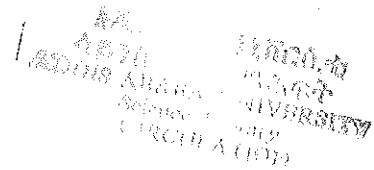
QUANTUM-CHEMICAL STUDY OF MOLECULAR CLUSTER OF SILICA



By

ADMASSU REGASSA

JUNE 1990

QUANTUM-CHEMICAL STUDY OF MOLECULAR CLUSTER OF SILICA

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE (M.SC) IN CHEMISTRY.

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LIST OF SYMBOLS AND ABBREVIATIONS

AAU	Addis Ababa University
AO	Atomic Orbital
A.U.	Atomic Unit
CNDO	Complete Neglect of Differential Overlap
CNDO/1	Complete Neglect of Differential Overlap Version 1
CNDO/2	Complete Neglect of Differential Overlap Version 2
CNDO/BW	Complete Neglect of Differential Overlap Boyd-Whitehead Version
CNDO/S	Complete Neglect of Differential Overlap Spectroscopic parameterization
Det	Determinant
GF	Gauss-type Functions
EHF	Extended Hartree-Fock Method
EHT	Extended Huckel Treatment
eV	Electron volt
HOMO	Highest Occupied Molecular Orbital
IBM	International Business Machines
INDO	Intermediate Neglect of Differential Overlap
IR	Infrared Spectoscopy
kJ	Kilo Joule
LCAO	Linear Combination of Atomic Orbitals
LUMO	Lowest Unoccupied Molecular Orbital
MINDO/3	Modified Version of Intermediate Neglect of Differential Overlap

MO	Molecular Orbital
Mol	Mole
MWH	Mulliken-Wolfsberg-Helmholtz Method
NCR	National Cash Register
NDDO	Neglect of Diatomic Differential Overlap
NMR	Nuclear Magnetic Resonance Spectoscopy
RHF	Restricted Hartree-Fock Method
SCF	Self-Consistent Field Method
SGS	School of Graduate Studies
SDDPC	Systems Design and Data Processing Center
STO	Slater - Type Orbitals
SW	Scatered Waves
THF	Tetrahydrofuran
UHF	Unrestricted Hartree-Fock Method
UV	Ultra-Violet Spectroscopy
ZDO	Zero Differential Overlap
A	An Interval
A_μ ,A_A	Atomic Electron Affinity
a_o	Atomic Unit of Length
α	The Step of Iteration in Variable Metrics Technique
B	Bond Order Between Bonded Atoms, An Interval
β_A^o, β_B^o	Atomic Bonding Parameters
β_{AB}^o	Bonding Parameter of AB Bond
C	Matrix of Coefficients in Roothaan Equation
χ_μ	Atomic Orbital Used in LCAO
d_i	Gradient of a Potential Energy Function
∇^2	Laplacian Operator

$G_{\mu\nu}$	The Contribution from the Electron-Electron Interaction to the Fock Matrix Element
G_{oo}	The Green Function for the Complete System
g_{nlm}	Gauss-Type Functions
$g_{i,i'}$	The Green Function for a Six-Ring Husimi Cactus Lattice
g_k	Occupation Number of Closed-Shell MOs
g_o	Occupation Number of Open-Shell MOs
g_{oo}	The Green Function for a Site
γ_{AB}	An Average Electrostatic Repulsion Between Any Electrons on A and B
$\gamma_{AA'}$ γ_{BB}	An Average Electrostatic Repulsion Between Any Two Electrons on A or Any Two Electrons on B
$\hat{H}$	Hamiltonian Operator
H	Hessian Matrix, Two-Band Hamiltonian of the Tight-Binding Type
$H_{\mu\nu}$	Matrix Elements of the Core Hamiltonian
$H_{\mu\mu}$, $H_{\nu\nu}$	Diagonal Matrix Elements of the Core Hamiltonian
$H^{(1)}$	One-Band Hamiltonian
H'	Effective Hamiltonian of a Hexagon
h	Planck Constant, an Effective Field Included in H'
$\hbar$	Dirac Constant; Reduced Planck Constant
$\hat{h}$, $\hat{H}^{core}$	Core Hamiltonian
H^*	Quasi- (Pseudo-) Hydrogen Atoms
$I_{\mu'_A}$ I_A	Ionization Potential of the Appropriate Average Atomic State
I	Unit Matrix, The Integrated Density of States

I_{fcc}	The Green Function for a Face-Centered Cubic Lattice
Im	The Imaginary Part of a Complex Number (Function)
I(R)	The Real Interval
∞	Infinity
$J_{\mu\nu}$,J_{ij}	Coulomb Integrals or Matrix Elements of the Coulomb Operator
$\hat{J}_j$	The Coulomb Operator
$K_{\mu\nu}$ K_{ij}	Exchange Integrals or Matrix Elements of the Exchange Operator
$\hat{K}_i$	The Exchange Operator
λ	The Step of Descent in Optimization
λ_1,λ_2	Eigenvalues, Points of a Given Interval
M_A	Mass of Nucleus A
M_{ij}	Matrix Elements of a Secular Equation
m, m_e	Mass of the Electron
μ_o	Slater Exponent
n(E)	Density of States
$\hat{O}_s$	Projection Operator
$P_{\mu\nu}$	Off-Diagonal Elements of the Density Matrix
$P_{\mu\mu}$, $P_{\lambda\lambda}$	Diagonal Elements of the Density Matrix
$P_l^{\|m\|}$	Associated Legendre Polynomials
q_A,q_B	Charges on Atoms A or B
q	Generalized Spatial Coordinate
q(A,B)	Distance Between Intervals A and B (Metric)
q^i	Sequence of Points in Minimization
q^{min}	Point of Minimum of a Function
ρ	Bond Order Between Atoms
S	Matrix of Overlap Integrals

$\hat{S}$	Overlap Operator
$S_{\mu\nu}$	Elements of the Overlap Matrix
$\vec{s}$	The Direction of Descent in Minimization
$\|s\rangle\langle s\|$	Operator of the s-like Combination of Basis Functions
$T_{\mu\nu}$	Contribution of the Kinetic Energy to the Matrix Elements of the Core Hamiltonian
$U(q^i)$	Potential Energy Function
$U^A_{\mu\mu}$	The One-Center Term of the Diagonal Matrix Elements of $H_{\mu\mu}$
V_1, V_2	Matrix Elements, Also Called "Banding" and "Bonding" Parameters, Respectively
$V_{\mu\nu}$	Contribution of the Potential Energy (of the Electron due to the Nucleus) to the Matrix Elements of the Core Hamiltonian
V_A, V_B	Core Potential of Atom A or B
V_{AB}	A Two-Center Integral Which is a Measure of the Interaction of any Valence Electron on Atom A with the Core of Atom B.
X_{nlm}	Slater-Type Functions
X	Nuclear Wavefunctions
x_i	Sequence of Points in Minimization
ξ	Slater Exponent
Z_A, Z_B	Nuclear charge of Atom A or B

ABSTRACT

The title study was undertaken to design an elaborated cluster model of silica gel and to investigate adsorption complexes of propene with silica using INDO method and optimization of geometry. The basic idea of cluster modeling entails substitution of the bulk of silica by terminal quasi-hydrogen is-atoms the quantum-chemical INDO parameters of which are strictly optimized to give adequate description of the electronic distributions in silica. Theoretical results for geometric parameters, electronic characterstics and band structure of the model studied were found to be in fairly good agreement with exdsting experimental data. Three stages of clusrter modeling were considered. The simplest model for hiydroxylated adsorbents is the hydroxide anion. In the second stage orthosilicic acid is used as a model of silica but the model has a basic drawback because there are no siloxane bridges in it. The third stage of modeling presupposes the incorporation of the siloxane network in the clusters. The cluster $Si(OSiH_3)_4$ is characterized by non-uniform electronic distribution in the bulk phase of silica and also gives inadequate description of the band structure of silica while the cluster $Si(OSiH_3^*)_4$ leads to more accurate and reliable description of the electronic and band structure of silica. The cluster model $Si(OSiH_3^*)_4$ is found to be optimum.

1. INTRODUCTION

The main objective for undertaking this study is to model the bulk and surface phases of silica using a quasi-atom cluster approach and to explore the merits of this approach over the existing models by studying the electronic and band structures (system of MO levels) of adsorbents and by comparing the results with experimental data.

The INDO method [1] gives a reliable description of open-shell systems and transition metal containing solids [2] and therefore is employed in the present work. The corresponding computer program was written by J.A. Pople et al [1].

The quasi-atom cluster approach eventually leads to a proper model of silica which allows calculation of more exact electronic densities and prediction of fairly accurate geometric structures of surface complexes of propene with silica. Such a modeling technique provides a more elaborated approach for theoretical consideration of the problem of adsorption and is applicable to surface complexes of propene with hydroxyl containing adsorbents with possible extensions to study surface complexes of propene with silicas chemically modified by metal salts.

The cluster models [3] used in the present study are chosen because of their simplicity and illustrative charcter. There are three stages of modeling. In the initial stage hydroxyl containing adsorbents are represented by hydroxyl anions.

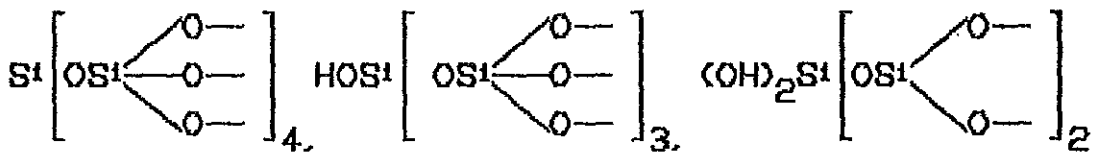
In the second stage of modeling orthosilicic acid [4] is used as a molecular model for the adsorbents. Finally, much more rigorous models are applied. The great merit of the third stage is that it takes into account the borderline effects between the fragment chosen and the solid [5]. The cluster models are useful to get a better insight into the process of adsorption and for the deeper understanding of surface complexes. The interpretation of results also becomes relatively easy.

The basic structural unit of silica is the Si, O-tetrahedron $[SiO_4]^{4-}$ [6]. The interatomic distances Si-O are in the range 0.161 - 0.162 nm and the nearset oxygen atoms are separated by a distance of 0.265 nm. Condensation of several tetrahedra into the complicated Si, O-structural networks inevitably leads to distortion of the basic Si, O-tetrahedral unit and this results in substantial deviations of the Si-O bondlengths from the average value and substantial variations of intra- and intertetrahedral angles OSiO and SiOSi [7].

Amorphous silicas consist of several tens of SiO_4 tetrahedra and contain β-cristobolite inclusions in regions of dimension 1.5 - 2.0 nm [8]. Such quasi-crystallic β-cristobolite inclusions are found even at elevated temperatures. The Si-O distance is 0.158 - 0.162 nm and the angle SiOSi is 140 - 180^{o} whereas the average statistical angle is 169^{o} [9].

The surface of dispersed silicas contains various macro- and micro-defects, the contacts of the globules, cavities, cracks and pores. OH-groups on the apices of the Si, O-tetrahedral surfaces form the hydroxyl carpet [10, 11].

The surface OH-groups of silica may enter substitution, isotopic exchange reactions and form hydrogen bonds with adsorbate molecules. The average distance between the surface OH-groups is estimated as 0.65 nm [12], though the surface hydroxyls are arranged non-uniformly. This is deduced from IR- [13 - 15] and NMR- [16 - 18] measurements. The estimated distance corresponds to the stastical average. However, it should be noted that depending on the conditions of pretreatment of silica (temperature and pressure of evacuation) some groups may be at a distance of 0.3 nm and interact by weak hydrogen bonds. In addition to silandiol groups $>Si(OH)_2$ [10]. The ^{29}Si NMR spectra clearly reveal the presence of



surface groups [17, 19]. From the previous discussion the difference between the isolated and bonded SiOH groups [13] and the distinction betwen the surface and internal silanol [20] should be clear. Not only hydroxyl groups but also silicon atoms [21] and oxygen atoms of the siloxane bridge [22] could be the active sites for adsorption of small nucleophiles.

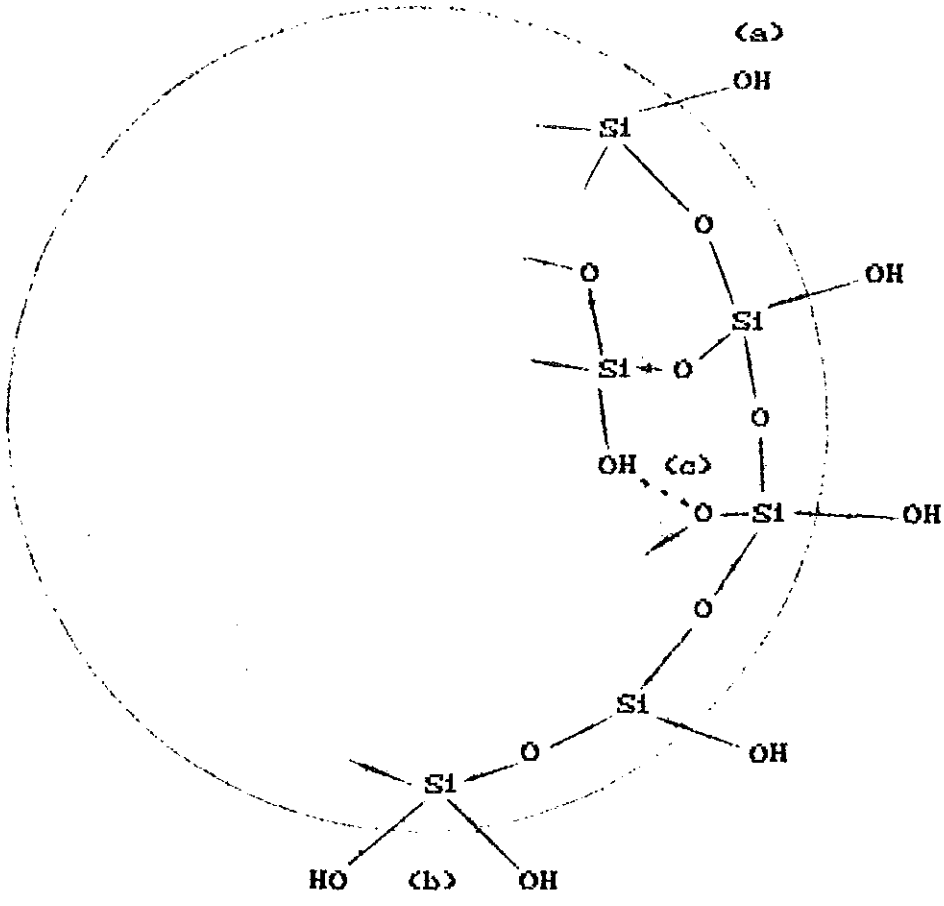


Fig. 1. Classification of surface hydroxyl groups in silica:
(a) isolated OH- group;
(b) hem-disilanol;
(c) internal H- bonded OH group.

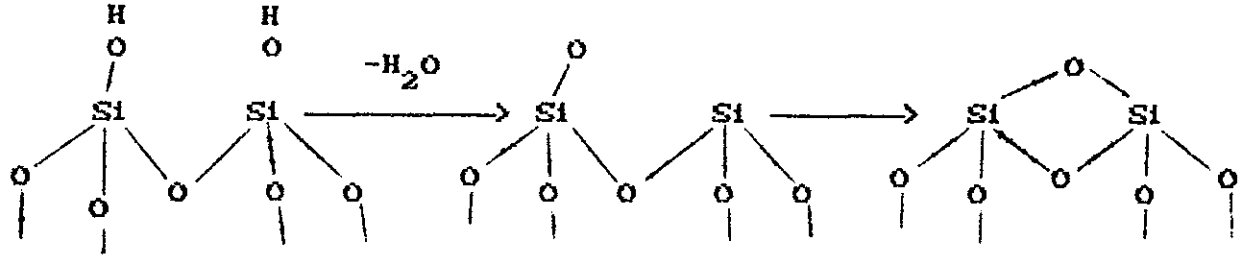


Fig. 2. Condensation of surface silanols in the rehydration process.

The various types of silica surface sites are generalized in the conventional scheme (fig. 1).

If silicas are evacuated at elevated temperatures, molecular water is evolved [23]. Adjacent OH-groups condense followed by the formation of the siloxane (SiOSi) bridges and some of the physically adsorbed water is desorbed (fig. 2).

This view follows from gravimetric [23] and molecular dynamics [24] studies.

The rate of adsorption or desorption of water as a function of pretreatment conditions of amorphous silicas could be monitored by gravimetric [23] and ^{29}Si NMR [25] studies.

2. MOLECULAR ORBITAL THEORY

2.1. SCHROEDINGER EQUATION AND VARIATIONAL PRINCIPLE

In principle all characterstic properties of a molecular system may be determined by solving the Schrödinger equation for the system. The resulting wavefunction is a function of the coordinates of all the particles (nuclei and electrons) in the system and time but most of the quantum-chemical calculations are based upon the time-independent Schrödinger equation. The solution of the time-independent Schrödinger equation is of great practical importance for the description of the motion of electrons in a given potential field (usually the field created by nuclei and electrons themselves). For a system of N nuclei and n electrons interacting with each other the time-independent Schrödinger equation is written as:

$$\hat{H}(1,2,\ldots,N;\ 1,2,\ldots,n)\ \psi(1,2,\ldots,N;\ 1,2,\ldots,n) = E\psi(1,2,\ldots,N;\ 1,2,\ldots,n) \qquad (2.1)$$

where $\hat{H}$ is the hamiltonian operator, ψ is the complete wavefunction of all the particles and E is total energy of the system; 1,2,...,N; 1,2,...,n are spatial coordinates of the nuclei and electrons, respectively.

$\hat{H} = \hat{H}_N + \hat{H}_e + \hat{H}_{eN}$ and

$\hat{H}_N$, $\hat{H}_e$ and $\hat{H}_{eN}$ are expressed in atomic units as

$$\hat{H}_N = -1/2 \sum_{A}^{N} M_A^{-1} \nabla_A^2$$

$$\hat{H}_e = \sum_{p}^{n} \hat{h}(p) + \sum_{p<q} \hat{g}(p,q)$$

where $\hat{h}(p)$ is the one-electron hamiltonian for the p-th electron

$$\hat{h}(p) = -1/2\nabla_p^2 - \sum_A Z_A r_{Ap}^{-1} \; ; \; r_{Ap}^{-1} = |r_p - R_A|^{-1}$$

and $\hat{g}(p,q)$ is the potential energy operator for interelectronic repulsive interaction between the p-th electron and all other electrons.

$$\hat{g}(p,q) = r_{pq}^{-1}$$

$$\hat{H}_{eN} = 1/2 \sum_A^N \sum_B^N Z_A Z_B R_{AB}^{-1}$$

A.U. for mass, length, charge, energy and action are defined as m_e, a_o, $e, e^2/a_o$, $\hbar$ respectively,

where

m_e is mass of the electron,

a_o is the Bohr radius,

e is the electronic charge and

$\hbar = h/2\pi$ where h is Planck constant ($\hbar$ is also known as Dirac constant [26]).

In the preceding equations, Z_A is charge on nucleus A; R_A and r_p are nuclear and electronic coordinates, respectively, R_{Ap} is the distance between nucleus A and electron p, R_{AB} is the internuclear distance between nuclei A and B, r_{pq} is the interelectronic distance between electrons p and q. ∇^2 is called the Laplacian operator which in cartesian coordinates is expressed as:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (2.2)$$

The various terms in the expression for the total hamiltonian represent operators for kinetic energy, electronic repulsion or attraction potentials. As was mentioned earlier the complete wavefunction depends upon the coordinates of all the electrons and nuclei but Born-Oppenheimer approximation allows the separation of the electronic and nuclear motions in which case the total wavefunction may be written as a product of two functions which are functions only of the electronic and nuclear coordinates, respectively, i.e.,

$$\psi' = \psi(r,q)\, X(q) \qquad (2.3)$$

where ψ and X are electronic and nuclear wavefunctions, respectively and r and q are generalized coordinates for the electrons and nuclei, respectively.

Thus, the problem of finding electronic wavefunctions for a given molecule reduces to solving its Schrödinger equation:

$$\left[-1/2 \sum_{p}^{n} \nabla_p^2 + \sum_{p<q} r_{pq}^{-1} - \sum_{A}^{N} \sum_{p}^{n} Z_A r_{Ap}^{-1}\right]\psi = E_{el}\psi \qquad (2.4)$$

where E_{el} is the electronic energy.

Under the Born-Oppenheimer approximation the total energy of the system is given as the sum of the electronic energy and total internuclear repulsion energy.

$$E = E_{el} + \sum_{A<B} Z_A Z_B R_{AB}^{-1} \qquad (2.5)$$

Equation (2.4) is a fundamental equation of quantum chemistry and various approaches (approximations) that are used to solve it led to the emergence of an emense variety of quantum chemical methods.

There are two general approaches to obtain approximate solutions of (2.4).

The approach known as orbital approximation in which one-electron orbitals are used to construct the molecular wavefunction, it is assumed that the motion of a single electron is governed by the average field created by the nuclei and the other electrons. Thus, for each electron it is possible to write a one-electron Schrödinger equation as:

$$\left[-1/2\nabla^2(1) + \sum_n Z_n r_{in}^{-1} + \sum_{j \neq i} \bar{r}_{ij}^{-1} \right] \varphi_i = E_i \varphi_i \qquad (2.6)$$

where $\bar{r}_{ij}$ is average interelectronic distance between electrons i and j, φ_i is one-electron wavefunction for electron i. One-electron wavefunctions are called orbitals.
The total electronic wavefunction of the many-electron system is then written as the product of one-electron wavefunctions or orbitals a procedure known as Hartree method. Besides, the electronic wavefunction must satisfy the antisymmetry condition. The antisymmetry principle states that the electronic wavefunction must be antisymmetric with respect to mutual permutation of a pair of electrons (interchange of their spatial and spin coordinates) in accordance with Pauli principle. Calculation of molecular orbitals by SCF one-electron approximations has computational simplicity but involves crude approximations as compared to LCAO SCF method. Therefore, ψ is not a single product but should be represented by a Slater determinant taking into account all the possible electron permutations of the different spin orbitals. This is referred to as Hartree-Fock method. For a system containing $n = N/2$ spatial orbitals (N spin orbitals) φ the

normalized wavefunction ψ for a closed-shell system is written as a single Slater determinant:

$$\psi = (N!)^{-1/2} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1)....\phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2)....\phi_n(2)\beta(2) \\ \vdots & \vdots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \phi_2(n)\alpha(n)....\phi_n(n)\beta(n) \end{vmatrix} \qquad (2.7)$$

or in compact form (using diagonal elements only)

$$\psi = (N!)^{-1/2} \left| \phi_1(1)\ \bar{\phi}_1(2)\phi_2(3)\bar{\phi}_2(4)....\bar{\phi}_n(N) \right|$$

or even more compactly as

$$\psi = (N!)^{-1/2} \left| \phi_1\bar{\phi}_1\phi_2\bar{\phi}_2...\phi_n\bar{\phi}_n \right|$$

where the spin components α and β are defined as $\pm 1/2$ in units of $\hbar$, respectively and $\phi = \varphi\ \alpha$, $\bar{\phi} = \varphi\ \beta$

In general it is necessary to consider the wavefunction as a linear combination of a finite (usually small) number of Slater determinants [27]. This is particularly true for MOs of systems containing unpaired electrons (open-shell systems).

The multi-determinantal description of the wavefunction may be written as:

$$\psi = \sum_i c_i D_i \qquad (2.8)$$

where the sum is taken over all possible configurations and c_i is a variational parameter (coefficient).

Slater determinants give only the means to express the total wavefunction as a product of spin-orbitals. To obtain the best approximate solution of (2.4) by this method, variational principle is used. The variational principle is based on the variational theorem which states that the average energy, E, of a system calculated using a well-behaved trial

wavefunction, ψ, is always greater than or equal to the true energy E_o obtained from the exact wavefunction ψ_o.

Mathematically, the variation theorem is expressed as:

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_o \qquad (2.9)$$

where equality holds when the trial function is the same as the exact wavefunction (ground state).

The expression (2.8) is substituted for ψ into the variational equation (2.9) which is minimized with respect to the coefficients of D_i and the parameters of the spatial orbitals, $\varphi_n(j)$. However, practical implementation of such minimization is very complicated because D_i depends on the shape of φ_n which in turn is determined by D_i. Such minimization is called multi-configurational SCF method but most SCF methods are based upon more simplified schemes (either φ_n or D_i is varied) than the multi-configurational approach. In particular, if $D_1 \neq 0$, $D_i = 0$, $i>1$, the whole calculation will be based on optimization of orbitals φ in this mere configuration.

The second approach involves approximation of φ as a linear combination of atomic orbitals (so-called LCAO MO).

$$\varphi_i = \sum_\mu C_{\mu i} \phi_\mu \qquad (2.10)$$

where C is a coefficient and ϕ is an atomic orbital (AO).

Intuitively, the nature of chemical problems makes it profitable to relate molecular orbitals to the corresponding atomic orbitals of the constituent atoms. However, to carry out such MO calculations a convenient analytical form for the AO of each type of atom in the molecule is required.

2.2 HARTREE-FOCK METHOD FOR CLOSED AND OPEN SHELL SYSTEMS

Roothaan's work [28] was the outstanding stage in the development of computational quantum chemistry.

As was mentioned the most widely used approximate calculations of the electronic structure of σ-systems are LCAO SCF MO procedures. Such procedures lead to the Roothaan equation [29]:

$$(\hat{F} - \varepsilon_i \hat{S})c_i = 0, \quad \mathrm{Det}(F - \varepsilon_i S) = 0 \qquad (2.11)$$

where F and S are matrices of the Hartree-Fock and overlap operators, respectively. The matrix elements are given as follows:

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \qquad (2.12)$$

where

$$H_{\mu\nu} = \int \phi_\mu(1)\, \hat{H}\, \phi_\nu(1)\, d\tau_1 \qquad (2.13)$$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}(J_{\mu\nu\lambda\sigma} - 1/2K_{\mu\nu\lambda\sigma}) \qquad (2.14)$$

where $H_{\mu\nu}$ and $G_{\mu\nu}$ are matrix elements of the core energy and interelectronic repulsion energy, respectively

$$P_{\lambda\sigma} = \sum_i c_{\lambda i} c_{\sigma i} \qquad (2.15)$$

$P_{\lambda\sigma}$ are the elements of the density matrix in AO basis set.

$$J_{\mu\nu\lambda\sigma} = \int\int \phi_\mu(1)\phi_\nu(1)\, \frac{1}{r_{12}}\, \phi_\lambda(2)\phi_\sigma(2)\, d\tau_1 d\tau_2 \qquad (2.16)$$

$$K_{\mu\nu\lambda\sigma} = \int\int \phi_\mu(1)\phi_\lambda(1)\, \frac{1}{r_{12}}\, \phi_\nu(2)\phi_\sigma(2) d\tau_1 d\tau_2 \qquad (2.17)$$

$J_{\mu\nu\lambda\sigma}$ and $K_{\mu\nu\lambda\sigma}$ are called coulomb and exchange integrals of the interelectronic interactions, respectively.

$$S_{\mu\nu} = \int \phi_\mu^*(1)\phi_\nu(1)\, d\tau \qquad (2.18)$$

The solutions of the Roothaan equation (2.11) are the eigenvectors, $c_i = c_{i1}, c_{i2}, c_{i3}, \ldots, c_{in}$, and the corresponding eigenvalues which are referred to as orbital energies, ε_i. In the unrestricted version of the Hartree-Fock method the wavefunction for the molecular system is written as a single determinant and different spatial MOs are used for different spins.

The procedure for solving the Roothaan equation is as follows. Determination of the roots of the secular equation (2.11) demands computation of the corresponding Fockian matrix elements, $F_{\mu\nu}$, which in turn depend upon the coefficients $c_{\mu i}$ of AO through $P_{\mu\nu}$ and may be computed only by solution of the secular equations. Therefore, it is necessary to make certain assumptions about the initial shapes of MO's (zero-ordrer approxdmation) and the corresponding values of $P^{o}_{\mu\nu}$. The latter are substituted to (2.11) and then (2.11) is solved, which gives matrix of electronic populations in the first approximation, say, $P'_{\mu\nu}$. This is again substituted into the initial equations. Such an iterative procedure of self-consistency is repeated unless the definite wavefunction is achieved which remains unchanged in subsequent iterations. Self-consistency is finished when

$$|\Delta E| = \left| E_{el}^{(n)} - E_{el}^{(n-1)} \right| < \varepsilon \qquad (2.19)$$

where $E_{el}^{(n)}$ and $E_{el}^{(n-1)}$ are the values of electronic energies obtained at n-th and (n-1)-th steps of iteration procedure, ε is a pre-defined very small quantity called accuracy of self-consistency. Sometimes, another criterion of the accuracy

of self-consistency is applied:

$$\Delta = \left| \frac{E_{el}^{(n)} - E_{el}^{(n-1)}}{E_{el}^{(n)}} \right| \qquad (2.20)$$

Open-shell systems appear in systems with the odd number of electrons and also with even number of electrons when one or several electrons are excited to virtual MOs

In general open-shell systems must be described by multi-determinant wavefunctions. However, such a description leads to substantial complication of the computational procedure which makes it impossible to treat complicated molecular systems, e.g., free radicals, low-lying triplets, etc. For some systems the situation becomes easier because quite accurate one-determinant description becomes possible. Corresponding subdivisions of SCF approaches are:

(i) restricted Hartree-Fock (RHF) method in which all the occupied MOs except the higher ones containing unpaired electrons are occupied by two electrons with anti-parallel spins;

(ii) unrestricted and expanded Hartree-Fock (UHF and EHF) methods in which variational procedure is fulfilled with the separate spin orbitals containing one electron each.

Generally the wavefunction of a system of N electrons is

$$\psi(1,2,\ldots,N) = \hat{G}\,\phi(1,2,\ldots,N)\,X(1,2,\ldots,N) \qquad (2.21)$$

where $\hat{G}$ is the operator of symmetry transformation; ϕ, X are functions of spatial and spin coordinates:

$$\left.\begin{aligned} \phi\ (1,2,\ldots,N) &= \varphi_{1\alpha}(1)\ldots\varphi_{n\alpha}(n)\varphi_{1\beta}(n+1)\ldots\varphi_{m\beta}(N) \\ X\ (1,2,..,N) &= \alpha(1)\ldots\alpha(n)\beta(n+1)\ldots\beta(N+m) \end{aligned}\right\} \qquad (2.22)$$

where $\left\{ \varphi_{i\alpha} \right\}$ and $\left\{ \varphi_{i\beta} \right\}$ are two orthonormalized sets of one-electron orbitals; $\alpha(i)$ and $\beta(i)$ are spin functions with spin projections of the i-th electron equal to +1/2 and -1/2, respectively in units of $h/2\pi$.

Substituting (2.21') into (2.22) and replacing of $\hat{G}$ by the antisymmetrization operator $\hat{A}$ ths wavefunctin of UHF, ψ^{UHF} is obtained. Imposing on ψ^{UHF} the condition $\varphi_{i\alpha} = \varphi_{i\beta}$ one arrives at the wavefunction of RHF. Finally, the wavefunction of EHF is obtained if $\hat{G} = \hat{A}.\hat{A}$ is substituted into (2.21), where projection operator $\hat{O}_S$ subtracts component of multiplicity (2S+1) from ψ^{UHF}.

RHF is the direct generalization of standard SCF theory. However, resultant equations are somewhat more complicated than equations for closed shells. Roothaan [30] proposed a scheme according to which total energy is

$$E = 2\sum_{k} H_k + \sum_{kl}(2J_{kl} - K_{kl}) + f\left[2\sum_{m} H_m + f\sum_{mn} 2(aJ_{mn} + bK_{mn}) + 2\sum_{km}(2J_{km} + K_{km})\right] \qquad (2.23)$$

where indices k,l and m,n refer to the orbitals of closed and open shells, respectively, and

$$H_i = \langle\varphi_i|\hat{H}|\varphi_i\rangle,$$

$$J_{ij} = \langle\varphi_i|\hat{J}_j|\varphi_i\rangle = \langle\varphi_j|\hat{J}_i|\varphi_j\rangle,$$

$$K_{ij} = \langle\varphi_i|\hat{K}_j|\varphi_i\rangle = \langle\varphi_j|\hat{K}_i|\varphi_j\rangle,$$

$$\hat{J}_i\varphi(1) = \left[\int \bar{\varphi}_i(2)\varphi_i(2)\frac{1}{r_{12}}d\tau_2\right]\varphi(1)$$

$$\hat{K}_i\varphi(1) = \left[\int \bar{\varphi}_i(2)\varphi_i(2)\frac{1}{r_{12}}d\tau_2\right]\varphi(1)$$

are coulomb and exchange operators, respectively.

The first two sums in (2.23) define energy of closed shells, the latter two - energy of open shells; f is equal to the number of occupied orbitals with open shell divided by the number of all the possible spin orbitals. Values of a and b are different for different states of one configuration, e.g., for the ground state of a radical f = 1/2, a = 1, b = 2. Procedure of finding of the wavefunction is to find combined solution of separate system of equations for open and closed shells:

$$\begin{cases} \hat{F}_c\varphi_k = \eta_k\,\varphi_k \\ \hat{F}_o\varphi_m = \eta_m\,\varphi_m \end{cases} \qquad (2.24)$$

where

$$\hat{F}_c = \hat{H} + 2\hat{J}_c - \hat{K}_c + 2\hat{J}_o - \hat{K}_o + 2\alpha\hat{L}_o - \beta\hat{M}_o,$$

$$\hat{F}_o = \hat{H} + 2\hat{J}_c - \hat{K}_c + 2a\hat{J}_o - b\hat{K}_o + 2\alpha\hat{L}_c - \beta\hat{M}_c,$$

$$\alpha = (1-a)/(1-f), \quad \beta = (1-b)/(1-f)$$

$$\hat{J}_c = \sum_k \hat{J}_k, \quad \hat{J}_o = f\sum_m \hat{J}_m,$$

$$\hat{K}_c = \sum_k \hat{K}_k, \quad K_o = f\sum_m K_m,$$

$$\hat{L}_i\varphi = \langle\varphi|\hat{J}_o|\varphi\rangle\varphi_i + \langle\varphi_i|\varphi\rangle\hat{J}_o\varphi_i,$$

$$\hat{M}_i = \langle\varphi_i|\hat{K}_o|\varphi\rangle + \langle\varphi_i|\varphi\rangle\hat{K}_o\varphi_i,$$

$$\hat{L}_c = \sum_k \hat{L}_k, \quad \hat{L}_o = f\sum_m \hat{L}_m,$$

$$\hat{M}_c = \sum_k \hat{M}_k, \quad \hat{M}_o = f\sum_m \hat{M}_m.$$

The difficulty of such an approach is the choice of the off-diagonal Lagrangian multipliers connecting open and closed shells. The role of these multipliers is that they make open and closed shells mutually orthogonal. However, hamiltonian of the system is too complicated and it becomes difficult to ascribe physical description to its separate constituents.

For the definite types of electronic configurations (non-excited doublets and lowest triplets) Roothaan [30] proposed a more realistic approach, in which unified system of equations is solved for open and closed shells:

$$\hat{F}\varphi = \varepsilon\varphi \qquad (2.25)$$

$$\hat{F} = \hat{H} + \hat{J}_t + \hat{K}_t + 2\alpha(\hat{L}_t - \hat{J}_o) - \beta(\hat{M}_t - \hat{K}_o),$$

$$\hat{J}_t = \hat{J}_c + \hat{J}_o, \quad \hat{K}_t = \hat{K}_c + \hat{K}_o,$$

$$\hat{M}_t = \hat{M}_c + \hat{M}_o, \quad \hat{L}_t = \hat{L}_c + \hat{L}_o.$$

In the case of doublets (one electron on non-degenerate φ_o) equation (2.23) reduces to

$$E = 2\sum_k H_k + \sum_{kl}(2J_{kl} - K_{kl}) + H_o + \sum_{ko}(2J_{ko} - K_{ko}) \qquad (2.26)$$

where the first two terms describe closed-shell energy. They may be rewritten as

$$E_R = \sum_k g_k H_k + 1/4\sum_{kl}(2J_{kl} - K_{kl})g_k g_l \qquad (2.27)$$

where $g_k = 2$ - occupation number of closed-shell MOs.

Formal generalization of (2.27) on the radical having $g_o = 1$ leads to the expression which besides a small number $1/4J_{oo}$ coincides with (2.26):

$$E_R = 2\sum_k H_k + \sum_{kl}(2J_{kl} - K_{kl}) + H_o + \sum_k (2J_{ko} - K_{ko}) + 1/4J_{oo} \qquad (2.28)$$

Thus, calculated approximate value of E_R may be associated with the accurate (Roothaan) value:

$$E = E_R - 1/4J_{oo} \qquad (2.29)$$

Energy of the excited triplet state is

$$E = E_R - 1/4J_{oo} - 1/4J_{o'o'} - 1/4K_{oo'} \qquad (2.30)$$

The last terms in (2.29) and (2.30) may be visualized as the result of the repulsion of two "halves" of electrons with different spins occupying orbitals φ_o (radical), φ_o and $\varphi_{o'}$ (in triplet).

The basic assumption of UHF method [31] is that electrons having α spin occupy spatial MOs different from MOs of electrons with β spin. In this case two combined eigenvalue problems are solved:

$$\begin{cases} (\hat{H} + \sum_j \hat{J}_j - \sum_j{}^{\alpha} \hat{K}_j)\varphi_{i\alpha} = \sum_j{}^{\alpha} \varepsilon_{ij}\varphi_{j\alpha} \\ (\hat{H} + \sum_j \hat{J}_j - \sum_j{}^{\beta} \hat{K}_j)\varphi_{i\beta} = \sum_j{}^{\beta} \varepsilon_{ij}\varphi_{j\beta} \end{cases} \qquad (2.31)$$

or in the matrix form

$$F_i^{\alpha} C_i^{\alpha} = \varepsilon_i^{\alpha} S C_i^{\alpha}$$

$$F_i^{\beta} C_i^{\beta} = \varepsilon_i S C_i^{\beta}$$

where F^{α} and F^{β} may be represented as the sum of one- and two-electron contributions, i.e.,

$$F^{\alpha} = H + G^{\alpha}, \quad F^{\beta} = H + G^{\beta} \qquad (2.32)$$

Matrix elements of G^{α} and G^{β} matrices are:

$$G^{\alpha}_{\mu\nu} = \sum_{\rho\sigma} \left[P_{\rho\sigma}(\mu\sigma|\nu\rho) - P^{\alpha}_{\rho\sigma}(\mu\nu|\rho\sigma) \right],$$

$$G^{\beta}_{\mu\nu} = \sum_{\rho\sigma} \left[P_{\rho\sigma}(\mu\sigma|\nu\rho) - P^{\beta}_{\rho\sigma}(\mu\nu|\rho\sigma) \right] \qquad (2.33)$$

where

$$P^{\alpha}_{\rho\sigma} = \sum_{i}^{\alpha} c_{\rho i}^{\alpha} c_{\sigma i}^{\alpha} , \qquad P^{\beta}_{\rho\sigma} = \sum_{i}^{\beta} c_{\rho i}^{\beta} c_{\sigma i}^{\beta},$$

$$P_{\rho\sigma} = P^{\alpha}_{\rho\sigma} + P^{\beta}_{\rho\sigma} .$$

From (2.31) - (2.33) it is seen that Fockians for electrons with different spins are connected by exchange terms and differ from each other because exchange interaction of electrons with equal and opposite spins is different.

In this thesis the program version based on UHF method is used.

2.3 NON-EMPIRICAL SCF MO LCAO METHODS AND SEMI-EMPIRICAL APPROXIMATIONS.

Calculation of electronic structure of a molecule or a molecular system reduces to solution of Hartree-Fock-Roothaan equations. Integrals entering these equations are determined in the basis of one-electron functions - AOs, χ_μ. Calculation of ψ demands a proper choice of AOs, χ_μ, which must give a good approximation to the true atomic wave functions, should ensure satisfactory convergence of iteration procedure and must have analytical (simple) expressions for the corresponding integrals.

Analytical approximations of the basis functions, parameters of which are optimized by solution of variational problem for atoms and small molecules, are well known.

Among such functions the most popular are STO:

$$\chi_{nlm} = \sqrt{\frac{2\xi}{(2n)!}}\,(2\xi)^n\, r^{n-1}\, e^{-\xi r}\, Y_{lm}(\vartheta,\varphi) \qquad (2.34)$$

where

$$Y_{lm}(\vartheta,\varphi) = \left[\frac{2l+1}{2\pi\delta_m}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\vartheta)\begin{cases}\cos m\varphi & (m \geq 0)\\ \sin m\varphi & (m < 0)\end{cases} \qquad (2.35)$$

are normalized spherical harmonics; $P_l^{|m|}(X)$- associated Legendre polynomials; $\delta_m = 2$ if $m = 0$ and 1 in all the other cases.

Orbital parameters (2.33) are quantum numbers n, l ,m and Slater exponents ξ selected according to the well-known Slater rules.

Therefore, the great majority of non-empirical calculations of polyatomic molecules is based upon Gauss-type functions:

$$g_{nlm} = \left[\sqrt{2/\pi} \; \frac{(4\alpha)^{n+1/2}}{(2n-1)!} \right]^{1/2} r^{n-1} \; e^{-\alpha r^2} \; Y_{lm}(\theta,\varphi) \qquad (2.36)$$

Their basic difference from STO (2.34) is their quadratic dependence on r in the exponential part. Owing to these products of functions g_{nlm} centered at different points which are met in computations of molecular integrals may be presented as LC of GF centered in a general case at any other point of space. This circumstance and possibility of factorization of the exponent relative to the three cartesian coordinates allows to calculate all the necessary integrals comparatively very easily and more effectively.

The most perspective in this sense is application of extended Gauss sets. Decomposition of STO to GF may be represented as

$$\chi = \sum_{i=1}^{N} c_i g_i \qquad (2.37)$$

where c_i is decomposition coefficient, N defines the number of GF by which STO function is approximated and is called parameter of the function STO-NG [32,33]. Practically basis sets are used after grouping of several GF entering the basis set, which gives economy of computer time. The recommendation along this line is to group GF and to vary not all the coefficients of MO LCAO decomposition but only those which refer to the given group of functions [34, 35]. This allows to decrease the number of Hartee - Fock Roothaan equations substantially.

The most popular schemes are STO - 3G, STO-4G. To improve the results each orbital of the inner shells is represented by

STO-NG but orbitals of the valence shell are subdivided into several (usually two-three groups) each of them is described by the corresponding number of GF: STO-4-31G [36,37] (orbitals of valence shell are subdivided into two groups, orbitals of the first group are described by three and the second - by one GF). Basis sets STO-6-31G, STO-6-311G are also known.

The other way of improvement of results is inclusion of polarization functions to the basis set (d for the second period atoms, p for hydrogen atom). Basis sets of this type are designated by one or two stars, respectively. This allows to obtain the more uniform electronic distribution, increases the relative contribution of the stabilizing non-valent interactions. For example, extended basis set of the type STO-6-311G* is widely used.

Application of non-empirical calculations of the electronic structure of molecules comes across serious computational difficulties connected with the necessity of computation of various integrals the number of which abruptly increases with molecular size.

In spite of rapid advancements of non-empirical quantum-chemical methods approximate semi-empirical schemes still continue to play a vital role in the calculation of molecular properties. Therefore, semi-empirical methods are widely used. Semi-empirical MO approximations are one of the most intensively used and highly developed methods of quantum chemistry. Semi-empirical MO methods based upon Parison-Parr-Pople approximations for π-electron systems are

described and analyzed in every detail [38]. Semi-empirical methods are also used to calculate the electronic structure of saturated organic compounds and thus take into account not only π- but also σ-electrons [1, 27, 39]. In recent years such methods were successfully employed to study various physico-chemical properties of compounds containing atoms up to the fourth period.

The impossibilty of getting exact solutions to the Schrödinger equation for many-electron systems eventually necessitates the introduction of approximations. Thus, MO method involves approximate quantum-mechanical treatment of a system containing a finite number of electrons and nuclei interacting with each other. The effects of approximations on the results of calculations were analyzed and discussed [1, 27, 38, 39].

Characterstic features of all the semi-empirical methods are:

(i) Several groups of electrons are not explicitly treated. For example, only valence (valent approximation) or π-electrons (π-electron approximation) are considered;

(ii) Several terms of hamiltonian (2.12) are ignored or expressed through empirical parameters;

(iii) A series of integrals necessary for calculation of the electronic energy are either accepted to have zero values or expressed through other integrals or empirical parameters.

Approximations however cannot be arbitrary. The basic features , interaction and effects, accurately taken into consideration in semi-empirical schemes, should be kept in

semi-empirical MO LCAO methods. One of the features of such a continuity is preservation of the invariancy of calculations under different transformations of basis sets and Hartree-Fock-Roothaan equations. From this point of view a series of levels of approximations are possible:

1. Approximations leading to violation of invariancy of the results relative to both rotation of coordinate axes and hybridization of AOs;

2. Approximations preserving invariancy relative to rotation of coordinate axes but violating invariancy relative to hybridization of AOs;

3. Approximations invariant to both rotation of coordinate axes and hybridization of AOs.

Computational methods corresponding to any type of approximation are possible but preservation of invariancy of the second or third level is practically essential. All the semi-empirical computational methods described below satisfy these conditions.

All the existing semi-empirical methods may be subdivided into two large groups. The first group includes methods taking into account overlap or methods of complete overlap. Equation of these methods is formally analogous to the accurate Roothaan equation:

$$H c_i = E S c_i \qquad (2.38)$$

but the expression for $\hat{H}$ depends on the level of approximation. The most known among these approaches is EHT method [40, 41]. Electron-electron interaction is not explicitly taken into account, diagonal elements of H matrix

are approximated by ionization potentials with reverse sign and for off-diagonal terms one of the expressions is applied:

(i) $H_{\mu\nu} = \frac{k}{2}(H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu}$ (2.39)

(Wolfsberg-Helmholtz version) [42];

(ii) $H_{\mu\nu} = kS_{\mu\nu}$ (2.40)

(Longuet-Higgins-Roberts version) [43];

(iii) $H_{\mu\nu} = k(H_{\mu\mu} H_{\nu\nu})^{1/2} S_{\mu\nu}$ (2.41)

(Ballhausen-Gray version) [44];

(iv) $H_{\mu\nu} = 1/2(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} (2 - |S_{\mu\nu}|)$ (2.42)

(Cusachs' version) [44].

The total energy in EHT is the sum of one-electron energies which is equivalent to proposal on mutual compensation of contributions from electron-electron and nuclear repulsion.

This method appears to be satisfactory for the systems with relatively uniform charge distribution, e.g., hydrocarbons. For the systems containing heteroatoms IEHT (iterative version) is more adequate [45]. Dependence of $H_{\mu\mu}$ on the charge of the given center is taken into consideration and is accepted to be linear. For transition-metal containing substances MWH method is more adjustable [44]. It is characterized by self-consistency relative to charge and electronic configuration of transition metal.

ZDO-approach [46] gives a variety of semi-empirical methods. It is based upon the assumption that $S_{\mu\nu} = 0$ at $\mu \neq \nu$, i.e., $S_{\mu\nu} = \delta_{\mu\nu}$. This reduces equations (2.11) to the form

$$\hat{F}c_i = \varepsilon_i c_i \qquad (2.43)$$

and substantially decreases the number of integrals of

interelectronic interaction subjected to computation. All the versions of ZDO-scheme follow Pople's classification [47 - 49] in accordance to which three levels of approximation may be noted, preserving invariancy at least to rotation of coordinate axes;

1. CNDO when all the products $\chi_\mu\chi_\nu$ are set zero. Only integrals of the type

$$U_{\mu\mu} = \langle\chi_{\mu_A}\left|-\frac{\nabla^2}{2} - V_A\right|\chi_{\mu_A}\rangle, \quad \langle\chi_{\mu_A}\left|V_B\right|\chi_{\mu_A}\rangle, H_{\mu_A\mu_B},$$

$$\langle\mu_A\mu_A|\nu_A\nu_A\rangle = \gamma_{AA}, \langle\mu_A\mu_A|\mu_B\mu_B\rangle = \gamma_{AB} \qquad (2.44)$$

are non-zero, where V_A and V_B - core potential of atoms A and B not containing valence electrons.

2. INDO differs from CNDO only by non-zero integrals of the type $\langle\mu_A\nu_A|\nu_A\sigma_A\rangle$.

3. NDDO when the products $\chi_\mu\chi_\mu$ are equal to zero only for AO refering to different atoms. Integrals $U_{\mu\mu}$, $\langle\chi_{\mu_A}|V_B|\chi_\mu\rangle_A$, $H_{\mu_A\nu_A}$, $\langle\mu_A\nu_A|\lambda_A\sigma_A\rangle$, $\langle\mu_A\nu_A|\lambda_B\sigma_B\rangle$ are kept in this scheme.

INDO scheme is equivalent to NDDO in one-center parts, to CNDO - in two-center parts.

For all the ZDO methods total energy of the molecule is

$$E = \sum_A E_A + \sum_{A<B} E_{AB} \qquad (2.45)$$

where E_A are one-center constituents containing only interatomic terms; E_{AB} are two-center constituents which in turn may be subdivided into covalent and electrostatic constituents.

Semi-empirical theories reproduce correctly the behaviour of one-center constituents of energy with the aid of such

values of one-center parameters which are determined from atomic spectra. The situation is worse with two-center interactions.

The difficulty is condition of rotational invariancy which necessitates to consider electrostatic constituent of two-center interaction to be isotropic:

$$E_{AB}^{el} = \left[(Z_A - q_A)q_B + (Z_B - q_B)q_A\right]\gamma_{AB} + Z_A Z_B V_{AB} \qquad (2.46)$$

where q_A and q_B are gross electronic densities on A and B atoms ($q_A = \sum_{\mu}^{A} P_{\mu\mu}$); Z_A and Z_B are core charges, V_{AB} is nomrmalized per unit of charge potential of core-core interaction.

This leads to serious consequences: (i) the scheme does not reproduce energy splitting in the crystal field;
(ii) character of steric interaction is violated.

The value of E_{AB}^{el} and the whole balance between E_{AB}^{el} and E_{AB}^{cov} is determined as

$$E_{AB}^{cov} = 2\beta_{AB} \sum^{A} \sum^{B} \rho_{rs} S_{rs} - 1/2\ \gamma_{AB} \sum^{A} \sum^{B} \rho_{rs}^2 \qquad (2.47)$$

where β_{AB} is empirical bond parameter depending on the nature of A and B atoms. They depend on the values of the coulomb integrals γ_{AB}. They may be evaluated by two methods: (i) purely theoretical computation on the basis of STO leading to the overestimation of E_{AB}^{cov} at large distances; (ii) empirical equations for γ_{AB} allowing to overcome this difficulty.

The expression for the electronic energy in the Hatree-Fock-Roothaan approximation is given [1].

$$E_{el} = 2 \sum H_{ii} + \sum_{i\,j\mu\nu}^{n} (2J_{ij} - K_{i\mu j\nu}) \quad \text{or}$$

$$E_{el} = \sum_{i}^{occ} E_i + \sum P_{\mu\nu} H_{\mu\nu} \qquad (2.48)$$

Application of the Mulliken-Ruldenberg approxdmation [28, 50] substantially signifies the computation of multi-center integrals of the type (2.16, 2.17) expressed in the following way:

$$\phi_{\mu_A}(1)\ \phi_{\mu_B}(1) \approx 1/2\ S_{\mu\nu}\left[\phi_{\mu_A}(1)\ \phi_{\mu_A}(1) + \phi_{\mu_B}(1)\ \phi_{\mu_B}(1)\right] \qquad (2.49)$$

Then the most complicated expressions for the three- and four-center integrals in the computation of electronic interactions are represented by much more simplified expressions, which contain only one-center and two-center integrals:

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\ \phi_\sigma(2)\ d\tau$$

$$\approx 1/4\ S_{\mu\nu}\ S_{\lambda\sigma}\left[(\mu\mu|\lambda\lambda) + (\mu\mu|\sigma\sigma) + (\nu\nu|\lambda\lambda) + (\nu\nu|\sigma\sigma)\right] \qquad (2.50)$$

Since the valence and inner core electrons abruptly differ in their orbital energies and spatial localization and since the basic contribution to the formation of a chemical bond originates from the highest filled and vacant orbitals, calculations of MOs for many-electron systems may be simplified by approximate SCF equations for valence electrons. The inner core electrons of atoms are considered as non-polarizable cores and their mutual interactions are described in approximate ways.

Moreover, solution of SCF equations even in the valence approximation is a rather complicated task due mainly to the computational difficulties of a large number of integrals. One of the most widely used techniques to overcome this difficulty is the application of ZDO approximation, which neglects integrals having small values from SCF matrix elements.

For π- and σ-systems ZDO approximation was formulated by Pople, Santry and Segal [1]. In general ZDO approximation may be characterized by the following simplifying assumptions:

(i) neglect of the overlap integrals in SCF equations. Then equation (2.18) becomes

$$S_{\mu\nu} = \delta_{\mu\nu} \qquad (2.51)$$

where $\delta_{\mu\nu}$ is the Kronecker delta.

(ii) neglect of all the integrals containing two-center distributions in the matrix elements of electron-electron interactions. Then equation (2.50) becomes

$$(\mu_A \nu_B | \lambda_C \sigma_D) = \delta_{AB}\, \delta_{CD}\, (\mu_A \nu_B | \lambda_C \sigma_D) \qquad (2.52)$$

Besides, in the various versions of ZDO approximation special rules for the evaluation of the core energy matrix elements (2.13) are introduced. For instance, Pople [1] introduced the scheme according to which $H_{\mu\nu}$ values are accepted to be different from zero for $\phi_\mu \equiv \phi_\nu$ and for $\phi_\mu \neq \phi_\nu$ only for orbitals belonging to the same atom or to the nearest (bonded) neighbours. Then in the Pople approximation the Hartree-Fock-Roothaan equations (2.11 - 2.14) are:

$$\sum_\nu F_{\mu\nu}\, c_{\nu i} = \varepsilon_i c_{\nu i} \qquad (2.53)$$

in which

$$F_{\mu\mu} = H_{\mu\mu} - 1/2\ P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda} (P_{\lambda\lambda}(\mu\mu|\lambda\lambda) \qquad (2.54)$$

$$F_{\mu\nu} = H_{\mu\nu} - 1/2\ P_{\mu\nu}\ (\mu\mu|\nu\nu) \qquad (2.55)$$

Theoretical substantiation of such an approach and discussion of various kinds of non-invariancy of the results of calculations in different ZDO approximations are given in detail [27, 38, 39].

In the following part some of the most widely used and thoroughly discussed versions of ZDO approxdmation are considered, which also makes it possible to analyze the main differences between the versions.

NDDO approximation fully employs ZDO method. In this version of ZDO no supplementary simplifying conditions are introduced to (2.52). Thus, NDDO approximation involves a large number of integrals to be computed, though the number is less than that of the initial SCF equations by an order of magnitude.

INDO approximation introduces simplifications to (2.52) in such a way that two-center integrals of the type $(\mu_A\nu_B|\lambda_A\sigma_A)$ are retained only if they have large values in the matrix of the interelectronic interaction.

$$(\mu_A\mu_A|\lambda_B\lambda_B) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu_A\mu_A|\lambda_B\lambda_B) \qquad (2.56)$$

Pople, Beveridge and Dobosh [1] proposed the computation of two-center integrals by using s-functions, i.e., s-orbitals with the corresponding quantum numbers:

$$(\mu_A\mu_A|\lambda_B\lambda_B) = \gamma_{AB} = (nS_A\ nS_A|mS_B\ mS_B) \qquad (2.57)$$

In the INDO version proposed by Brown and Roby [51, 52] the values of two-center coulomb integrals are used. Such

integrals are averaged separately relative to AO of each type are calculated using the corresponding AO of the valence shells of A and B atoms, e.g.,

$$\gamma_{AB}^{sp} = 1/3 \sum_{\alpha=1}^{3} (nS_A\ nS_A | mP_B^{\alpha}\ mP_B^{\alpha}) \qquad (2.58)$$

where $\alpha = x, y, z$.

CNDO is the most familiar version of ZDO approximation. Besides condition (2.56), CNDO introduces additional limitations to (2.52). Thus, in CNDO approximation only the following one-center integrals of the matrix of interelectronic interaction are taken into account.

$$(\mu_A \nu_A | \lambda_A \sigma_A) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu_A\mu_A | \lambda_A\lambda_A) \qquad (2.59)$$

Equations (2.54) and (2.55) are also rewritten as follows:

$$F_{\mu_A\nu_B} = H_{\mu_A\nu_B} - 1/2\ P_{\mu\nu}\gamma_{AB} \qquad (2.60)$$

where $$P^B = \sum_{\lambda}^{B} P_{\lambda\lambda} \qquad (2.61)$$

Solution of SCF equations by ZDO approximations leads to considerable reduction of computational work. Besides, there are additional semi-empirical techniques for the evaluation of the terms in the SCF equations.

In the most widely accepted version of CNDO which was proposed by Pople, Santry and Segal [1], the following parameterization is used.

$$H_{\mu_A\mu_A} = \langle \mu_A | -\frac{\nabla^2}{2} - V_A | \mu_A \rangle - \sum_{B\neq A} \langle \mu_A | \hat{V}_B | \mu_A \rangle$$
$$\equiv U_{\mu\mu}^{A} - \sum_{B\neq A} V_{AB} \qquad (2.62)$$

where $U_{\mu\mu}^{A}$ is the diagonal matrix element of the core hamiltonian of atom A for AO ϕ_{μ_A} and $U_{\mu\mu}^{A}$ is evaluated from the

ionization potential of atom A corrected for the charge it possesses in the molecule (i.e., CNDO/1 version:

$U^{A}_{\mu\mu} = -I_{\mu} - (Z_A - 1)\gamma_{AA}$).

In CNDO/2 approximation $U^{A}_{\mu\mu}$ is determined from the ionization potential I_{μ_A} and the electron affinity A_{μ_A}, i.e., as the orbital electronegativity according to the Mulliken scale.

$$U^{A}_{\mu\mu} = -1/2(I_{\mu_A} + A_{\mu_A}) - (Z_A - 1/2)\gamma_{AA} \qquad (2.63)$$

V_{AB} values characterize averaged interactions of any AO ϕ_{μ_A} of atom A with potential V_B created by atom B in the molecule. V_{AB} is estimated as:

$$V_{AB} \approx -Z^{*}_{B}\,\gamma_{AB} \qquad (2.64)$$

The off-diagonal elements of the core matrix are:

$$H_{\mu_A\nu_B} = \langle \mu_A \left| -\frac{\nabla^2}{2} - \hat{V}_{AB} - \hat{V}_B \right| \nu_B \rangle - \sum_{C \neq A,B} \langle \mu_A | \hat{V}_C | \mu_B \rangle \qquad (2.65)$$

Atomic bonding parameters β^{o}_{AB} are introduced and are supposed to be dependent only on the properties of A and B atoms. Thus, the expresion for the off-diagonal elements becomes:

$$H_{\mu_A\nu_B} = \beta^{o}_{AB}\, S_{\mu_A\nu_B} \; ; \quad \beta^{o}_{AB} = 1/2\,(\beta^{o}_{A} + \beta^{o}_{B}) \qquad (2.66)$$

Besides, direct computations on s-functions as in CNDO/2 method, the Pariser-Parr relation [53] is applied for the evaluation of the one-center integrals enetring the matrix of interelectronic repulsion in (2.14).

$$\gamma_{AA} = I_A - A_A \qquad (2.67)$$

and for two-center integrals empirical relations of

Mataga-Nishimoto [54] are used:

$$\gamma_{AB} = \left[R_{AB} + \frac{2}{\gamma_A + \gamma_B} \right]^{-1} \qquad (2.68)$$

or Ohno relation [55] is used.

$$\gamma_{AB} = \left[R_{AB}^2 + \left[\frac{2}{\gamma_A + \gamma_B} \right] \right]^{-1/2} \qquad (2.69)$$

The higher sensitivity of calculations to a selected system of atomic parameters caused the development of the whole series of different parameterizations which differ in the way the atomic parameters are selected and in the computation of β_{AB}^{o} to correctly reproduce the definite characteristics of the system under study: binding energy, CNDO/SW [56], CNDO/BW [57], electronic spectra, CNDO/S [58] and so on.

The various approximations of LCAO MO SCF equations within the framework of the CNDO version led to the development of a variety of computational schemes that ensure the accurate reproducibility of the definite characteristics of molecular systems.

However application of such techniques for the evaluation of other characteristics which are taken into account in the method may lead to absolutely distorted predictions, i.e., complete discrepancy with experiment. Hence, to calculate new characteristics it is necessary to apply a new computational scheme with its own parameterizations. Such an approach essentially means the use of the whole set of different computational schemes to give a complete description of the system. Each of the schemes fairly describes only characteristics and class of parameters incorporated in the

method. It is evident that such a trend leads to specialization of semi-empirical methods of quantum chemistry.

Hojer and Meza made an enormously interesting approach to construct such schemes to obtain reasonable results for various properties of molecular systems containing atoms up to bromine. Such a broad scale of studies required the development of sufficiently simple computational schemes with the least possible number of parameters. Bond energies, dipole moments, ionization potentials, molecular geometries and barriers to internal rotations of several molecules predicted by such schemes are in satisfactory agreement with experimental data. However, such schemes have not been developed further.

3. QUANTUM-CHEMICAL DESCRIPTION OF CLUSTERS

3.1. INVESTIGATION OF BULK AND SURFACE PROPERTIES OF SOLIDS

Theoretical study of any electron-nuclear system is based upon the solution of the Schrödinger equation which gives the possibility to describe the system by its wavefunctions. However, for many electron systems exact solution of the Schrödinger equation is impossible. Thus, for practical applications several simplifications must be introduced in order to get approximate solutions to the problem. In the case of solids a possible simplification is made by considering a solid as a system consisting of many electrons in the field of the atomic nuclei of the solid. Such calculations are important for the most exact elucidations of the electronic (band) structure of a solid, the nature of its bonding, electrical conductivity, work function and optical adsorption. In an alternative approach a solid is considered as a system consisting of atoms and the properties and interaction modes of the constituent atoms govern the electronic structure of the system.

Quantum chemistry of solids is based upon various methods [4, 59 - 62]. Such quantum chemical methods are used for adequate description of the bulk properties of solids, the influence of local surface defects on the band structure, densities of electronic states and other properties of solids. Quantum theory is very important not only to study the electronic structure of the crystalline and amorphous surfaces of different nature but also to gain a better insight into adsorption processes [4, 63]. However, quantum-chemical

calculations of adsorption have been fulfilled only for very simple adsorbents.

Methods of molecular quantum chemistry [59] are applied to molecular models to study complicated complexes on crystal and amorphous surfaces and systems containing defects of various kinds. Quantum-chemical study of solids requires abstarction of fragments or clusters containing the structural elements of the modeled solid from the solid matrix [64]. The cluster presentation of solids simplifies not only modeling but also interpretation of theoretical results. Consideration of adsorption processes demands that the factors governing the surface states must be taken into account. In the limiting case of one-point adsorption the surface site is modeled by one atom [65] and the two-point- by two atoms [66]. Quantum-chemical parameters of such atoms are selected as atomic parameters or may contain corrections on the atomic state in the bulk or at the surface of the solid. However, the interactions of adsorbate-adsorbent is extremely deformed in this case because atom interacts not only with the nearest surface atoms but also with the more remote ones [67 - 69]. Meanwhile from the local character of adsorbate-adsorbent interaction it can be inferred that the model of quasi-isolated molecule may contain relatively small number of atoms and simultaneously reproduces the peculiarities of the adsorption process quite satisfactorily [4].

Generally the choice of the cluster as a model for a solid is rather ambiguous. Most importantly, the model should take

into account both the peculiarities of the object and the borderline conditions that arise when the bonds are artificially cut. Abstarction of the cluster from the condensed system leads to the problem of borderline effects which cause the appearance of localized energy states on borderline atoms and disposed in the forbidden band [70]. Besides, borderline effects cause artificial heterogenity of electron distribution on spatially equivalent atoms in the macrosystem [71 - 73]. Omission of the borderline effects or their rough compensation leads to the discrepancy between the model and the object studied. It is natural that if rather large clusters are considered, the influence of the lattice termination effects on the local properties of a definite site disposed far from the borderlines of the cluster will be small [72]. However, as the cluster size is increased the computational difficulties become quite enormous.

One of the possible ways for at least partial compesation of the borderline effects involves termination of the broken bonds by hydrogen atoms, leading to substitution of the nearest neighbours outside the cluster [74]. However, even in this case heterogenity of electron distribution is preserved and this inevitably leads to non-adequate description of the properties of the solid.

If the broken bonds are not terminated at all the description is very rough except for some narrow range of properties to give qualitative description of adsorption complexes [74].

Models of condensed systems and adsorption complexes based upon separate surface sites only and with the nearest neighbours ignored [75] seem to be oversimplified and thus bear no information on the role of solid matrix in adsorption phenomena.

The set of recommendations for the construction of a model may be classified as follows [64].

1. Parameterization to ensure equivalence of the definite properties of the cluster and the modeled solid [76,77];

2. Imposition of borderline conditions to ensure equivalence of all the physically similar cluster atoms [67, 68, 78];

3. Ensuring the convergence of the results as the cluster size increases [79].

3.2 QUASI-ISOLATED MOLECULAR MODEL OF SILICA

It has been pointed out that one of the basic surface sites of silica is the hydroxyl group. Likewise, the first cluster for silica consisted of only two atoms - hydrogen and oxygen, so that the model represented hydroxide anion, cation or radical. Certainly this model gives the minimum amount of information concerning the influence of the bulk phase and is considered to be naive. Nonetheless, it still has practical significance because it gives the most general trends of electronic and spectral behaviour of adsorbed organic substances.

The adsorption process for oxygen, nitrogen and nitric oxide on silica gels was modeled by surface complexes of O_2, N_2 and NO with OH, OH^- or OH^+ frameworks [80]. Their configurations were found to be linear or T-shaped. The CNDO/2 method predicts the linear configuration to be more stable. Nitric oxide is coordinated via nitrogen atom. OH-group possesses very weak proton-donor ability. The linear configuration is the most stable for carbon monoxide and coordination is via carbon atom [74].

The CNDO/2 method was also applied to study the interaction of benzene and toluene molecules with hydroxide anions [81]. For benzene the OH^- groups lie vertically under the C-C bond of benzene at a distance of 0.187 nm with the stabilization energy of -22.7 kJ. For toluene the OH^- anion is vertically under the methyl group bearing carbon atom of the benzene ring

at a distance of 0.160 nm with the stabilization energy of 39.9 kJ.

Model CNDO/S calculations were performed to describe the electronic spectra of the complexes of p-aminobenzene with hydroxide anions [82]. Both weak-basic and weak-acidic OH groups cause bathochromic shift of absorption bands. Thus, electronic spectra are not able to differentiate protic from aprotic groups. These three examples were extracted from numerous sources to show that the oversimplified clusters give only a limited volume of information about the behaviour of surface complexes.

3.3 CHARGED CLUSTERS AND CLUSTERS WITH TERMINAL HYDROGEN ATOMS

The preceding discussions revealed that the basic task in cluster modeling is to formulate a molecular model of the solid phase [83].

Molecular models facilitate quantum-chemical description of catalytic systems and the processes occuring at the electronic level (σ, π-, covalent, ionic and donor-acceptor interactions) [84]. Applications of quantum- chemical methods to catalysis specifically demands the study of the elementary act of a reaction stage including chemisorption (coordination stage). Structural problems in chemisorption may be subdivided into the following three groups [85].

(i) calculation of the electronic structure of the active sites - structural defects and admixtures, surface functional groups, and trends of their electronic structure under chemical modification of the catalyst surface;

(ii) estimation of the location of chemisorption of atoms and molecules, the geometry and energetics of chemisorption, comparison of chemisorbed states, estimation of the energy barriers of the transitions between these surface states, elucidation of the features of chemisorption (molecular or dissociative, activational or non-activational), determination of the degree of covalency or ionicity in chemisorbed states, analysis of modification of these parameters as a function of surface coverage and study of the possibility of formation of ion-transfer structures or charged molecular fragments (carbonium ions) [86];

(iii) direct analysis of different pathways in the reactions of adsorbed molecules at the surface or in the reactions of the adsorbed molecules with the surface structures, comparison of Eley-Rideal- and Langmuir-Hinshelwood mechanisms of adsorptions, consideration of the stepwise and deformation mechanisms and study of the dependence of the reaction pathways on various catalyst modifications [87].

As mentioned before the basic drawback of the cluster approach is the existence of the broken (cut) chemical bonds at the borderline between the terminal cluster atoms and the rest of the lattice.

Calculated characteristics and collective properties of the solid such as electronic structure Fermi energy levels, ionization potential, electron affinity, atomization energy converge too slowly with the cluster size. Cluster approach is quite satisfactory in chemisorption calculations when local interactions are the determining factors.

3.4 CLUSTERS CONTAINING QUASI- (PSEUDO-) ATOMS

A method of cluster modeling was proposed [88, 89] that uses pseudo atom A instead of terminal cluster atoms to compensate for borderline effects. The quantum-chemical parameters of the pseudo-atoms can be varied in a wide range. Thus, the parameters are chosen in such a way that a molecular cluster description will be compatible with the actual solid state. Besides, it is possible to discuss trends of the electronic structure of the cluster and the adsorbate in the process of such variation of parameters. Hence within the framework of the proposed approach different possibilities of the cluster environment existing in real systems can be discussed and also the influence of different factors on the state of adsorbed molecules can be analyzed.

From the methodological point of view it is of interest to study the stability of quantum-chemical solutions of different properties as a function of the cluster size and the parameters chosen for borderline pseudo-atoms. The first set of properties includes electronic density distribution, energy diagram, the composition of occupied and vacant MOs and the energy differnce between HOMO and LUMO while the second set of properties constitutes the characterstics of surface acidity. The solutions appeared to be stable relative to the first set of properties [90] whereas the variation of the cluster size and the nature of the pseudo-atoms leads to substantial discrepancy in surface acidity parameters [91]. This is a basic drawback of the proposed approach. The approach seems to be adequate only for comparison of results obtained for

optimal structures of clusters of the same type or cluster with optimal parameters.

CNDO/BW method was used to study the interaction of water molecule with surface hydroxyl group of silica gel represented as cluster $HOSi(OA)_3$ [88]. It was shown that proton exchange reaction occurs through the intermediate that has two equivalent protons (C_{2v} symmetry). The reaction does not involve the intermediate with three equivalent protons (C_{3v} symmetry).

The cluster model $HOSi(OA)_3$ appeared to be quite effective for the discussion of the properties of terminal hydroxyls [92].

A group of calculations generalized in [93] were based upon firm theoretical principles. The borderline atoms are called quasi-hydrogen atoms and their parameters were thoroughly optimized to give equal electronic densities on the central and peripheral atoms in the clusters $(H^*_3SiO)_3SiOH$, $(H^*_3SiO)_2Si(OH)_2$, $H^*_9Si_8O_{10}(OH)_3$, where H^* is the quasi-1s-atom with a non-standard set of quantum-chemical parameters. Adsorption of several electron-donors was studied. Such studies led to the conclusion that formation of weak surface hydrogen bonds is of low probability. The mode of electronic distribution in the plane passing through the hydroxylated silicon atoms of the cyclic framework suggests the possibility of non-activation or penetration of the smaller electron-donor molecules into the hexagonal cavities followed by their localization in the proximity of the least shielded silicon atoms. Unfortunately, these calculations were mostly based on

the application of CNDO/2 – spd basis set and are not suitable for rigorous comparison of the results of this thesis. Under the preceding conditions the coordination number of silicon atom is increased to five or six as is known from some ab initio calculations [94] but sometimes the results cause some doubts especially when theoretical and experimental data are analyzed together. In the quasi-hydrogen approach adsorption complexes are usually considered by the method of atom-atom potentials and SCF perturbation theory. Six kinds of water adsorption complexes were considered [95]. The conclusion is that H-bonded adsorption complexes are weak but the stability of donor-acceptor complexes increases by a factor of 3 - 5.

3.5 A FORTRAN-IV COMPUTER PROGRAM FOR CNDO AND INDO CALCULATIONS [1].

Several years have already elapsed since the computer has become a universal and highly versatile tool of research. The computer plays a very special role in computational chemistry, particularly in quantum chemistry which exclusively involves enormous computational tasks that are virtually impossible without the intervention of modern high speed computers.

Accordingly, most of the data reported in this thesis were generated by computers. In this part, a qualitative description and brief assessment of the computer program originally developed by Pople and co-workers [1] for approximate molecular orbital calculations within the framework of CNDO and INDO will be given. For the present study this program and its extended version INDO88 were adopted and rewritten for execution on the NCR system V-8555 mainframe digital computer at AAU. The programs are also saved on the auxiliary storage device (magnetic disk) of the mainframe computerat the Systems Design and Data Processing Center (SDDPC) of AAU.

The program CNINDO was written for the IBM system 360/65 digital computer and is capable of computing molecular wavefunctions for open and closed shell molecules containing atoms from H to Cl (CNDO) and from H to F (INDO).

Allowed AO basis functions are: one for hydrogen (1s), four each to the elements Li through F (2s, $2p_x$, $2p_y$, $2p_z$) and nine each to the elements Na through Cl (2s, $2p_x$, $2p_y$, $2p_z$, $3d_{z^2}$, $3d_{xz}$, $3d_{yz}$, $3d_{xy}$, $3d_{(x^2-y^2)}$.

The operation of the program requires input of molecular data with proper formats for identification and comments; specification of method (CNDO or INDO and open or closed options depending upon the type of calculation desired); number of atoms, charge and multiplicity; and atomic number and cartesian coordinates of each atom. Then the MAIN calls the subroutines (COEFFT and INTGRL) which evaluate the integrals needed for MO calculation and the subroutines which perform MO calculation (HUCKCL, SCFCLO, CPRINT for a closed-shell molecule; HUCKOP, SCFOPN, OPRINT for an open-shell molecule).

The qualitative description of the function of each subroutine is outlined as follows:

COEFFT assigns the coefficients used in the evaluation of overlap and coulomb integrals of the type expressed by previous equations (2.1).

In subroutine INTGRL the overlap matrix and coulomb interaction matrix are computed and stored in labelled common arrays.

The subroutine HARMTR generates the rotation matrix which is used to transform the overlap integrals from a local diatomic coordinate system to the molecular coordinate system.

Subroutine HUCKCL first forms a ZDO EHT-type approximation to the Fock matrix and after diagonalization of this matrix an initial density matrix is constructed which in turn is taken as an input by the subroutine SCFCLO. The iteration continues until the electronic energy converges to 10^{-6}. A limit of 25 iterations is allowed.

Subroutine CPRINT computes dipole moments, atom densities and nuclear repulsion energies.

HUCKOP is similar to HUCKCL except that α and β density matrices are formed from the initial Huckel eigenvectors. All computed molecular properties are stored in their respective predefined storage locations (labelled common arrays).

SCFOPN has the same basic structure as SCFCLO except that it makes allowance for P^{α}, P^{β}, F^{α} and F^{β}.

Subroutine OPRINT calculates the same properties as CPRINT. Besides, it forms a spin density matrix from which it computes isotropic hyperfine coupling constants.

The subroutines SS, HARMTR, RELVEC. FACT, BINTGS, AINTGS and MATOUT are called only by INTGRL.

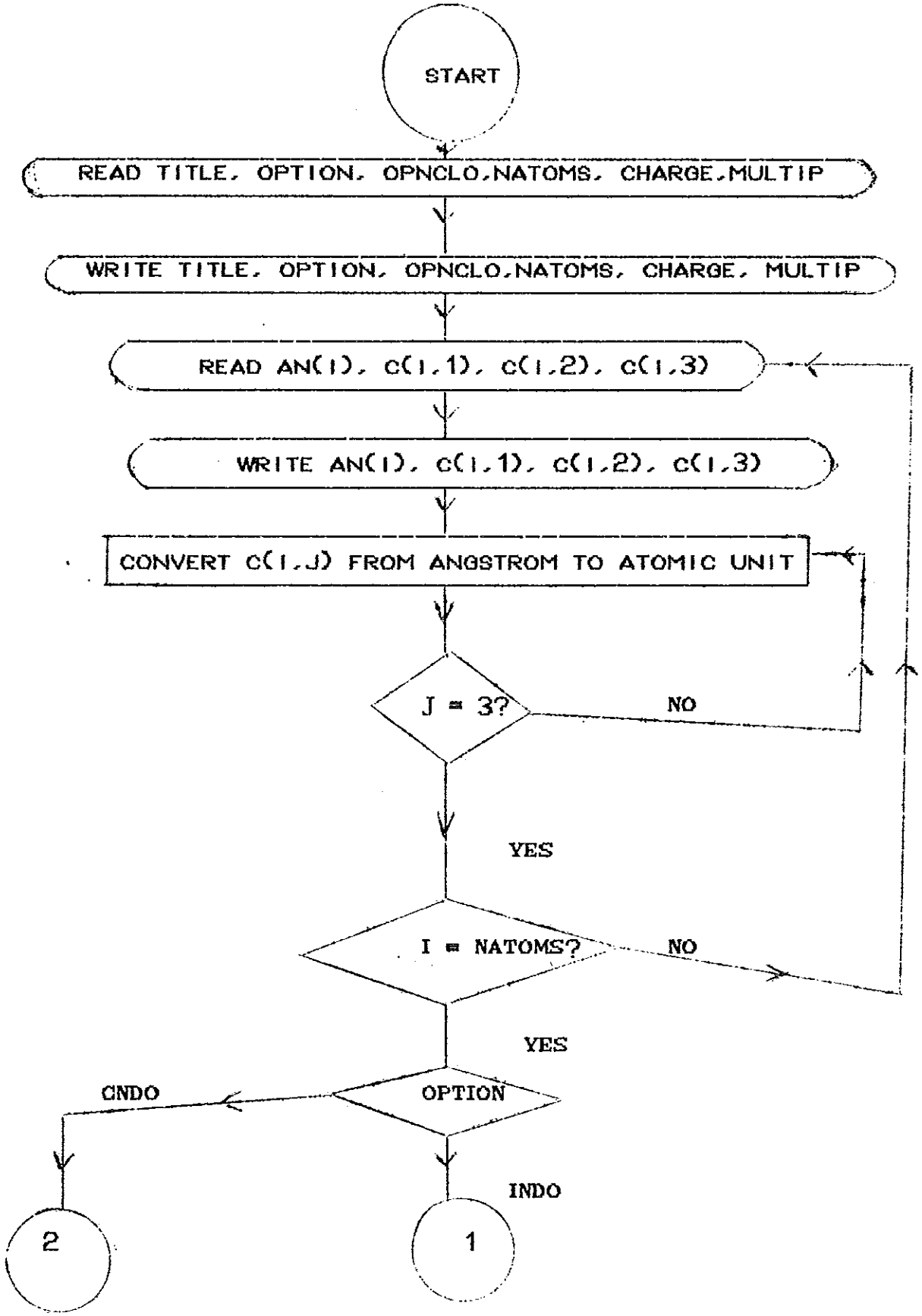
EIGIN, SCFOUT and EIGOUT are needed in the subroutines HUCKCL through OPRINT.

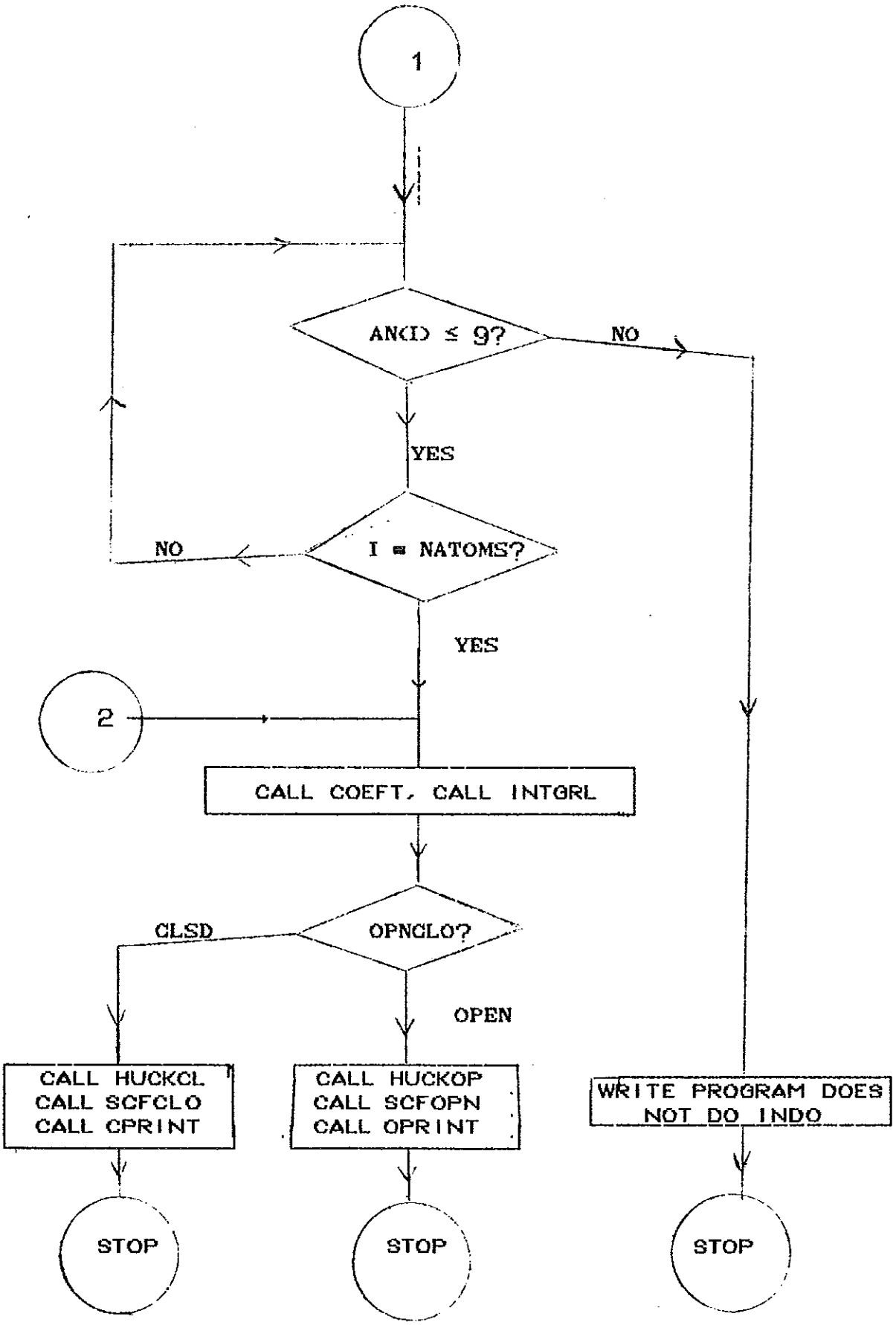
For further details, a complete listing of the program is given in Appendix E.

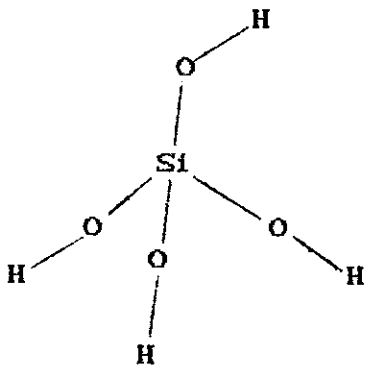
A careful survey of the program list with a closer look at each segment will certainly indicate the role and out puts of the subroutines. A generalized flow chart of the MAIN program, CNINDO, is given below.The flow chart is merely a summary of the foregoing discussions using

programming symbolism to show the hierarchy of the subroutines and flow of information in the program. Flow charting is usualyy required at the initial stages of program development. Therefore, a detailed and more sophisticated flow chart is ommited as it gives no additional information in lieu of the complete program list in Appendix E.

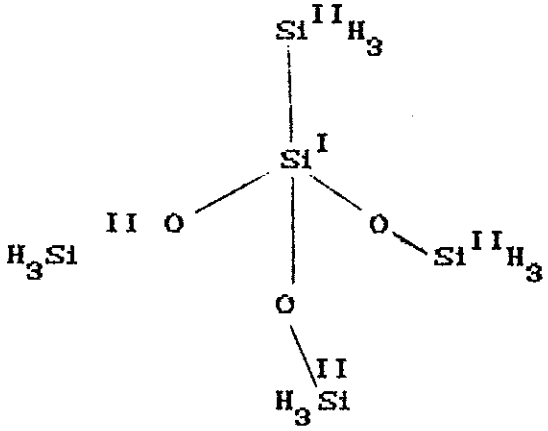
GENERALIZED FLOW CHART OF PRGRAM CNINDO [1].



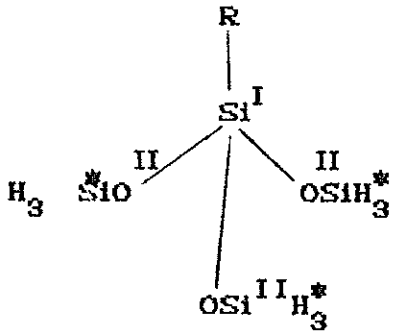

1
ANCI ≤ 9?
NO
YES
I = NATOMS?
NO
YES
2
CALL COEFT, CALL INTGRL
OPNCLO?
CLSD
OPEN
CALL HUCKCL
CALL SCFCLO
CALL CPRINT
CALL HUCKOP
CALL SCFOPN
CALL OPRINT
WRITE PROGRAM DOES NOT DO INDO
STOP
STOP
STOP



(a)



(b)



R = $OSiH_3^*$, OH, Cl, NH_2, MCl_n, ...

(c)

Fig. 3. Cluster models of Silica

(a). Orthosilicic Acid

(b). Initial Approach to Cluster Model of Silica

(c). Cluster Model of Silica by quasi-Atom approach

4. RESULTS AND DISCUSSIONS

4.1. CLUSTER MODEL OF SILICA GEL

As was pointed out before the majority of articles on silica have certain limitations. The treatments are inaccurate and do not correctly reproduce the electronic distribution on the atoms because they do not fully take into account the influence of the solid environment on the fragment chosen as the cluster model. This defficiency is also intrinsic for pseudo-atom approach [88], in spite of the illustrative character and simplicity of the model which gave it wide popularity in quantum chemical research. The way the influence of the solid environment on the cluster fragment is treated has a series of drawbacks. In the first place, the quantum chemical parameters of pseudo atoms are varied in a rather wide range. There is a limitation on the equality of the electron densities of the physically equivalent atoms. No other limitations are imposed on the parameters.

Consequently, the parameters of pseudo-atoms substantially depend on the geometry and size of the cluster, which in the authors' opinion [90, 91] limits the construction of the cluster model.

Termination of the unsaturated bonds of the Si, O- fragment by hydrogen atoms [74] disposed in the sites of the nearest bonded neighbours could compensate the unsaturation but this is an oversimplification and such simple approaches should lead to a predetermined wrong electron density distribution partly due to the absence of surface siloxane groups. The problem is preservation of its simplicity and illustrative

character along with minimization of its principal drawbacks.

In the case of silica gel such an approach may imply substituion of one of the silicon or oxygen atoms by a hydrogen atom.

In the case of $Si(OH)_4$ (fig. 3a) silicon is substituted for hydrogen atom producing a molecule that differs from orthosilicic acid essentially by the estimated O-H bond length. In other words, the resulting molecule is the analogue of the silicon containing molecule, $Si(OH)_4$. Naturally, this cluster describes the properties of silica gel very roughly . In the first place the model does not contain the siloxane group whereas the geometry of the siloxane group, i.e., the Si- O bond length and the SiOSi bond angle, is known to be responsible for a variety of structural modifications of silica [23].

It is possible to extend this cluster by adding one (fig. 3b) or more coordination spheres. The resulting cluster contains the SiOSi groups and thus, it gives a better description of the system. Charge equivalence of Si^I and Si^{II} atoms may be achieved by increasing the cluster size through the addition of oxygen and silicon atoms in the outer coordination spheres [79]. However, in this case the cluster size of the system will be too extended leading to enormous computational difficulties.

These difficulties may be overcome if pseudo-atoms [96] with arbitrary basis set and atomic parameters [97] are used instead of hydrogens (fig. 3b) with INDO parameters [1]. The parameters necessary for INDO calculations may be chosen in

such a way that the most characterstic features of the system studied: electron distribution, width of the forbidden band, ionization potential, cohesion energy, etc., are correctly reproduced. There is a more or less similar approach to study the adsorption of hydrogen on tungsten [98]. This is especially the case when parameters of the borderline atoms in a cluster are modified to produce a uniform charge distribution over the whole fragment.

Cluster (fig. 3b) was selected for theoretical study of the properties of silica. The hydrogen atoms in fig. 3b were replaced by quasi-hydrogens $(H)^*$. As was indicated earlier quasi-hydrogens have parameteters substantially different from the INDO standard sets. Directed variaton of the parameters is designed to reproduce the influence of the outer part of the modeled solid (this was not taken into account before) on the mode of electron distribution in the Si, O- fragment. Si^I and Si^{II} atoms are equivalent in the macrosystem. Hence, by varying the set of parameters for H^* it is possible to achieve unfform electron distribution on Si^I and Si^{II} atoms. This cluster may be used as a theoretical model for a stationary state description of the electronic characterstics of the system.

Substitution of the $OSiH_3^*$ group by other groups or atoms keeping the parameters of H^* constant gives the possibility to study the influence of the surface on the electron distribution in the modeled solid. The cluster containing a functional group allows to study the role of the surface active sites in adsorption and heterogeneous catalysis.

The proposed cluster model (fig. 3c) of silica may easily be used to study the processes of chemical modifications of highly dispersed silicas. This has a great practical importance.

The quality of the quantum-chemical description of a molecular system depends to a large extent on the accuracy of the MO construction. This process should ensure not only the minimum total energy of the system but also calculation of the electronic structure using optimum geometries at the given level of approximation [99]. This is especially important in reaction mechanism studies and activation energy estimations for different processes.

Optimization of geometry for $Si(OSiH^{*}_{3})_4$ was fulfilled using parameters obtained from the equilibrium geometric structure of β-cristobolite [7]. The procedure employs the algorithm of direct minimization of the energy functional over all the independent coordinates by the method of configurations [100]. To reduce the computational labour techniques based on the decrease of the accuracy of self-consistent cycle were used.

The borderline effects which manifest themselves in the non-uniform electron distribution of the Si^{I} and Si^{II} atoms of the cluster (fig. 3b) are eliminated by replacing quasi-hydrogens for hydrogen atoms. Determination of parameters for quasi hydrogens is an independent task.

The variation of parameters of quasi-atoms for the cluster $Si(OSiH^{*}_{3})_4$ containing 48 AO's is a rather complicated problem as it involves three independent variables:

(i) the average (arithmetic mean) of the orbital ionization potential and electron affinity: 1/2 (I_H^* + A_H^*);

(ii) the resonance atomic parameters and

(iii) the Slater exponent.

For such a cluster a single computation alone requires about 15 minutes of computer time. Self-consistency is achieved only after 18 - 20 iterations. Hence, after four iterations the Hartree procedure of acceleration of self-consistency was applied. This remarkably reduces the computer time. The dependence of the electronic densities of atoms in the cluster $Si(OSiH_3^*)_4$ on the independent variables or parameters, i.e., μ_H^{0*}, 1/2(I_H^*+ A_H^*) and β_H^{0*} can readily be seen from equations 2.34 or 2.36, equations 2.62 or 2.63 and equation 2.66, respectively, which together with other equations discussed in section 2.3 allow the evaluation of the desired properties. More specifically, the secular equations arising from the Hartee-Fock-Roothaan methods contain variation coefficients which depend on the matrix elements of the Fockian ($F_{\mu\nu}$ = $H_{\mu\nu}$ + $G_{\mu\nu}$(eqn. 2.12)) and the Slater exponent appears in the basis functions (eqns. 2.34 or 2.36) used for the evaluation of the matrix elements $H_{\mu\nu}$ and $G_{\mu\nu}$. In particular, 1/2(I_H^*+A_H^*) is encountered as a parameter in $H_{\mu\mu}$ (eqns. 2.62 and 2.63) and β_H^{0*} is incorporated into $H_{\mu\nu}$ (eqn.2.66) whereas μ_H^{0*}enters all the matrix elements. Thus, the variation coefficients are solved in terms of the matrix elements containing the parameters for quasi-hydrogens and are used to form a density matrix (eqn. 2.15) the elements of which are functions of the parameters described above.

In other words, the parameters for quasi-hydrogens must be optimized in contrast to the standard set of INDO parameters estimated semi-empirically for hydrogen atoms.

Therefore, the search for optimum parameters of H^* reduces to minimization of the following functional:

$$f\left[1/2\ [I_{H^*} + A_{H^*}],\ \beta_{H^*},\ \mu^{o}_{H^*}\right] = \left| \sum_{i \in Si}^{I} P_{ii} - \sum_{j \in Si}^{II} P_{jj} \right| \qquad (4.1)$$

where $\sum_{i \in Si^I}^{I} P_{ii}$ is the electronic density on Si^I atom and

$\sum_{j \in Si^{II}}^{II} P_{jj}$ is the electronic density on Si^{II} atom.

The energies of the cluster before and after optimization of the parameters were found to be -95.3814 and 97.0446 a.u., respectively, which on comparison with experimental data led to the justification of the need for optimization of the parameters.

The method applied to solve conformational problems (geometry optimization) is not applicable for finding the parameters of H^* atoms because the diagonal elements of the density matrix depend on the variation of parameters in different ways. This circumstance makes it quite difficult to choose the iteration step. Moreover, if the initial approximation is not good the method will lead to low convergence. Hence, minimization of the functional (4.1) was fulfilled using the method of variable metrics [100], (Appendix C) which is based upon direct calculation of derivatives using difference scheme (Appendix B).

Table 1. Calculated optimum parameters for H^* and standard parameters for H (for notations see the text)

Atom	1/2(I + A, eV)	β °eV	μ , a.u.
H	7.1761	-9.0	1.200
H^*	9.3050	-7.9	0.876
H^{*a}	8.2701	-7.9	0.826

[a] CNDO spd [93].

Table 2. Charges on atoms (q) in silica gel clusters

No.	Cluster	Basis	$q_{Si\,I}$	$q_{Si\,II}$	q_O	$q_{H(H^*)}$
1	$Si(OH)_4$	sp	1.694	-	-0.628	0.204
2	$Si(OH)_4^a$	spd'	0.984	-	-0.496	0.250
3	$Si(OSiH_3)_4$	sp	1.348	0.946	-0.694	-0.211
4	$Si(OSiH_3)_4^a$	spd'	0.385 (0.780)	0.550 (0.568)	-0.340 (-0.357)	-0.103 (-0.140)
5	$Si(OSiH_3^*)_4^a$	sp	1.301 (0.805)	1.301 (0.805)	-0.643 (-0.376)	-0.331 (-0.210)
6	$Si[OSi(OH)_3]_4$	sp	1.424	1.644	-0.681	0.204
7	Experimental		1.300	1.300	-0.650	-0.325[b]

[a] The data in brackets refer to CNDO spd results [93].

[b] The estimate for the oxygen atoms in the coordination sphere of the deepest layers in the bulk.

The values of the optimized parameters for quasi-hydrogens in $Si(OSiH^{*}_{3})_{4}$, based on β-cristobolite structure, are given in table 1 together with standard quantum-chemical parameters for hydrogen atoms.

As can be seen from table 1, the Slater exponents for H^{*} are less than μ_{H} for the normal hydrogen atoms. The more diffuse character of $\mu^{0}_{H^{*}}$ from [93] is due to CNDO spd calculations wherein the influence of the diffuse d-orbitals is incorporated in the basis set. Orbital electronegativity in the INDO sp calculations approach that of the oxygen atom much better than in the CNDO spd approach [93]. This is an indicative of the more adequate description of the bulk phase in the present work, since quasi-hydrogens stand for oxygens of the real silica.

The decrease in the orbital exponent of quasi-hydrogen to 0.876 a.u. leads to increased diffuse character of 1s-AO of the quasi-hydrogen in comparison with that of the normal hydrogen atom. This leads to the formation of a more effective bond with a bond distance shorter than that formed by a hydrogen atom. Meanwhile, the increase in the half-sum of the ionization potential and electron affinity is the measure of the increase in its electronegativity. It should be noted that this value is even higher than that for the p-orbitals of oxygen (9.111 eV). The oxygen atoms take direct part in the formation of the chemical bonds. Before proceeding to the consideration of the numerical results a brief discussion of the role of the outer vacant 3d-orbitals of silicon in the formation of a chemical bond will be given. spd and spd' basis

sets may be used [1] to account for the interactions arising from the 3d-orbitals. In spd basis set equal values of the orbital exponents of the 3s-,3p- and 3d-orbitals of silicon are used as if the 3d-orbital directly takes part in bonding [48, 49]. In the spd' basis set the orbital exponent selected for the 3d-orbital is much less than that of the 3s- and 3p-orbitals of silicon [101]. This is more realistic and may be qualified since it has a stabilizing effect on the chemical system as a polarizing addition. Analysis of the literature data shows that spd' calculations for silica systems have never been fulfilled. On the other hand spd - calculations [102] give highly overestimated results comprable with that of the forbidden band and thus, calculations employing the spd - basis set are usually inadequate.

All in all, the following clusters were studied in the indicatd basis sets:

(i) OH^-: sp - basis set

(ii) $Si(OH)_4$: sp - basis set was used

(iii) $Si(OH)_4$: spd' - basis set was used to study the influence of the 3d - functions in the basis set on the electronic and band structures.

(iv - v) $Si(OSiH_3)_4$: both basis sets were used to elaborate the non-uniform character of the electronic distribution and to illustrate that this system is a reliable and good precursor for a more refined model as well as to study the influence of 3d - polarization functions.

(vi) $Si(OSiH_3^*)_4$: sp - basis set was applied to obtain a reference used in subsequent calculations.

(vii) $Si[OSi(OH)_3]_4$: sp - basis set was used to determine whether termination of the borderline by O quasi-atoms is reasonable or not.

Considering charges on atoms (table 2) the discussion of the charge distribution is based upon the experimental data for the effective charges on silicon and oxygen atoms obtained by the method of annihilation of positrons for silica [103]. The initial geometric structures of $Si(OH)_4$ in the sp - basis functions were taken from x-ray structural data for β-cristobolite (R_{SiO} = 0.190 nm, R_{OH}= 0.150 nm, < OSiO = 109.5°, <HOSi = 180°) [7]. Optimization of geometry over the whole set of spatial variables led to R_{SiO} = 0.200nm, R_{OH}= 0.102 nm while the bond angles remained unchanged. Calculated charges are 1.30 for the silicon atom and -0.65 for the oxygen atom. Besides the use of the more sophisticated X_α SW calculations give a charge of 1.329 on the silicon atom. As may be seen the charge on the silicon atom in the model, $Si(OH)_4$, is an overestimation. Thus, this model is rejected as it has no potential use in the discussion of the electronic properties of silica. The trends in the optimized geometries are: R(SiO) = 0.196 nm, R(OH) = 0.103 nm, and the bond angles remain unchanged.

For $Si(OSiH_3)_4$ clusters the following β-cristobolite data were used: R(SiO) = 0.200nm, (R(SiH) = 0.162 nm, <OSiO = 109.5°, <SiOSi = 180°, <OSiH = 109.5°. Geometry optimization in the sp - calculations leads to R(Si) = 0.205 nm, <OSiH = 107.5°.

Table 3. Bond characteristics of cluster models of silica: bond orders (B), two-center covalent (E_{cov}) and ionic (E_{ion}) consitituents for Si-O bond, contribution of $d_\pi \leftarrow\!\!- p_\pi$ back-donation effect to Si-O bond.

No	Cluster	Basis	B_{SiO}	$B_{SiH(H^*)}$	E^{cov}_{SiO} a.u.	E^{ion}_{SiO} a.u.	$d_\pi \leftarrow\!\!- p_\pi$ contribution to SiO bond
1	$Si(OH)_4$	sp	0.724	-	-0.549	-0.114	-
2	$Si(OH)_4$	spd'	1.035	-	-0.884	0.0235	31
3	$Si(OSiH_3)_4$	sp	0.705	0.902	-0.513	-0.063	-
4	$Si(OSiH_3)_4$	spd'	1.088	0.897	-0.877	0.159	36
5	$Si(OSiH_3^*)_4$	sp	0.705	0.839	-0.486	-0.077	-
6	$Si[OSi(OH)_3]_4$	sp	0.700	-	-0.520	-0.040	-

Apparently, this model leads to non-uniform electron distributions on silicon atoms which are equivalent in the real system but the central silicon atom and the oxygen atom attain charges that are closer to the experimentally estimated values [103]. Hence, the cluster is considered as a precursor for a more adequate model of silica.

INDO results for geometry optimization in the spd' - basis set are: RSiO = 0.188 nm, R(SiH) = 0.166 nm, <OSiO = 109.5°, <SiOSi = 180° <OSiH = 103.1°. The resulting hypersurface contains underestimated charges on silicon and oxygen atoms and overestimated values of the $P_{\pi} \longrightarrow d_{\pi}$ contribution to the O - Si bonds. Thus, it appears that application of spd' basis set within the framework of INDO approxdmation is unreasonable for solid state modeling

In the proceeding discussions the basic model, $Si(OSiH_3^*)_4$, used in this work will be considered. The optimized geometric parameters were: R(SiO) = 0.205 nm, $R(SiH^*)$ = 0.162 nm, <OSiO = 109.5°, <SiOSi = 180°, <OSiH* = 107.5° and generally reflect the trends observed in β-cristobolite. Substitution of hydrogens by quasi - hydrogens equalizes the effective charges on the central and peripherial silicon atoms in good agreement with experimental data. This gives the first justification for the success of the model.

Finally, the following optimized geometric parameters were obtained for the cluster $Si(OSi(OH)_3)_4$ in the sp - basis set: R(SiO) = 0.204 nm, R(OH) = 0.102 nm, <OSiO = 109° <SiOSi = 180°, <SiOH = 180°. Non-uniform electron distribution was observed. Evidently, this is one of the consequences of

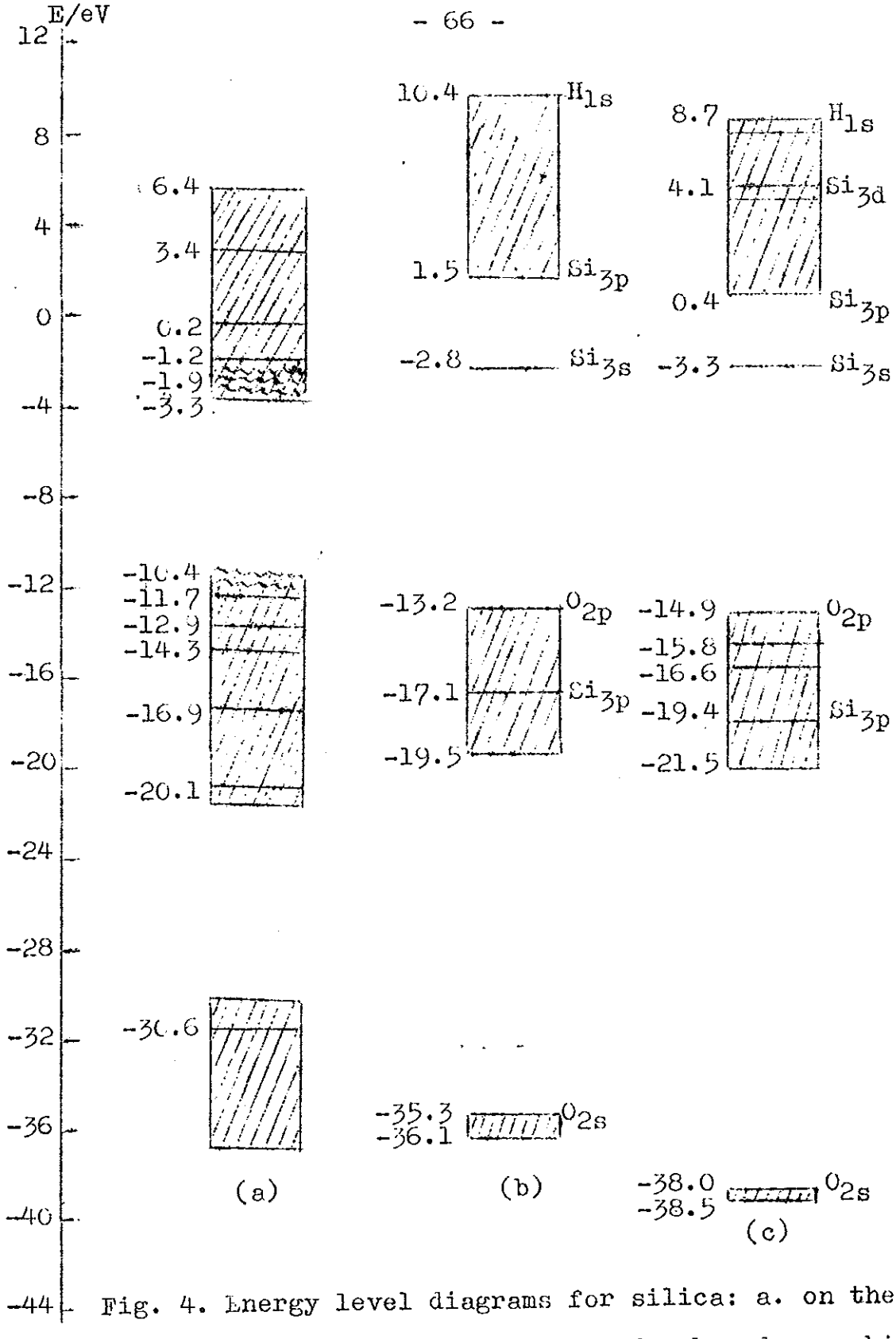
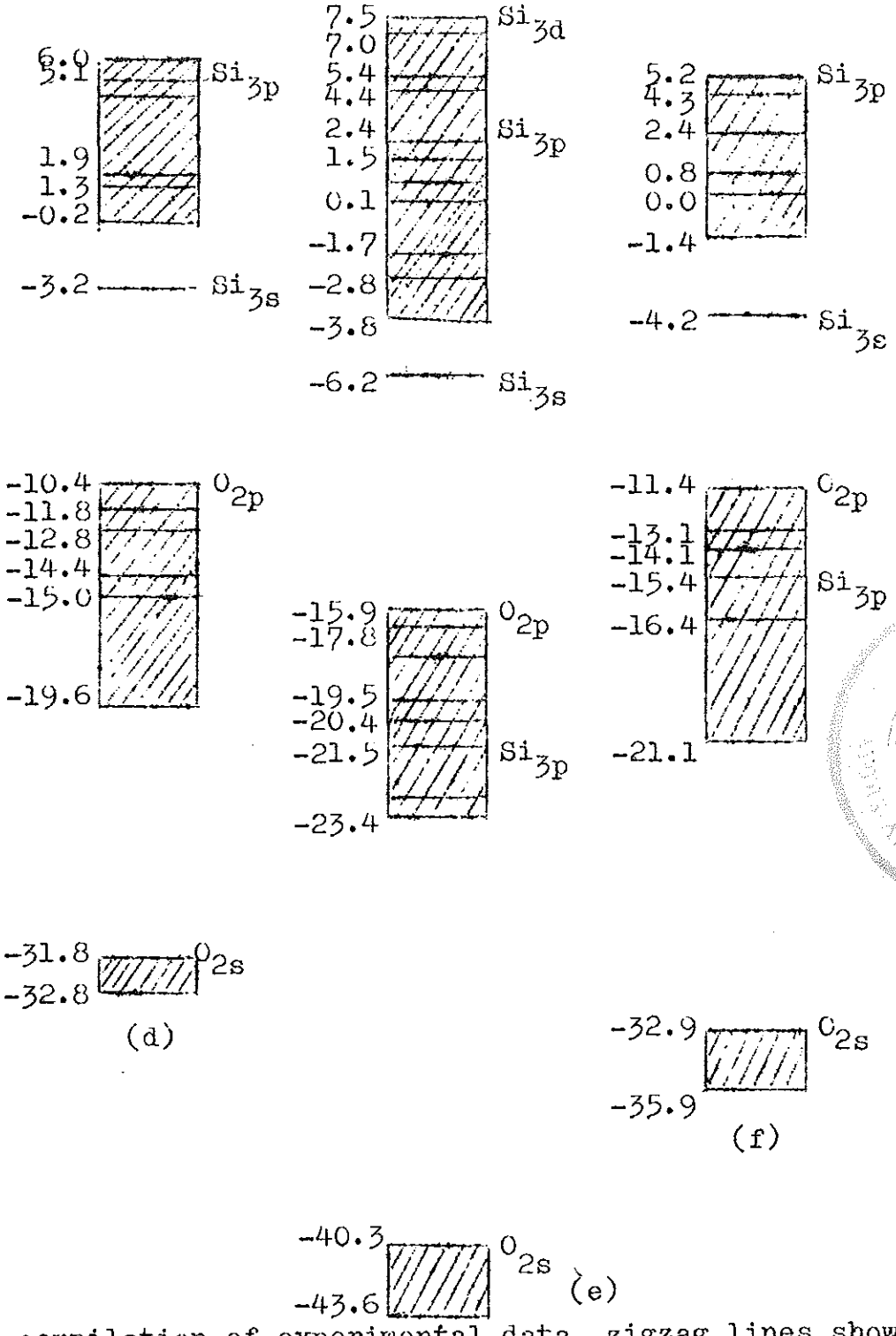
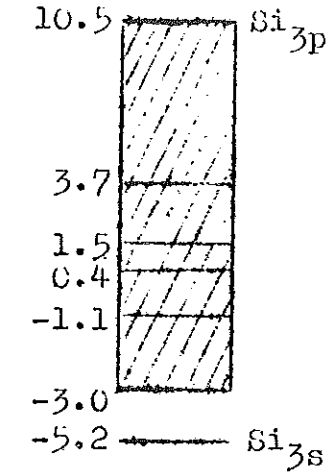


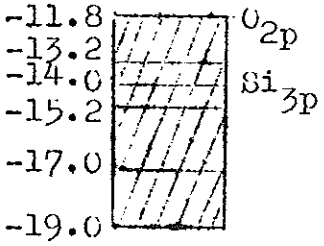
Fig. 4. Energy level diagrams for silica: a. on the basis of of experimental estimates for boundary orbitals; c. for $Si(OH)_4$ spd'; d. for $Si(OSiH_3)_4$ sp; e. for



compilation of experimental data, zigzag lines show the range

b. for $Si(OH)_4$, sp in the framework of INDO calculations; $Si(OSiH_3)_4$, spd'; f. for $Si(OSiH_3^*)_4$, sp; g. for $Si[OSi(OH)_3]_4$


10.5
Si 3p
3.7
1.5
0.4
-1.1
-3.0
-5.2
Si 3s


-11.8
-13.2
-14.0
-15.2
-17.0
-19.0
O 2p
Si 3p


-33.8
-35.7
O 2s

(g)

inaccurate treatment of the borderline effects.

The general trends of bond characteristics, especially that of the Si- O bond, are given in table 3 Analysis of this table reveals that only calculations in the sp - basis set reproduce the ionicity of the bonds in silica. Results derived from other basis sets are unsatisfactory. 'Even the spd' basis set gives eroneous results because the tabulated data indicate that there is a substantial $p_\pi \longrightarrow d_\pi$ character in the O - Si bond with non-ionic structures (the ionic contribution to the total energy is positive). In other words, the 3d - orbitals of silicon in the cluster are considered as the real bonding orbitals. However, such assumptions are unrealistic.

Further discussions and arguments in favour of the cluster, $Si(OSiH_3^*)_4$ may be obtained from a comparative analysis of the band structure of silica and the experimental data [18].

But before presenting theoretical data obtained in this work it seems reasonable to make some generalizations of the existing data with formulation of empirical schemes for electronic levels. Such an approach may serve as a reference tool for comparative analysis of the cuister model elaborated in this work.

Most of the information about the sequence of energy levels in amorphous silicas was obtained by spectroscopic methods.

The positions of the peaks in the valence band were determined by vacuum UV-, UV-, photoelectronic and x-ray photoelectronic spectroscopy. Vacuum UV - reflectance measurements [104 - 107] produced the following peaks:

-10.2, -11.7, -14.7, -17.0 and -20.5 eV.

Both kinds of photoelectronic spectroscopy revealed that the violet band has a width of 11 eV [108]. Several peaks were obtained below the lower edge of the valence band. The most interesting peaks for the present discussion are: -26.9 and -40.8 eV [108] and -30.6 eV [108,109]. The top of the valence band was estimated to be at -10.2 eV [110] or -10.6 eV [111]. There is a shoulder located at -11.7 eV [108,109] below the top of the valence band and the prominent peak is at -12.9 eV [108,111].

Photo conductivity data are usually employed to locate the bottom of the conduction band. The given data [110] reveal a band width (energy gap) equal to 9.0 eV.

X-ray emission data give totally independent estimates of the band structure within the valence band and also of the O_{2s} states [112], in good agreement with the presented data.

The very top of the valence band of silica is characterised by a higher density of non-bonding oxygen 2p - orbitals. Some authors [113], however, criticize the position of the top of the valence band and assert that it should be lower by 1 eV. According to various estimates the true band width (energy gap) in amorphous silica should be in the range 8.3-10.0 eV while the true position of the top of the valence band is found in the range -10.4 - - 11.5 eV and that of the bottom of the conduction band is in the range -3.3 -- 1.4 eV [7]. The level preceeding the bottom of the conduction band (-3.3 eV) is usually attributed to the silicon atom [114].

This brief review of the spectroscopic data on silica allows to deduce a generalized system of energy levels (Fig.4a), which serves as a reference tool for analysis of results obtained in this work.

These results for the cluster, $Si(OH)_4$ in the sp - basis set are shown in fig. 4b. The calculations qualitatively predict the existence of the following levels:

(i) a narrow O_{2s} band, (ii) the valence band which is represented by the contributions from the O_{2p} and Si_{2p} AO's (iii) the lone energy level corresponding to Si_{3s} contribution (iv) the conduction band represented by MO with predominant Si_{3s} and H_{1s} contributions. Evidently, this cluster cannot be used as an adequate model for silica due mainly to the presence of several inherent de ficiencies in the cluster. In the first place, the band width (energy gap), 14.7 eV is outside the experimental range. Secondly, the widths of the filled bands are underestimated. Thirdly, although the width of the conduction band seems reasonable, the structure of the levels and their distribution do not agree with experiment.

Inclusion of 3d - orbitals in the basis set for $Si(OH)_4$ cluster leads as usually to the stabilization of all the energy levels (Fig. 4c) but simultaneously the energy gap increases to 15.3 eV. The O_{2s} band becomes narrow and the Si_{3s} electronic states appear in the conduction band. All these circumstances uncover not only the inadequacy of the model but also the deficiency of 3d - containing basis sets.

The description based upon the cluster $Si(OSiH_3)_4$ (fig.4d) seems much more successful. Despite overestimation

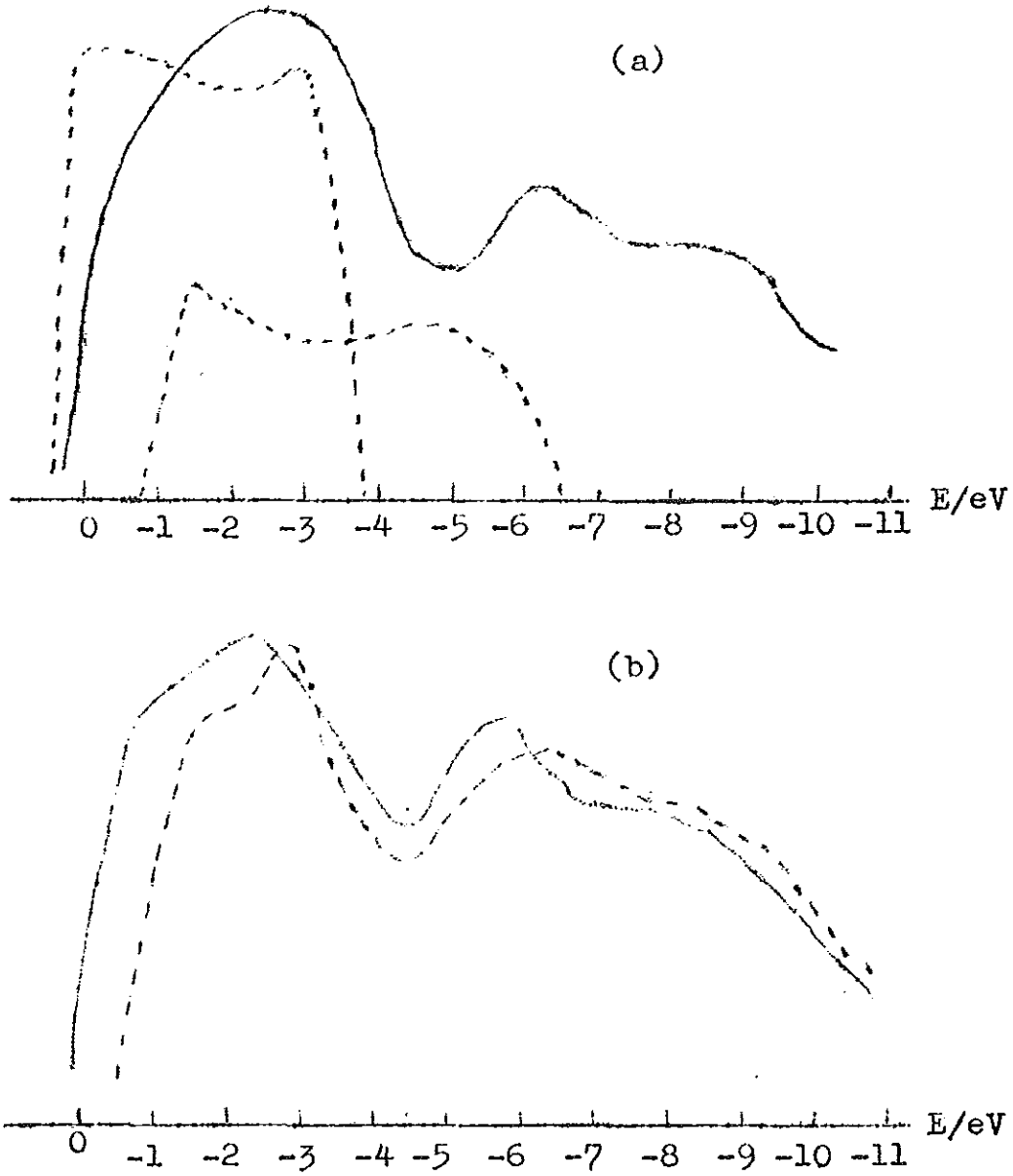


Fig. 5. Theoretical density of states (---) and photoemission spectrum (——) of silica:

a. theoretical quantities obtained for cluster $Si(OSiH_3)_4$, spd';

b. theoretical quantities obtained for cluster $Si(OSiH_3^*)_4$, sp.

of the O_{2s} - band width the description of the valence band seems reasonable. The bottom of the conduction band is overestimated leading to slightly overestimated energy gap (40.2ev) but this value seems quite reasonable for such quantum - chemical methods as INDO.

Inclusion of 3d - valence orbitals of silicon to the basis set leads to stabilization of all the energy levels, with major reductions of the energy of the valence band and minor reduction of that of the conduction band (fig. 4e). Consequently, the energy gap, 12.1 eV becomes overestimated which is naturally the case for existing spd - calculations [93, 99,102]. This makes the spd - basis set hardly applicable for practical calculations. All the other drawbacks of spd'-basis set were discussed for the $Si(OH)_4$ cluster (fig. 4f).

The analysis of the band structure for the cluster $Si(OSiH_3^*)_4$ (fig. 4f) shows that the calculated results fairly fit experimental data (fig.4a). First of all, it is the best model among the models studied in terms of the most accurate reproduction of the O_{2s} - band. The energy levels of both the bottom and top of the band fall within the energy range predicted by experiment. Most importantly, the valence band is reproduced with great accuracy. Apparently, it would suffice to compare the positions of the corresponding energy levels inside the band. The top of the valence band is just within the range of the corresponding energy levels described by different experimental groups. The same is true for the bottom of the conduction band. The energy gap is equal to 10.0 ev, in agreement with experimental data. The success of this cluster

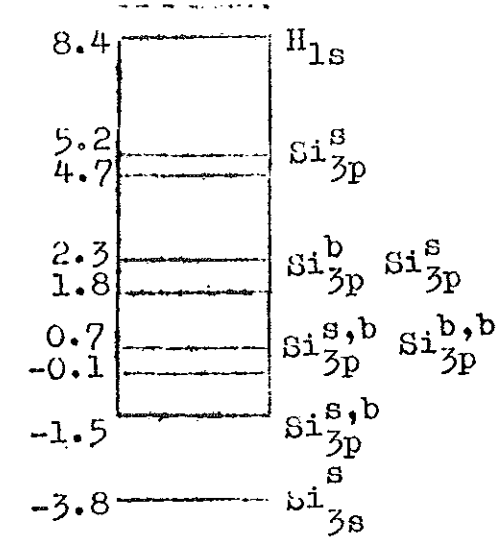
Table 4. Charges on atoms (q), bond orders (B), the energy gap (ΔE, eV) in the cluster models $Si(OSiH_3^*)_4$ and $H(s)O(s)Si(s)(OSiH_3^*)$[a]
The experimental values estimated for q_{Si}, q_O and ΔE were 1.300, -0.650 and 9.0, respectively.

Electronic characteristics	$Si(OSiH)_3$	$HOSi(OSiH_3^*)_3$	SW X_α
$q_{Si(s)}$	-	1.264	1.20[b]
$q_{O(s)}$	-	-0.452	-0.55[b]
$q_{H(s)}$	-	0.130	-
q_{Si}	1.302	1.305	1.33[c]
q_O	-0.634	-0.627	-0.73[b]
q_{H^*}	-0.331	-0.330	-
$B_{Si(s)O(s)}$	-	0.790	0.82[b]
$B_{O(s)H(s)}$	-	0.972	0.94[b]
$B_{Si(s)O}$	-	0.698	0.76[b]
B_{SiO}	0.705	0.721	0.80[c]
B_{SiH^*}	0.839	0.840	—
ΔE	10.0	9.9	9.8[b]

[a] H(s), O(s), Si(s) imply the corresponding surface sites, all the other atoms are in the bulk phase.

[b] $HOSiO_3^{-3}$ [116].

[c] $Si_2O_5^{2-}$ [116].



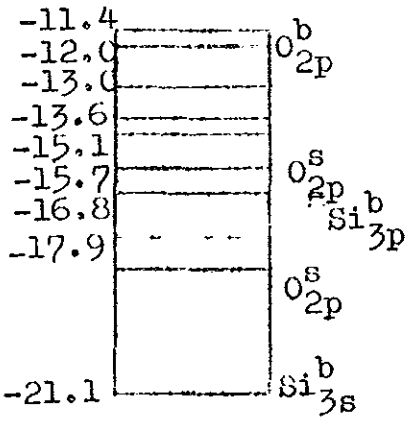
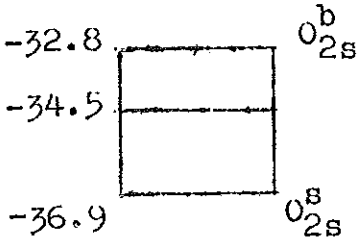


Fig. 6. Band structure of $HOSi(OSiH^{*}_{3})_{3}$. (superscripts s and b are used for surface and bulk atoms, respectively).



may be justified by the fact that the valence band energy levels corresponding to Si_{3p} bear admixtural character containing significant contributions from is - orbitals of quasi - atom though major contributions still come from Si_{3p}. Quasi-atoms seem to be partners in bonding, apparently having equal status with oxygen atoms in the solid. The optimized bond length $R_{(SiH^*)}$ is equal to 0.162 nm, a value typical for $R_{(SiO)}$ bonds in the corresponding organosilicon compounds [115]. Some inaccuracies concerning the spacings between energy levels and their distributions within the conduction band may easily be ascribed to the well-known de. ficiencies of the INDO method. Nevertheless, such de ficiencies were presumed to have little influence on the quality of calculations performed in this work because the decisive role was played by boundary orbitals with correct electronic distributions in $Si(OSiH^*)_4$ cluster model.

The cluster $Si[OSi(OH)_3]_4$ gives a proper description of the boundary orbitals which fall within the experimental range and the energy gap, 8.8 ev, is quite good, but all the other aspects are not so appealing. For instance, it was found that the O_{2s} and valence bands are too narrow whereas the conduction band is too wide. However, the main argnement against this model comes from its inadequate prediction of the electronic distribution.

The last point to be considered is the analysis of partial densities of states. Here, the discussions will focus on two clusters: $Si(OSiH_3)_4$ in the spd' basis set and $Si(OSiH_3^*)_4$ in

the sp - basis set (The latter cluster was found to be optimum in this work). Comparing the densities of states of the model of amorphous β-cristobolite $Si(OSiH_3)_4$ in spd' basis set and the corresponding result obtained from photoemission spectrum [108] (fig. 5a) it may be noted that the widths of the separate bands and the total width of the valence band as well as the shapes of isoenergetic surfaces are reproduced satisfactorily while the densities of the highest occupied sub-band and the sub-band of the O-SiO bonds overlap. Experimental spectral data reveal a band width of 2-3 eV between the filled sub-bands. Thus, the descripancy of the former model may be explained in terms of the inherent deficiencies of the spd' - basis set. On the other hand the $Si(OSiH_3^*)_4$ is characterized by non-overlaping filled sub-bands in agreement with photoemission spectra.

The present results of INDO calculations of the models of silica show that the $Si(OSiH_3^*)_4$ employing is - quasi - atoms to account for boundary effects may be successfully used to describe a series of solid-state features of silica, which from a practical point of view is a very important adsorbent. In the foregoing discussions possible appliciations of this model to study electronic structure, surface properties and the nature of active sites of silica will be considered.

4.2. ELECTRONIC STRUCTURE OF THE SURFACE OF SILICA WITHIN THE FRAMEWORK OF THE CLUSTER APPROACH

As was mentioned before (4.1), the proposed cluster model of the bulk of SiO_2 may be easily transformed to the model readily applicable to study the properties of silica surface. Substitution of the group $OSiH_3^*$ (fig. 3b) by an atom or a group of atoms leads to a model of a hydroxyl framework (R = OH) and chemically modified surface of silica. In the proceeding part the electronic characteristics of the model fragments of silica surface will be considered.

The fully optimized geometry of the surface structure $HOSi(OSiH_3^*)_3$ contains the surface hydroxyl groups with the following geometric parameters: R(OSi) = 0.207 nm, R(OH) = 0.104 nm, ∠HOSi = 104.5° in agreement with the existing experimental estimates [23]

Table 4 contains calculated electronic structural data of the model fragments of the silica surface which bears active hydroxyl groups in contrast with the bulk model. It was observed that when one of the silicon atoms transforms from the bulk to the surface site its charge decreases. However, such changes do not practically extend beyond the first coordination sphere of silicon because the electronic densities on the bulk silicon atoms, the bulk oxygen atoms and quasi - hydrogen atoms remain practically unchanged in the bulk and surface clusters. These data indicate the local character of the adsorption process in silica gel.

But certainly the idea of modeling of silica surfaces by considering only separable active sites or small fragments

without taking into account the influence of the bulk phase is a rather weak arguement.

When quasi - hydrogens are used in the cluster to account for the influence of the solid state environment on the fragment the electronic charges on the quasi - hydrogens remain constant (Table 4). This shows the adequacy of the application of quasi - hydrogens to study the surface properties of SiO_2. The band structure of the model surface cluster $HOSi(OSiH_3^*)_3$ is shown in fig. 6.

Analysis of MO of the model fragment of silica (fig. 6) shows that the general band structure is not changed but many levels are split and are represented mainly by the bulk or surface silicon and oxygen atoms. There is the whole set of the vacant MO's disposed in the conduction band and mainly localized on the surface silicon and hydrogen atoms.The latter is presumably responsible for physisorption which results in the formation of weak H - complexes. The silicon atom is considered to be a potential active site for chemisorption relative to electron donor molecules, especially small nucleophiles [71].

It should be noted that the surface OH groups are characterized by substantial ionicity which is the basis for their definite H - bonding ability with the silanol group. However, it is considerably weak but more realistic than follows from [75]. This discrepancy may be attributed to the neglect of the influence of the solid matrix on the hydroxyl group. The energy gaps in the bulk and surface clusters were found to be practically the same.

4.3. ADSORPTION COMPLEXES OF PROPENE WITH SILICA

A series of adsorption complexes of propene with silica were considered, among which only the two clusters which appeared to be energetically stable and therefore are discussed in detail here.

The most stable adsorption complex of propene is the σ-complex which is also the case with the free hydroxide anion [119]. The surface hydroxyl group interacts with the propene in a direction perpendicular to the plane of the molecule from the side of the methylene group (fig. 7). The optimized geometric parameters and the stabilization energy indicate that the surface complex is weaker than the complex of propene with the hydroxide anion. This is inferred from the longer distance between propene and OH-group as well as from the lower stabilization energy -59.7 kJ mol^{-1}. This corresponds to the H-bonding energy from the INDO method which is characterized by overestimation of interaction energies.

The next adsorption complex in order of stability is the classical π-complex of the Dewar type (fig. 8). The comparison between this complex and the related complex with the hydroxide-anion shows that the surface structure is more stable, though the stability is less than that of the corresponding σ-surface complex shown in fig. 7. The distance between the double bond and the surface hydroxyl group shown

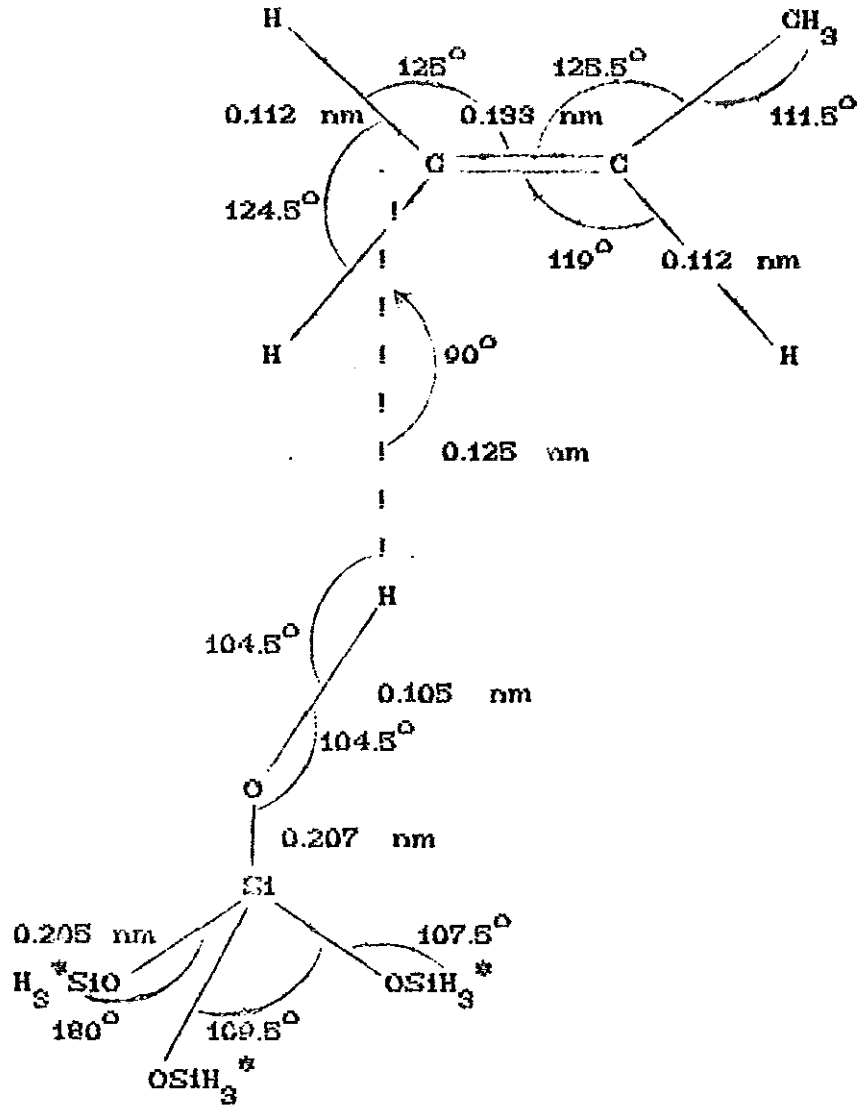


Fig. 7. σ -adsorption complex of propene with silica gel.

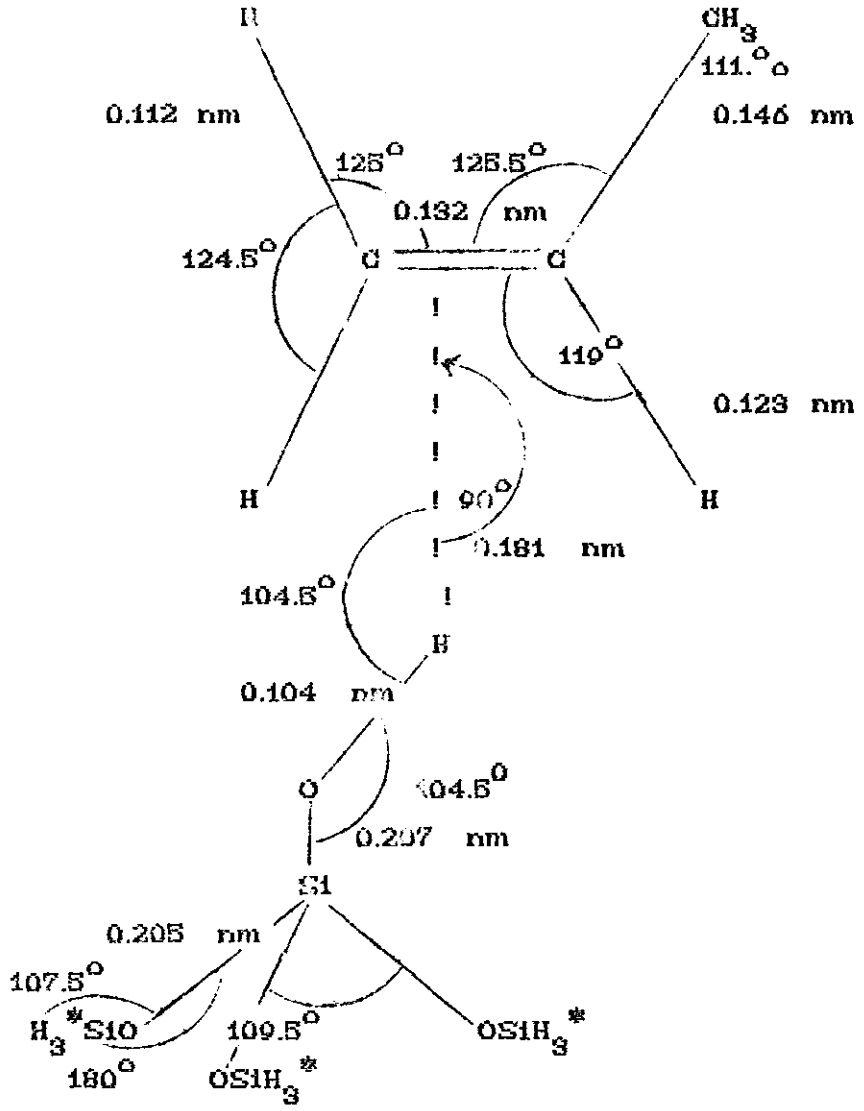


Fig. 8. π-adsorption complex of propene with silica gel.

in fig. 8 and the value of the interaction energy -29.7 $kJ.mol^{-1}$ clearly indicate the formation of a weakly H-bonded complex.

By and large, the surface complexes are more stable than the corresponding complexes with the hydroxide anion and there are no principal differences in the electronic distribution upon complex formation. Thus, it may be concluded that the construction of elaborated models accounting for the solid matrix may not be necessary. Nevertheless, even the first results mentioned before show that proper consideration of the solid matrix leads to more realistic estimates of the energy and geometry of the system.

Analysis of the electronic structure shows that there is a remarkable electronic redistribution in propene after adsorption and complex formation. The direction of electron transfer and the changes of electronic characteristics of OH group are of fundamental importance. The corresponding values are given in table 5. Analysis of charges on atoms and bond orders clearly indicates that the direction of electron transfer is from silica to the propene molecule. However, the trends of electron redistribution are not so uniform in hydroxylated and surface complexes. It should be noted that the formation of the σ-OH complex leads to a decrease in the charge of the hydrogen atom while upon propene adsorption the opposite trend is observed. For the π-complexes similar trends of electronic charge distribution are found whereas the bond orders show the surface π-complex to be stronger than the σ-complex with OH-anion.

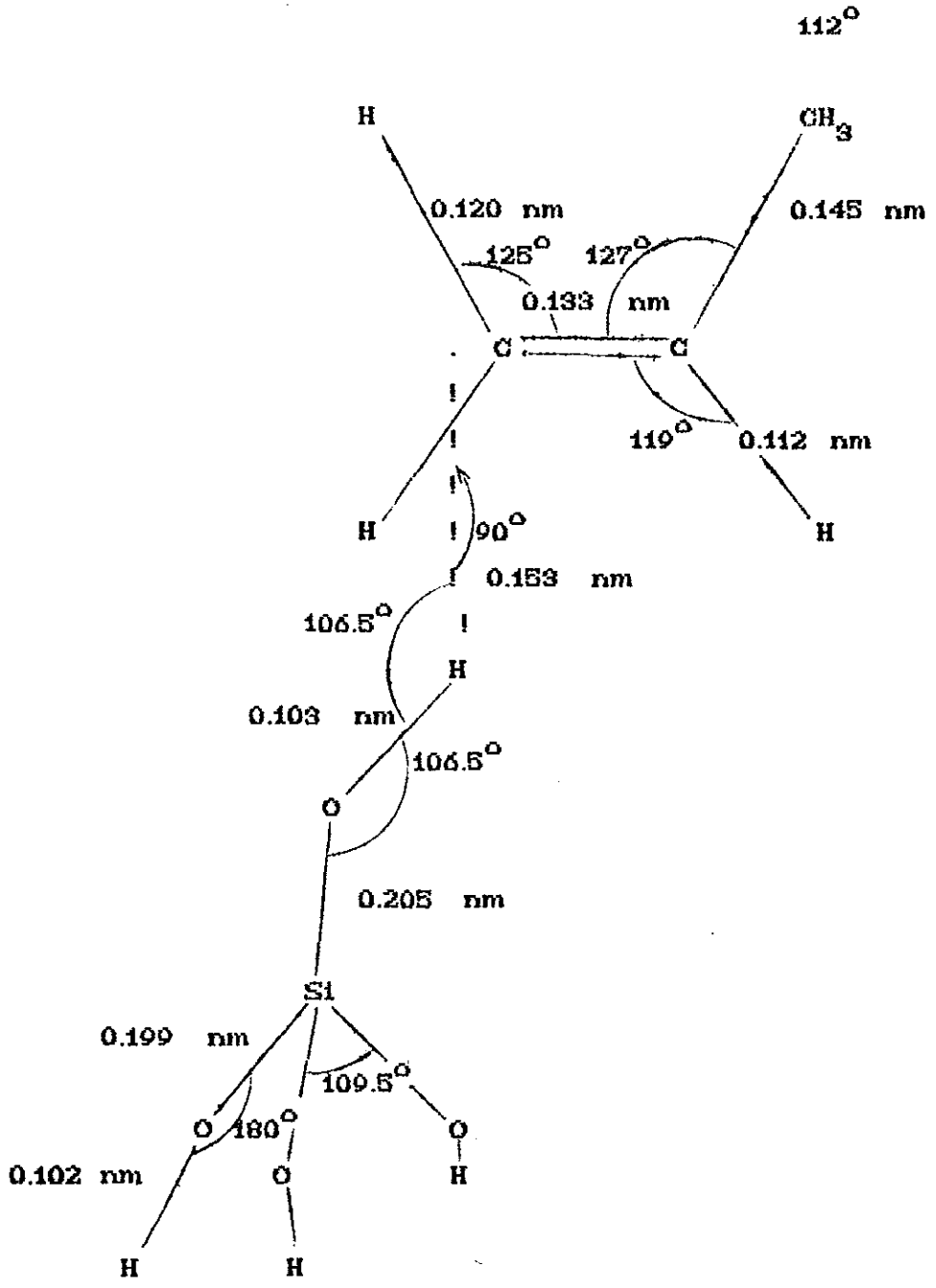


Fig. 9. Adsorption σ-complex of propene with minimum cluster $Si(OH)_4$.

In order to elucidate these differences more explicity table 5 is given in a generalized form and it includes all the quantum-chemical results on propene and its complexes with the OH-group and silica surface.

Finally, the σ-complex of propene through the methylene group with the minimum cluster, $Si(OH)_4$ (fig.9), will be briefly discussed. Eventhough the intermolecular distance is quite the same as in the $HOSi(OSiH_3^*)_3$ complex (fig. 7) the interaction energy in the former case is overestimated (-67.4 kJ mol^{-1}) and is intermediate between that of the hydroxylated complex (-100.6 kJ mol^{-1}) and the surface complex with $HOSi(OSiH_3^*)_3$ (-59.7 kJ mol^{-1}). In most cases the electronic characteristics (charges on atoms and bond orders) are intermediate between that of the hydroxylated and surface complexes given in table 5. For instance the charge on the $\equiv C(H)CH_3$ carbon atom in the complex of propene with $Si(OH)_4$ is practically the same as that in propene itself (0.045) while the charge on the same carbon atom is 0.146 in the σ-hydroxylated complex and 0.002 in the complex of propene with $HOSi(OSiH_3^*)_3$. And all the other characteristics follow the same trend. Thus, the cluster model, $Si(OH)_4$, seems to be insufficient to give a detailed account of the properties of silica matrix.

Evidently, the cluster model $HOSi(OSiH_3^*)_3$ appears to be successful in the description of the weak adsoption complex of the silica surface.

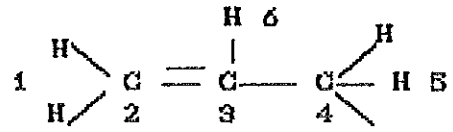


Table 5. Charges on atoms (q) and bond orders (B) in propene and its complexes with the hydroxyl and with the surface of silica.

(a) Charges on atoms

No	Structure	q_1	q_2	q_3	q_4	q_5	q_6
1	Propene	-0.013	-0.007	0.042	0.073	-0.023	-0.017
2	σ-OH complex	-0.051	0.169	0.152	0.146	-0.080	-0.044
3	π-OH complex	-0.029	0.039	0.067	0.091	-0.036	-0.028
4	σ-Surface complex	-0.001	0.041	0.002	0.075	-0.021	-0.022
5	π-Surface complex	-0.009	0.009	0.049	0.066	-0.018	-0.002

(b) Bond orders

No	B_{12}	B_{23}	B_{34}	B_{45}	B_{36}
1	0.961	1.982	1.076	0.962	0.934
2	0.948	1.718	1.102	0.947	0.933
3	0.959	1.976	1.076	0.960	0.932
4	0.946	1.872	1.083	0.960	0.935
5	0.960	1.933	1.072	0.963	0.933

(c) Electronic characteristics of OH group in hydroxylated complexes and surface OH-group in adsorption complex of propene.

No	Type of OH Group	q_O	q_H	B_{OH}
1	Free OH	-0.853	-0.147	0.978
2	σ-OH complex	-0.749	-0.228	0.753
3	π-OH complex	-0.866	-0.039	0.974
4	Surface OH	-0.453	0.131	0.972
5	Surface σ-OH complex	-0.425	0.188	0.869
6	Surface π-OH complex	-0.461	0.173	0.926

5. CONCLUSION

1. Quantum-chemical modeling of bulk phases of silica has been proposed. The proposed approach is applicable to a wide range of solids in general. Computer programs were developed for practical implementation of the modeling techniques. The new modeling approach presupposes termination of the fragment isolated from the solid matrix by quasi-hydrogen atoms. Determination of semi-empirical quantum chemical parameters of quasi-hydrogens was made on the basis of adequate description of the electronic distribution and other pecularities for the optimum geometries of the model fragments.

2. Parameters of quasi hydrogens for the optimum structure of silica model have been calculated by INDO method within the framework of the proposed cluster approach. This allowed not only to present correct description of X-ray and photoelectronic spectra of silica but also to obtain good agreement between calculated values and experimental data for energy gaps, geometric structures and electronic distributions.

3. The investigated cluster approach has been found to be applicable for the analysis of processes occuring in the surface layer of the modeled solid. The geometric and electronic structures of the hydroxylated silica surface were studied.

PERSPECTIVES FOR FURTHER STUDY.

The computer program CNINDO written by J.A. Pople et al [1], was used as a basis for the present calculations. However, most of the data in this thesis were generated by a substantially modified program called INDO88. The modified program is supplemented by Sargent-Murtagh [117] double self-consistency geometry optimization procedure. The capability of the program is increased by introducing the possibility of working in cartesian, polar and natural coordinates, addition of subroutines for the mapping of the electronic density and electrostatic potential, the densities of electronic states in solids, decomposition of the total energy into one-center and two-center constituents [118] as well as some other service subroutines and finally the parametrization for transition metals based upon a series of papers by Bohm [2, 119].

The programming job is still in progress to write the modified program in a form compatible with the NCR century Full Fortran compiler at SDDPC of AAU and then to use it for the investigation of the catalytic behaviour of transition metal salts supported on the surface silica towards propene oxidation (selective and complete pathways) or other reactions and surface complexes.

Thus, the main perspectives for future study are summarized as follows.

1. To obtain cluster models of transition metal oxides by quasi-atom approach and to take into account the borderline effects and the electrostatic environment of the

cluster in point charge approximation. To establish a series of catalytic activity for simple transition metal oxides relative to propene oxidation in comparison with the experimental interaction energies of cuprous and cobaltic-cobaltous oxides as a reference.

2. To design cluster models of surface immobilized silicas modified by chemisorbed transition metal species and to analyze the trends of electronic and energy level redistribution in light of various experimental estimates. To use elaborated models for theoretical studies of adsorption complexes of propene [120] and to make prediction of the reaction paths of propene oxidation and to set criteria for the selectivity of propene oxidation by studying the electronic characterstics in the limiting and adsorbed structures.

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APPENDIX A. THE SCHROEDINGER EQUATION AND APPROXIMATION METHODS FOR MANY ELECTRON SYSTEMS

For a system consisting of N nuclei and n electrons the Schrödinger equation is a function of the coordinates of the N+n particles [1].

$$\hat{H}\psi = E\psi \qquad (A.1)$$

where

$\hat{H} = \hat{H}(1,2,\ldots,N;1,2,\ldots,n)$

$\psi = \psi(1,2,\ldots,N;1,2,\ldots,n)$

E = Constant

The total hamiltonian could be broken down into three components:

$$\hat{H} = \hat{H}_N + \hat{H}_e + \hat{H}_{eN} \qquad (A.2)$$

The explicit expression in a.u. for each of the terms on the right hand side of (A.2) are given by

$$\hat{H}_N = \sum_{A}^{N} \hat{h}(A), \quad \hat{H}_e = \sum_{p}^{n} \hat{h}(p) + \sum_{p<q} \hat{g}(p,q), \quad \hat{H}_{eN} = \sum_{A<B} \hat{g}(A,B)$$

where

$$\hat{h}(A) = -1/2M_A^{-1}\nabla_A^2, \quad \hat{g}(A<B) = Z_A Z_B R_{AB}^{-1}$$

$$\hat{h}(p) = -1/2\nabla_p^2 - \sum_{A} Z_A r_{Ap}^{-1}, \quad \hat{g}(p,q) = r_{pq}^{-1}$$

$\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$; $\nabla^2 = \nabla.\nabla = (\partial^2/\partial x^2, \partial^2/\partial y^2, \partial^2/\partial^2)$

The existence of the internuclear distance R_{AB} in $\hat{H}$ makes it difficult to obtain the exact solution of (A.1) by the separation of variables technique but a reduction in the total hamiltonian is made by the use of the Born-Oppenheimer approximation [2], under which (A.2) yields

$$\hat{H} = \hat{H}_e + \hat{H}_{eN} \qquad (A.3)$$

This gives the possibility to separate the total wave function into the nuclear and electronic functions. Accordingly, the total energy is given by

$$E = E_{el} + \sum_{A<B} Z_A Z_B R_{AB}^{-1} \qquad (A.4)$$

The Born-Oppenheimer approximation states that the motion of the electrons is so rapid that they can instanteneously adjust their positions to the slow nuclear motion which eventually leads to the neglect of the term containing the kinetic energy operator of the nuclei from the total hamiltonian thereby giving the possibility to write the total wave function as the product of the nuclear and electronic wave functions. Therefore, a Schrödinger equation analogous to A.1 can be set up for electronic motion wherein the energy of the system will be expressed by (A.4).

Evenso, the solution of the resulting equation requires the introduction of some sort of approximations due to the presence of the interelectronic separations r_{pq}.

Some of the best approximations are obtained by the so-called SCF procedures or Hartree-Fock methods which are broadly subdivided into two. In the orbital approxdmation an antisymmetrized total electronic wave function is approximated by the linear combination of one-electron wave functions (Hartree product) which for a closed shell system is written in a compact form as the Slater determinant.

$$\psi = (N!)^{-1/2} \left| \varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2 \cdots \varphi_n \bar{\varphi}_n \right| \qquad (A.5)$$

where $\varphi = \varphi\,\alpha$, $\bar{\varphi} = \varphi\,\beta$

In a more general approach multi-configurational SCF or configuration interaction (CI) is applied where the wave function is written as a linear combination of the Slater determinants.

$$\psi = \sum_i c_i D_i \qquad (A.6)$$

Evaluation of the energy and optimum parameters (coefficients) is based upon the variation theorem mathematically stated as

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_0 \qquad (A.7)$$

In an alternative approach SCF LCAO scheme is used to construct molecular wave functions.

$$\varphi_i = \sum_{\mu} c_{\mu i} \phi_\mu \qquad (A.8)$$

Application of the variation method to LCAO leads to Hartree-Fock-Roothaan equations which emerge as a result of certain simplifying assumptions in the secular determinant obtained from the secular equations. The hartree-Fock equations are eigenvalue equations.

$$\hat{F}\psi = E\psi \qquad (A.9)$$

whereas the Roothaan equations constitute algebraic equations.

$$\sum_{\nu} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0; \quad \mathrm{Det}(F - \varepsilon S) = 0. \qquad (A.10)$$

where the matrix elements are given by

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu}, \quad H_{\mu\nu} = \int \phi_\mu(1) \hat{H} \phi_\nu(1) d\tau_1$$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} (J_{\mu\nu\lambda\sigma} - 1/2 K_{\mu\nu\lambda\sigma})$$

$$J_{\mu\nu\lambda\sigma} = \iint \phi_\mu(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2) \phi_\sigma(2) d\tau_1 d\tau_2$$

$$K_{\mu\nu\lambda\sigma} = \iint \phi_\mu(1) \phi_\lambda(1) \frac{1}{r_{12}} \phi_\nu(2) \phi_\sigma(2) d\tau_1 d\tau_2$$

J and K are called coulomb and exchange integrals, respectively, and P is the density matrix.

Solution of the Roothaan equation requires an initial guess at the form of the molecular orbitals leading to the following SCF scheme.

$$P^{0}_{\mu\nu} \longrightarrow F'_{\mu\nu} \longrightarrow \varepsilon'_{i} \longrightarrow P'_{\mu\nu} \longrightarrow F'_{\mu\nu} \longrightarrow \varepsilon''_{i} \longrightarrow P''_{\mu\nu} \longrightarrow \text{etc.}$$

In the solution of (A.10) by non-empirical methods, the basis functions (AO) are given in convenient analytical forms in terms of STOs.

$$\chi_{nlm} = \sqrt{\frac{2\xi}{(2n)!}}\,(2\xi)^{n}\, r^{n-1}\, e^{-\xi r}\, Y_{lm}(\vartheta,\varphi) \qquad (A.11)$$

$$Y_{lm} = \left[\frac{2l+1}{2\pi\delta_{m}}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P^{|m|}_{l}(\cos\vartheta) \begin{cases} \cos m\varphi & m \geq 0 \\ \sin m\varphi & m < 0 \end{cases} \qquad (A.12)$$

$$\delta_{m} = \begin{cases} 2 & m = 0 \\ 1 & m \neq 0 \end{cases}$$

where n is the effective principal quantum number, ξ is the Slater exponent evalauted by the well known Slater rules and $P^{|m|}_{l}$ is the associated Legendre polynomial [1].

The main features of STOs are that they lead to non-degenerate sets of energy states and are not orthogonal at all but they can readily be orthogonalized by various methods. Other classes of convenient analytical functions include GFs which have essenetially the same form as STOs except that the exponential part is a quadratic function of r. GFs are characterized by fast convergence and many of the integrals involvong GFs are easily evaluated.

$$g_{nlm} = \left[\sqrt{\frac{2}{\pi}}\,\frac{(4\alpha)^{n+1/2}}{(2n-1)!}\right]^{1/2} r^{n-1}\, e^{-\alpha r^{2}}\, Y_{lm}(\vartheta,\varphi) \qquad (A.13)$$

Sometimes, a group of STOs are approxdmated by LCGF as

$$X = \sum_{i}^{n} c_{i} g_{i} \qquad (A.14)$$

The following notations are widely used in the literature [3].

STO-NG (STO-3G or STO-4G)

STO-NG-KLG (STO-4-31G)

STO-NG-KLMG (STO-6-311G)

STO-NG-KLMG* (STO-6-311G*) etc.

where STO in a given group is approximated by the indicated GFs.

The computational difficulties impose severe limitations on the range of applicability of non-empirical methods to large molecular systems. On the other hand, semi-empirical approximations use simple computational schemes and yet produce fairly accurate results and give good correlations between theoretical and experimental results.

In the solution of the Roothaan equations written in the matrix form as HC = SCE, the matrix elements are obtained in the following ways by a semi-empirical scheme known as method of complete overlap. $H_{\mu\mu}$ are estimated from I_{μ}.
Expressions for the off-diagonal elements are given by

(i) $H_{\mu\nu} = k/2(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$ (A.15)

(Wolfsberg-Helmholtz version)

(ii) $H_{\mu\nu} = kS_{\mu\nu}$ (A.16)

(Longuet-Higgins-Roberts version)

(iii) $H_{\mu\nu} = k(H_{\mu\mu}H_{\nu\nu})^{1/2}S_{\mu\nu}$ (A.17)

(Ballhausen-Gray version)

(iv) $H_{\mu\nu} = 1/2(H_{\mu\mu} + H_{\nu\nu})^{1/2}S_{\mu\nu}\,(2-|S_{\mu\nu}|)$ (A.18)

(Cusachs' version)

ZDO is another widely used semi-empirical scheme based upon the approximations:

$$S_{\mu\nu} = \delta_{\mu\nu};\quad (\mu_A\nu_B|\lambda_C\sigma_D) = \delta_{AB}\delta_{CD}(\mu\nu|\lambda\sigma)$$

where δ is the Kronecker delta.

Various versions of ZDO are known. In CNDO the matrix elements of the Roothaan equations are estimated by

$$H_{\mu_A\mu_A} = \left\langle \mu_A \left| -\frac{\nabla^2}{2} - V_A \right| \mu_A \right\rangle - \sum_{B\neq A} \left\langle \mu_A \left| \hat{V}_B \right| \mu_A \right\rangle$$

$$\cong U^A_{\mu\mu} - \sum_{B\neq A} V_{AB} \qquad \text{(A.19)}$$

Then to achieve computational simplicity the following parameters were introduced.

$$U^A_{\mu\mu} = -I_\mu - (Z_A - 1)\gamma_{AA} \qquad \text{(CNDO/1)} \qquad \text{(A.20)}$$

$$U^A_{\mu\mu} = -1/2(I_\mu + A_\mu) - (Z_A - 1/2)\gamma_{AA} \qquad \text{(CNDO/2)} \qquad \text{(A.21)}$$

$$H_{\mu_A\nu_B} = \beta^0_{AB} S_{\mu_A\nu_B}; \quad \beta^0_{AB} = 1/2(\beta^0_A + \beta^0_B) \qquad \text{(A.22)}$$

and furthermore, in CNDO/2 V_{AB} is parametrized as

$$V_{AB} = -Z^*_A \gamma_{AB} \qquad \text{(A.23)}$$

Evaluation of one-center and two-center integrals are based on

$$\gamma_{AA} = I_A - A_A \qquad \text{(A.24)}$$

(Parisor-Parr approximation)

$$\gamma_{AB} = \left[R_{AB} + \frac{2}{\gamma_A + \gamma_B} \right]^{-1} \qquad \text{(A.25)}$$

(Mataga-Nishomoto relation)

or

$$\gamma_{AB} = \left[R^2_{AB} + \left[\frac{2}{\gamma_A + \gamma_B} \right] \right]^{1/2} \qquad \text{(A.26)}$$

(Ohno relation)

In INDO all one-center integrals are retained, i.e., $(\mu_A\nu_A|\lambda_A\sigma_A) \neq 0$. Hence INDO is superior to CNDO in many respects. A version ZDO so-called NDDO is even less approximate and retains all one-cneter and two-center

overlaps, i.e., $(\mu_A \nu_A | \lambda_B \sigma_B) \neq 0$. INDO is identical to CNDO in two-center parts and NDDO in one-center parts.

ZDO approximation makes it possible to decompose the total energy into one-center and two-center contributions.

$$E = \sum_A E_A + \sum_{A<B} E_{AB} \qquad (A.27)$$

and the two-center part is further broken down into two components.

$$E_{AB} = E_{AB}^{cov} + E_{AB}^{el} \qquad (A.28)$$

where the electrostatic and covalent terms are given by

$$E_{AB}^{el} = \left[(Z_A - q_A)q_B + (Z_B - q_B)q_A\right]\gamma_{AB} + Z_A Z_B V_{AB} \qquad (A.29)$$

$$q_A = \sum_{\mu}^{A} P_{\mu\mu}, \quad q_B = \sum_{\mu}^{B} P_{\mu\mu}$$

$$E_{AB}^{cov} = 2\beta_{AB} \sum_{r}^{A}\sum_{s}^{B} \rho_{rs} S_{rs} - 1/2\, \gamma_{AB} \sum_{r}^{A}\sum_{s}^{B} \rho_{rs}^2 \qquad (A.30)$$

The Hartree-Fock-Roothaan equations are greatly simplified in the CNDO/2 version of the Pople approximation. Thus, the matrix elements in the equation $\sum F_{\mu\nu} c_{\nu i} = \varepsilon_i c_{\nu i}$ become

$$F_{\mu\mu} = H_{\mu\mu} - 1/2 P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda} P_{\lambda\lambda}(\mu\mu|\lambda\lambda) \qquad (A.31)$$

$$F_{\mu\nu} = H_{\mu\nu} - 1/2 P_{\mu\nu}(\mu\mu|\nu\nu) \qquad (A.32)$$

$$E_{el} = 2\sum H_{ii} + \sum_{i}^{n}\sum_{j\mu\nu} (J_{ij} - K_{i\mu j\nu}) \qquad (A.33)$$

or

$$E_{el} = \sum_{i}^{occ} E_i + \sum P_{\mu\nu} H_{\mu\nu} \qquad (A.34)$$

Mulliken-Ruldenberg approximation is used to make further reduction of two-center integrals as follows.

$$\phi_{\mu_A}(1)\phi_{\mu_B}(1) \approx 1/2 S_{\mu\nu}\left[\phi_{\mu_A}(1)\phi_{\mu_A}(1) + \phi_{\mu_B}(1)\phi_{\mu_B}(1)\right] \qquad (A.35)$$

For instance,

$$(\mu\nu|\lambda\sigma) \approx 1/4 S_{\mu\nu} S_{\lambda\sigma}\left[(\mu\mu|\lambda\lambda)+(\mu\mu|\sigma\sigma)+(\nu\nu|\lambda\lambda)+(\nu\nu|\sigma\sigma)\right] \qquad (A.36)$$

Pople-Beveridge-Dobosh approximation is used to estimate γ_{AB} from s-functions, i.e., s-orbitals and the corresponding quantum numbers.

$$(\mu_A\mu_A|\lambda_B\lambda_B) = \gamma_{AB} = (nS_A nS_A|mS_B mS_B) \qquad (A.37)$$

Therefore, γ_{AB} for s and p orbitals could be evaluated as

$$\gamma_{AB}^{sp} = 1/3 \sum_{\alpha=1}^{3} (nS_A nS_A|mp_B^{\alpha}\ mp_B^{\alpha}), \quad \alpha = x, y, z. \qquad (A.38)$$

References

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APPENDIX B. DIFFERENCE EQUATIONS

Numerical solution of a differential equation is usually obtained by the difference scheme which is based upon the transformation of the differential equation into the approximating difference equation [1]. Eventually, the computer plays a very vital role in the solution of the difference equation by an iterative process. The difference scheme is particularly important for the determination of optimum values of a function. Detailed discussion of difference equations is given elsewhere [2 - 4].

A difference equation [5] is an equation which involves an independent variable, dependent variable and successive differences of the dependent variable. A difference equation of order n is written as:

$$F\left[x,\ f(x),\ \Delta f(x),\ \ldots,\ \Delta^{n} f(x)\right] = 0 \qquad (B.1)$$

where F is a known function and f(x) is an unknown function and $\Delta f(x) = f(x+1) - f(x)$. The difference equation [6] for a first order differential equation could be derived as follows. For a given first order differential equation

$$y' = F(x,y) \qquad (B.2)$$

where $y' = dy/dx$ and y shall have the value y_0 when $x = x_0$. We seek a solution

$$y = f(x) \qquad (B.3)$$

such that $y_0 = f(x_0)$. Let x_0, x_1, x_2, ... be equally spaced values of x so that $x_{n+1} - x_n = h$, a constant for $n = 0, 1, 2, \ldots$. Hence, in place of the given differential equation (B.1), we deal with the difference equation (B.4).

$$\frac{y_{n+1} - y_n}{h} = F(x,y)$$

or

$$y_{n+1} = y_n + hF(x_n,y_n) = y_n + y'_n h \qquad (B.4)$$

One fairly obvious way to proceed would be to choose a small value of h and with $n = 0$ $y_1 = y_0 + hF(x_0,y_0)$ is computed; with $n = 1$ $y_2 = y_1 + hF(x_1,y_1)$ is computed; and so on until the approximation y_N for the value of y corresponding to $x = x_N$ is obtained.

The Taylor series expansion for the unknown function f(x) is powers of $x - x_n$ is written as:

$$f(x) = f(x_n) + f'(x_n)(x-x_n) + \frac{f''(x_n)(x-x_n)^2}{2!} + \ldots \qquad (B.5)$$

Let $x = x_{n+1}$, so that $x-x_n = x_{n+1}-x_n = h$; also using $y_n = f(x_n)$ for convenience, we then have

$$y_{n+1} = y_n + y'_n h + \frac{y''_n h^2}{2!} + \frac{y'''_n}{3!} + \ldots \qquad (B.6)$$

Comparing (B.4) and (B.6) we see that the error introduced by the difference equation (B.4) is due to dropping of the terms involving h^2 and higher powers of h. We say that the error involved is of the order of h^2.

The efficiency of the method could be improved by letting $x = x_{n-1}$ in (B.5) so that

$$x - x_n = x_{n-1} - x_n = -h.$$

Then

$$y_{n-1} = y_n - y'_n h + \frac{y''_n}{2!} - \frac{y'''_n}{3!} + \ldots \qquad (B.6')$$

$$y_{n+1} = y_{n-1} + 2y'_n h + \frac{y'''_n}{3!} + \ldots \qquad (B.7)$$

Accordingly, we may use, instead of (B.4) the relation

$$y_{n+1} = y_{n-1} + 2y'_n h \qquad (B.8)$$

Then, the error will be of the order h^3, which, for h sufficiently small may be expected to be less than when the h^2 term is neglected. Since y_{n-1} appears in (B.8) this formula first gives for n = 1 $y_2 = y_0 + 2y'_1 h$. Accordingly, y_1 and y'_1 must be computed by other means to get started by the iteration process. To be consistent with the wish to neglect only terms involving third and higher powers of h, the first three terms of (B.6) may be used in the computation of y_1; that is,

$$y_1 = y_0 + y'_0 h + 1/2 y''_0 h^2 \qquad (B.9)$$

is calculated.

The values of x_0 and y_0 being given, $y_0 = F(x_0,y_0)$ is evaluated from the given differential equation (B.2) and then y''_0 from the result of differentiating (B.2).

$$y'' = \frac{\partial F}{\partial x} + \frac{\partial F}{\partial y} y' \qquad (B.10)$$

wherein we put $x = x_0$, $y = y_0$, $y' = y'_0$.

The method therefore involves the following successive steps.

1. Use the given differential equation (B.2) to get $y'_0 = F(x_0,y_0)$ and (B.10) to compute y''_0.
2. Using y_0, y'_0 and y''_0 together with a chosen value of h, find y_1 from (B.9). With $x_1 = x_0 + h$ and y_1, calculate y'_1 from (B.2).
3. From formula (B.8) get $y_2 = y_0 + 2y'_1 h$; with $x_2 = x_1 + h$, find y'_2 from (B.2).

4. Repeat step 3 for y_3 and y_3', y_4 and y_4' and so on, through as many stages as required.

In dealing with functions of several variables, the function U(x,y,z) will have optimum values (maxima or minima) with respect to all the three variables x, y, z if the following conditions are fulfilled.

$$U(x,y,z) = F(x,y,z) = 0 \qquad \text{(B.11)}$$

$$U(x,y,z) = F(x,y,z) = 0 \qquad \text{(B.12)}$$

$$U(x,y,z) = F(x,y,z) = 0 \qquad \text{(B.13)}$$

where $U_\alpha = \frac{\partial U}{\partial \alpha}$ (α = x, y, z) and U shall have the valueU_0 when $x = x_0$, $y = y_0$, $z = z_0$. Then by the same arguements, equations analogous to equations (B.4) and (B.8) can be derived for each of the partial derivatives U_x, U_y, U_z to solve for the optimum (extremum) values U(x,y,z) [6].

In the optimization of the INDO parameters for quasi-hydrogen atoms by the difference scheme, the variables x, y, z in (B.11) - (B.13) are replaced by $1/2(I_H^* + A_H^*)$ (eqns. 2.62 and 2.63), β_H^{0*}(eqn. 2.66) and μ_H^{0*} (eqns. 2.34 or 2.36), respectively, in equation (4.1).

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APPENDIX C. POTENTIAL ENERGY SURFACES AND OPTIMAL GEOMETRIC STRUCTURES OF MOLECULAR SYSTEMS.

C.1. GENERAL CHARACTERISTICS OF MINIMIZATION METHODS.

Potential energy of a system is a function of (3N-6) internal coordinates, $U(q_i)$. Minimization problems are generally called optimization problems [1].

The problem of minimization involves construction of a sequence of points (q^i) such that $q^i \dashrightarrow q^{min}$, where q^{min} is the point, in which minimum of the given function is achieved. The majority of algorithms for the construction of the minimizing surface are subdivided into two groups: direct search methods and methods using derivatives. Substantial part of methods is based on subseuqent determination of the direction $\vec{s}$ and the step λ of descent so that the i-th iteration step may be presented as

$$\vec{q}^{\,i} = \vec{q}^{\,i-1} + \lambda^i \vec{s}^{\,i} \qquad (C.1)$$

where $\vec{s}^{\,i}$ is normalized vector, $\lambda_i > 0$.

The λ value is often determined by condition of minimization of the function along the direction of $\vec{s}$. Therefore essential part of many algorithms is one-dimensional minimization of the function.

Efficiency of algorithms of minimization is often estimated by the rate of convergence. The sequence $\vec{q}^{\,i}$ is said to converge to $\vec{q}^{\,min}$ linearly if the sequence of distances $||\vec{q}^{\,i} - \vec{q}^{\,min}||$ decreases as geometric progression, i.e.

$$||\vec{q}^{\,i+1} - \vec{q}^{\,min}|| \leq j||\vec{q}^{\,i} - \vec{q}^{\,min}||, \quad 0 < j < 1 \qquad (C.2)$$

If the sequence $\vec{q}^{\,i}$ decreases faster so that the estimate

$$||\vec{q}^{\,i+1} - \vec{q}^{\,min}|| \leq c||\vec{q}^{\,i} - \vec{q}^{\,min}||^k, \quad c > 0, \; k > 1 \qquad (C.3)$$

is true, then this implies hyperlinear convergence (quadratic convergence in the case k = 2).

If a function U is differentiable and if its gradient is known

$$d = \begin{bmatrix} 1 \\ \vdots \\ d_m \end{bmatrix}, \quad d_i = \frac{\partial U}{\partial q^i} \qquad (C.4)$$

then at least in a proximity of a point function U decreases along the direction $\vec{s}$, if

$$\vec{s} \cdot \vec{d} < 0 \qquad (C.5)$$

In particular a function decreases in the direction

$\vec{s} = -\vec{d}/||\vec{d}||$ and in general in any direction

$$\vec{s} = -A\vec{d}/||A\vec{d}|| \qquad (C.6)$$

where A is an arbitrary positively determined matrix.

The problem of search of stationary points is connected with the problem of solution of the system of non-linear equations

$$d_i(\vec{q}) = 0 \qquad (C.7)$$

Let in proximity of a point $\vec{q}^{\,o}$ function $U(\vec{q})$ be approximated quadratically.

$$U(\vec{q}) = U^o + (\vec{q} - \vec{q}^{\,o})d^o + 1/2(\vec{q} - \vec{q}^{\,o})\Theta^o(\vec{q} - \vec{q}) \qquad (C.8)$$

Conditions of extremum (C.7) reduce to linearized equations:

$$\Theta^o(\vec{q} - \vec{q}^{\,o}) + d^o = 0 \qquad (C.9)$$

If matrix Θ^o is known and its inverse $(\Theta^o)^{-1}$ could be found, extremum $\vec{q}^{\,ex}$ (C.9) may be determined for one step:

$$\vec{r} = \vec{q}^{\,ex} - \vec{q}^{\,o} = (\Theta^o)^{-1}d^o \qquad (C.10)$$

Since equations (C.8) and are approximate, (C.10) gives only approximate value of extremum. The iteration process for which one step is determined by (C.10) is called Newton-Raftson method. If function $U(\vec{q})$ satisfies definite conditions, convergence to minimum of Newton-Raftson method is quadratic. This method is characterized by fastest convergence but necessity of calculation of both gradient and Hessian matrix makes its application in quantum chemistry difficult.

C.2. ONE-DIMENSIONAL OPTIMIZATION

Primarily it is useful to localize a minimum over some segment $0 \leq \lambda \leq 1$. The simplest procedure uses division of the segment into parts. If two points are given $0 < \lambda_1 < \lambda_2 < 1$, $f(0) \leq f(1)$, then comparing the values of the function at the points λ_1 and λ_2 it is possible to decrease the interval in which λ^{min} is localized:

$$0 \leq \lambda^{min} \leq \lambda_2 \quad \text{if} \quad f(\lambda_2) > f(\lambda_1) \qquad (C.11)$$

$$\lambda_1 \leq \lambda^{min} \leq 1 \quad \text{if} \quad f(\lambda_1) > f(\lambda_2)$$

The most effective procedure is division of a segment according to "gold section" rule, i.e.,

$$\lambda_1 = \varphi_1 \equiv (3 - \sqrt{5})/2 \cong 0.38 \qquad (C.12)$$

$$\lambda_2 = \varphi_2 \equiv (\sqrt{5} - 1)/2 \cong 0.62$$

Since $\varphi_1 = \varphi_2^2$, $\varphi_1 + \varphi_2 = 1$, in subsequent division of a segment, one of the points for which the value of the function was calculated at preceding iteration, satisfies condition (C.12), so that at each step of the next iteration calculation of the function in one new point is needed.

The number of calculation of the function is connected with the accuracy of λ^{min}.

In quantum-chemical problems it is preferable to use methods based on interpolation by polynomial of low degree, particularly on quadratic or cubic interpolation [2 - 4]. If only the values of the function are known, quadratic interpolation over three points is used. If three points, a,b,c are given and the values of the function in these points are f_a, f_b, f_c then the minimum of a parabola passing through three points is determined according to the formula

$$\tilde{\lambda}^{min} = 1/2 \; \frac{(b^2-c^2)f_a+(c^2-a^2)f_b+(a^2-b^2)f_c}{(b-c)f_a+(c-a)f_b+(a-b)f_c} \qquad (C.13)$$

If derivatives are known it is possible to construct a tangent parabola. In this case it is necessary to know the value of the function at two points and its derivative at one

point, but it is possible to use cubic interpolation over the values of the function and its derivative at two points. Then if f_a, g_a, and f_b, g_b are respectively the values of the function and its derivative at the points a and b (a < b), then approximate value of the minimum of the function is determined according to

$$\bar{\lambda}_{min} = \left[1 - \frac{g_b + w + z}{g_b - g_a + 2w} \right] (b - a) \qquad (C.14)$$

where

$$W = (Z^2 - g_a g_b)^{1/2}, \qquad Z = \frac{3(f_a - f_b)}{b - a} + g_a + g_b$$

C.3. MANY-DIMENSIONAL OPTIMIZATION

The simplest methods of search are based on the definite strategy of subsequent sorting out of points in multidimensional space. Thus, in Hook-Jeaves method finite increment is given in turn to each coordinate at each separate iteration and if the function decreases a new value of the coordinate is used instead of the old one. alternatively, the step over the given coordinate is made in the opposite direction. Then further treatment of other coordinates is made. After sorting out all the coordinates the next iteration is fulfilled unless all the old values are kept unchanged. This method appears to be quite simple for programming but convergence is quite slow.

The simplest method of movement along directions is cyclic coordinate descent. Sequence of one-dimensional minimizations is fulfilled along each of the coordinates in turn. The process is repeated cyclically unless the minimum is achieved over all the coordinates simultaneously. This method has slow convergence but may be effective if generalized coordinates are successfully chosen.

Consider a series of methods based on derivatives.

In the method of fastest descent it is assumed that

$$\vec{s}^{\,i} = -\vec{d}^{\,i} \qquad (C.15)$$

i.e. in (C.6) A = I. Thestep along the direction mass be chosen in different ways. It is possible to use one-dimensional minimization, i.e. $\lambda^i = \lambda^{min,i}$.However even the constant step guarantees convergence if inequality $0<\lambda<2/M$ is satisfied, where M is the greatest eigenvalue of Hessian.

If the distance between two intervals $A = [a_1,a_2]$, $B = [b_1,b_2]$ in the real interval I(R) is defined by

$$q(A,B) = \max\left\{|a_1 - a_2|,\ |b_1 - b_2|\right\} \qquad (C.16)$$

then the map q introduces a metric in I(R) [6]. In other words, a metric is a distance function which fulfills certain requirements [7]. The most effective procedures used for function minimization constitute a group of so called variable metric methods [8, 9] which are iterative methods using the steepest descent in the first step.

Nowadays the method of variable metrics proposed by Davidon-Fletcher-Powell is the most popular approach. Although this method demands more computer memory it is more effective. It is not necessary to determine the step from condition of the minimum of a function along a given direction and it may be even chosen as constant value. The direction of descent is determined according to (C.6), the A matrix being specified at each iteration step. In the beginning of the process initial approximation is given, $(\vec{q}^{\,o}, A^o)$. The matrix A^0must be positively determined, usually $A_o = I$. At the k-th step

$$\vec{s}^{\,k} = -A^{k-1}\vec{d}^{\,k-1},\quad \lambda^k = \lambda^{min,k},$$

$$A^k = A^{k-1} + \left[\Delta q^k - A^{k-1}\Delta d^k\right]\left[(\Delta d^k)^+ (\Delta q^k - A^{k-1}\Delta d^k)\right]^{-1}\left[\Delta q^k - A^{k-1}\Delta d^k\right]^+ \qquad (C.17)$$

where $\Delta q^k = q^k - q^{k-1}$, $\Delta d^k = d^k - d^{k-1}$,

aa^+ is direct vector product,

a^+a^- is scalar product.

The sequence of directions appears to be conjugate in the case of positively determined quadratic function and method of converges during k iterations, in the end of iterations it appears that $A = G^{-1}$, i.e. method ensures automatic construction of the inverse of the Hessian matrix.

Methods of variable metrics, penetrated into the fields of quantum chemistry during the last two decades. It is very convenient that on the basis of the known wave function for some configuration of muclei it is possible to calculate not only the energy at the given point but its derivatives, if

derivatives of molecular integrals are known.

$$\frac{\partial E}{\partial q_a} = S_p P \frac{\partial H}{\partial q_\alpha} + 1/2 \frac{\partial G}{\partial q_\alpha} - 1/2 S_p P \mp P \frac{\partial S}{\partial q_\alpha} \qquad (C.18)$$

where E is the total energy, D is density matrix, H and G are one- andtwo-electron parts of Fockian. F is Fockian (Fock hamiltonian), S is overlap matrix.

Calculation of derivatives is a very laborous procedure, particularly of derivatives of integrals of electron-electron repulsion. Computation of one component of gradient vector demands computation of the same quantity of additional integrals as calculation of the energy at one point. Moreover in the process of differentiation over coordinates the degree of polynomial is increased by 1, i.e. computation of integrals of derivatives is equivalent to computation of integrals of functions with a higher (by one) orbital quantum number. In semi-empirical methods computation of integrals takes only a small part of the whole computational time. Therefore application of gradient methods is especially effective. Thus, in the procedure of variable metrics in Murtagh-Sargent version the k-th iteration looks like:

$$q^{k+1} = q^k - \alpha_k A^k d^k \qquad (C.19)$$

$$A^k = A^{k-1} + Z^k (z^k)^+ / c^k$$

where $Z^k = - A^{k-1}\left[d^k - d^{k-1}(1-\alpha^{k-1})\right]$, $c^k = (d^k - d^{k-1})^+ Z^k$

The step α_k is assumed to be constant, $\alpha_k = 1$, but if thisstep leads to energy increase it is decreased in two times. Since the method preserves symmetry automatically and excludes pure translations and rotations, cartesian but not internal coordinates may be used.

Refined version of Murtagh-Sargent method was proposed by Pancir [8]. Geometry optimization is fulfilled together with self-consistent procedure, i.e. after each SCF-cycle geometry correction is fulfilled according to (C.19) (methods of double iterations [8].

To calculate derivatives it is enough to consider two-center components of energy, E_{AB}, since overlap matrix in this case is constant and equal to unitary matrix and one-center terms do not depend on geometry.

In the optimization procedure based on variable metrics [8] the Hessian matrix arises in the course of computation and makes the computation quadratically convergent [10]. The variation step is perfomed according to the following formula.

$$x_i = x_{i-1} - \alpha H_{i-1}^{-1} g_{i-1} \qquad (C.20)$$

where α is a scalar so chosen that the term $E(x_{i-1} - \alpha H_{i-1}^{-1})$ is minimal.

The way the Hessian matrix is constructed depends on the individual methods.

Davidon made use of (C.21).

$$H_i^{-1} = H_{i-1}^{-1} + q^T q/c_1 - Z^T Z/c_2 \qquad (C.21)$$

where $q = x_i - x_{i-1}$, $y = g_i - g_{i-1}$, $Z = (H_{i-1}^{-1})y$,

$c_1 = y^T q$, $c_2 = y^T Z$

Murtagh and Sargent suggested (C.22).

$$H_i^{-1} = H_{i-1}^{-1} + (q^T q - q^T Z - Z^T q + Z^T Z)/(c_1 - c_2) \qquad (C.22)$$

Broyden and Goldfarb used

$$H_i^{-1} = H_{i-1}^{-1} + \left[(1 + a_2/a_1)q^T q - q^T Z - Z^T q - Z^T Z\right]/(a_1 + a_2) \quad (C.23)$$

and Hoshino used (C.23).

$$H_i^{-1} = H_{i-1}^{-1} + \left[(1 + 2a_2/a_1)q^T q - q^T Z - Z^T q - Z^T Z\right]/a_1 \quad (C.24)$$

The starting H^{-1} matrix is chosen as the unit matrix, the choice of α is done by quadratic or cubic minimization in a given direction (vide infra). The value of α was chosen by

$$\alpha = r^T g_{i-1}/(r^T g'_{i-1} - r^T g_{i-1}) \quad (C.25)$$

where $r = x'_{i-1} - x_{i-1}$ and x'_{i-1} lies in the vicinity of x_{i-1} in the direction given by $(H_{i-1}^{-1})^T g_{i-1}$.

Searching the value of α by minimization of a cubic function is equivalent to minimization by means of gradients computed at two points of the same distance from x_{i-1} in the directions $(H_{i-1}^{-1})^T g_{i-1}$ and $-(H_{i-1}^{-1})^T g_{i-1}$ (double iteration technique). On the other hand, the Murtagh-Sargent method is quadratically convergent [10] for any α. For $\alpha = 1$ the number of variable metric iterations increased insignificantly.

Algorithm:

a) Proceed in the SCF iterative procedure at point x_{i-1} until the convergency criterion is less than an a priori given value, say ε.

b) Perform a step according to eqn. (C.1).

c) Perform the stability test (vide infra). If the tests are not satisfied reset the H_{i-1} matrix and continue with a).

d) Update the H_i^{-1} matrix according to any of eqns. (C.21) - (C.24).

e) If the norm of gradiaent is higher than a prescribed value, say δ, go back to a). If necessary, lower ε in the next calculation step.

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APPENDIX D. DENSITY OF STATES IN THE FORBIDDEN AND ALLOWED BANDS

Some generalized approaches for theoretical derivation of the density of states are given elsewhere [1, 2]. The density of states, $G(\varepsilon)$, is the number of electron states in a unit interval of energy. Thus, the number of electron states with an energy in the interval between ε and $\varepsilon + d\varepsilon$ is equal to $G(\varepsilon)d\varepsilon$ [3].

From the study of the electronic properties of amorphous solids using a simple hamiltonian of the tight-binding type, rigorous bounds were derived for the density of states of a tetrahedrally bonded solid [4 - 6]. In the derivations only perfect coordination of nearest neighbours was assumed. Various other results were obtained for the fraction s- and p-like character of wave functions, the attainment of bounds and other features of the density of states.

The two-band hamiltonian for the determination of the band structure of a topologically disordered system [4] is given by

$$H = \sum_{i,\, j \neq j'} V_1 \left|\phi_{ij}\right\rangle \left\langle\phi_{ij'}\right| + \sum_{i \neq i',\, j} V_2 \left|\phi_{ij}\right\rangle \left\langle\phi_{i'j}\right| \qquad \text{(D.1)}$$

where V_1 and V_2 are defined to be real and ϕ_{ij} are localized functions that form an orthonormal set and may be visualized as the familiar sp^3 hybridized orbitals of tight-binding theory, i is the index for the atoms and j for the bonds.

As can be seen from eqn. (D.1) for $V_2 = 0$ the hamiltonian describes completely decoupled atoms, each with a singly degenerate eigenstate at energy $E = 3V_1$ and triply degenerate eigenstates at $E = -V_1$. On the other hand, for $V_1 = 0$ the hamiltonian describes decoupled bonds each of which is associated with eigenstates at $E = \pm V_2$. Thus, the two matrix elements V_1 and V_2 might be called "banding" and "bonding" parameters, respectively.

Then the Schrödinger equation gives

$$M\vec{u}(i) = -V_2\vec{v}(i) \quad (D.5)$$

where

$$M_{ij} = \begin{cases} -E & i = j \\ V_1 & i \neq j \end{cases}$$

The matrix M has the eigenvalues

$$\lambda_1 = -E + 3V_1 \quad \text{(singly regenerate)} \quad (D.6)$$

and

$$\lambda_2 = -E - V_1 \quad \text{(triply degenerate)} \quad (D.7)$$

Tkaing the scalar product of both sides of (D.4) with their respective conjugate vectors one obtains

$$\vec{u}^{*}.M^2\,\vec{u} = V_2^2\,|\,\vec{v}\,|^2 \quad (D.8)$$

By expanding $\vec{u}$ in eigenvectors of M, the following inequalities were readily obtained from (D.8).

$$\max(\lambda_n^2)|\,\vec{u}\,|^2 \geq V_2^2|\,\vec{v}\,|^2 \geq \min(\lambda_n^2)|\,\vec{u}\,|^2 \quad (D.9)$$

It can be shown that if the energy E is such that

$$\max(\lambda_n^2) < V_2^2 \quad (D.10)$$

or

$$\min(\lambda_n^2) > V_2^2 \quad (D.11)$$

(D.9) implies a zero bulk density of states at that energy. One should first note that either of the inequalities (D.10) or (D.11) together with (D.9) implies that

$$\left|\,|\,\vec{u}\,|^2 - |\,\vec{v}\,|^2\right| > \theta|\,\vec{u}\,|^2 \quad (D.12)$$

where $\theta > 0$ and further $|\,\vec{v}\,|^2 - |\,\vec{u}\,|^2$ has the same sign for all atoms. Then considering the range of energy $E_0 \leq E \leq E_1$ for which such relations hold and letting θ to denote its maximum value in that rnage ($\theta \neq 0$), an integrated density of states, I, was defined by

$$I = \int_{E_0}^{E_1} dE\; n(E) \quad (D.13)$$

Weaire and Thorpe express the density of states in terms of the Green's functions for the face-centered cubic lattice $I_{fcc}(\varepsilon)$ as follows [4].

$$I_{fcc}(\varepsilon) = \left(\frac{1}{2\pi}\right)^3 \int_{-\pi}^{\pi}\int\int \frac{dxdydz}{\varepsilon - (\cos x\cos y+\cos y\cos z+\cos z\cos x)} \quad (D.2)$$

and the density of states is related to the imaginary part of the Green' functions by the relation

$$n(\varepsilon) = -\frac{1}{\pi}\left[\frac{[(E - V_1)^2 - 4V_1^2 - V_2^2]}{2V_1^2 V_2^2}\right] \mathrm{Im} I_{fcc}\left[\frac{[(E-V_1)^2-4V_1^2-V_2^2]^2}{4V_1^2V_2^2 - 1}\right] \quad (D.3)$$

Expressions are known for I_{fcc} in terms of the complete elliptic integrals of the first kind and an elegant discussion of Green's functions and their role in the calculation of the density of states is given elsewhere [7, 8].

By projecting out that part of the Scrödinger equation $(H-E)\psi = 0$ which lies in the subspace spanned by ϕ_{ij} for some given i and j=1 - 4, the coefficients a_{ij} are defined by

$$\psi = \sum_{i,j} a_{ij}\phi_{ij} \quad (D.4)$$

and a_{ij} for j = 1 - 4 are considered as the components of a vector $\vec{u}(i)$. The components $a_{i',j}$ associated with other orbitals (fig. D1) associated with these bonds may be considered as a second vector $\vec{v}(i)$.

Fig. D1. Coefficients of the basis functions 1 - 4 associated with a given atom in the expansion of a given wave function are elements of the vector $\vec{u}$ and the coefficients of 1' - 4' form the vector $\vec{v}$.

where n(E) is the normalized density of states, that is,

$$4 = \int_{-\infty}^{\infty} dE\ n(E) \qquad (D.14)$$

Considering a particular state with wave function ψ_n corresponding to an energy between E_0 and E_1 the quantity $|\vec{u}|^2 - |\vec{v}|^2$ was summed over all atoms for such a wave function which with the cancellation of terms in the interior interior of the structure and the assumption of "free" boundary condition reduces to

$$\sum_i \left(|\vec{u}(i)|^2 - |\vec{v}(i)|^2\right) = \sum_{\substack{\text{surface} \\ \text{atom } i \\ \text{component } m}} |\vec{u}(i)|^2 \qquad (D.15)$$

A surface atom is defined as an atom with at least one surface bond, i.e., one not connected to another atom in the structure. For large N the number N_s of atoms in the surface layer satisfies $N_s < \nu N^{2/3}$ (D.16)

where ν is a constant independent of N. Then eqns. (D.12) and (D.15) (using the constancy of the sign of $|\vec{u}|^2 - |\vec{v}|^2$) give for any wave function:

$$9 \sum_{i=1}^{N} |\vec{u}(i)|^2 < \sum_{i=1}^{N} \left| |\vec{u}(i)|^2 - |\vec{v}(i)|^2 \right| < \sum_{\substack{i,\text{surface} \\ \text{layer only}}} |\vec{u}(i)|^2 \qquad (D.17)$$

$$\sum_{i=1}^{N} \left| |\vec{u}(i)|^2 - |\vec{v}(i)|^2 \right| = \left| \sum_{i=1}^{N} \left(|\vec{u}(i)|^2 - |\vec{v}(i)|^2\right) \right| \qquad (D.18)$$

$$\left| \sum_{i=1}^{N} \left(|\vec{u}(i)|^2 - |\vec{v}(i)|^2\right) \right| < \sum_{\substack{i,\text{surface} \\ \text{layer only}}} |\vec{u}|^2 \qquad (D.19)$$

Combining eqns. (D.17) - (D.19) together with the normalization condition for the wave function

$$\sum_{i=1}^{N} | \vec{u}(i)|^2 = 1 \qquad (D.20)$$

one obtains

$$\sum_{i,\text{surface layer only}} | \vec{u}(i)|^2 > \vartheta \qquad (D.21)$$

Then it can be readily shown that

$$NI\vartheta < 4N_s \qquad (D.22)$$

where NI is the number of wave functions with energies between E_0 and E_1.

Therefore, it follows that

$$I < 4\vartheta^{-1}(N_s/N) \qquad (D.23)$$

Since $\vartheta > 0$ and is independent of N

$$\lim_{i\to\infty} I = 0 \qquad (D.24)$$

Similar procedures were used to derive certain properties of the allowed bands. In particular, it has been shown that the average fractional s- and p-character and the average bonding and anti-bonding character of a wave function are functions only of the energy E. Considering a particular normalized wave function over the whole system and expanding the eigenvectors of M the eigen vector $\vec{u}(s)$ with eigenvalue eqn. (D.6) is called s-like and any eigenvector $\vec{u}(p)$ with eigenvalue eqn. (D.7) is called p-like.

$$\vec{u} = c^{(s)} \vec{u}(s) + c^{(p)} \vec{u}(p) \qquad (D.25)$$

Then eqn. (D.8) may be written as

$$\lambda_1^2 |c^{(s)}|^2 + \lambda_2^2 |c^{(p)}|^2 = V_2^2 | \vec{v}|^2 \qquad (D.26)$$

or

$$| \vec{v}|^2 - | \vec{u}|^2 = (\lambda_1^2 V_2^2 - 1)|c^{(s)}|^2 + (\lambda_2^2 V_2^2 - 1)|c^{(p)}|^2 \qquad (D.27)$$

For quasiperiodic conditions and as N $\longrightarrow \omega$ the quantity

$$b = \sum_{i=1}^{N} (|\vec{v}(i) - |\vec{u}(i)|^2) \qquad (D.28)$$

vanishes and

$$F_s/F_p = (\lambda_2^2 - V_2^2)/(\lambda_1^2 - V_2^2) \qquad (D.29)$$

where

$$F_s = \sum_{i=1}^{N} |c^{(s)}|^2 \qquad (D.30)$$

$$F_p = \sum_{i=1}^{N} |c^{(p)}|^2 \qquad (D.31)$$

F_s and F_p may be called the fractional s- and p-like characters of the wave function.

Using $F_s + F_p = 1$ we obtain

$$F_s = (\lambda_2^2 - \lambda_1^2)/(\lambda_2^2 - V_2^2) \qquad (D.32)$$

The fractional bonding character was obtained by taking the scalar product of eqn. (D.4) with $\vec{u}^*$.

$$\vec{u}^*.M\,\vec{u} = -V_2^2\,\vec{u}^*.\,\vec{v} \qquad (D.33)$$

which may be written as

$$\lambda_1|c^{(s)}|^2 + \lambda_2|c^{(p)}|^2 = -V_2\,\vec{u}^*.\,\vec{v} \qquad (D.34)$$

Then the fractional bonding character is defined by

$$F_b = 1/2 + 1/2 \sum_{i=1}^{N} \vec{u}^*.\,\vec{v} \qquad (D.35)$$

in which case eqns. (D.34) and (D.35) yield

$$F_b = 1/2 - 1/2\, V_2^{-1}(\lambda_1 F_s + \lambda_2 F_p) \qquad (D.36)$$

The results (D.30) and (D.36) entail sum rules on the density of states n(E). The appropriate operator in the case of eqn. (D.30) is

$$S = \sum_{i=1}^{N} |s\rangle\langle s| \qquad (D.37)$$

where s is the s-like combination of basis functions ϕ_{ij} associated with atom i. The resultant sum rule is

$$\int_{-\infty}^{\infty} dE\ n(E)\ F_s(E) = 1 \qquad (D.38)$$

while eqn. (D.36) yields

$$\int_{-\infty}^{\infty} dE\ n(E)\ F_b(E) = 2 \qquad (D.39)$$

The Green function [5] for the six-ring Husimi cactus lattice [4] is defined by

$$g_{i,i'} = \left\langle \phi_i \left| (\varepsilon - H')^{-1} \right| \phi_{i'} \right\rangle \qquad (D.40)$$

where H' is an effective hamiltonian of a hexagon including an eefective field h.

$$H' = 1/4 \sum_{i,i' \text{neighbours}} |\phi_i\rangle\langle\phi_{i'}| + h \sum_{i=1}^{6} |\phi_i\rangle\langle\phi_{i'}| \qquad (D.41)$$

and ε are reduced energies of one-band hamiltonian $H^{(1)}$ [4].

$$H^{(1)} = 1/4 \sum_{i,i' \text{ neighbours}} |\phi_i\rangle\langle\phi_{i'}| \qquad (D.42)$$

The relation between E and ε is geven by the special case of the so-called one-band-two-band transformation [5]:

$$E(\varepsilon) = V_1 - (4V_1^2 + V_2^2 + 4V_1V_2\varepsilon)^{1/2} \qquad (D.43)$$

From eqns. (D.40) and (D.41), the Green function g_{00} for a site is evaluated as

$$g_{00} = 1/(\varepsilon - h) \qquad (D.44)$$

and the Green function for the complete system is given by

$$G_{00} = 1/(\varepsilon - 2h) \qquad (D.45)$$

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APPENDIX E. PROGRAM LIST OF CNINDO

```
C       PROGRAM CNINDO
C
C
C
        IMPLICIT DOUBLE PRECISION (A - H, O - Z)
        COMMON/ARRAYS/ABC(19200)
        COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
        COMMON/PERTBL/EL(18)
        COMMON/ORB/ORB(9)
        COMMON/GAB/XYZ(2000)
        COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35)NELECS,OCCA,OCCB
        COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLSED,OPEN
        COMMON/AUXINT/A(17),B(17)
        INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
        INTEGER ORB,E,AN,CHARGE,CZ,U,ULIM,OCCA,OCCB
C       INPUT IS READ IN THE FOLLOWING ORDER
C (1)   AN IDENTIFICATION CARD WHICH IS PRINTED AT THE BEGINNING OF THE
C (1)   OPTION (WVAE FUNCTION OPTION) AND OPNCLO (OPEN OR CLOSED SHELI
C       THE FORMAT A4,1X,A4 AND THE KEY WORDS ARE
C       FOR THE WAVE FUNCTION (4)  CNDO  INDO
C       FOR THE OPEN-CLOSED OPTION (A6)  OPEN  CLSD
C (3)   NATOMS,CHARGE,MULTIP,  FORMAT(3I4)
C (4)   ATOMIC NUMBER, X COORDINATE,Y COORDINATE,Z COORDINATE-1 CARD/A
        READ(2,20) (AN(I), I = 1,20)
        WRITE(3,30) (AN(I), I = 1,20)
        READ(2,40) OPTION,OPNCLO
        WRITE(3,45) OPTION,OPNCLO
        READ(2,50) NATOMS,CHARGE,MULTIP
        WRITE(3,60) NATOMS,CHARGE,MULTIP
        DO 10 I = 1,NATOMS
        READ(2,70) AN(I),C(I,1),C(I,2),C(I,3)
C       CONVERSION OF COORDINATES FROM ANGSTROMS TO ATOMIC UNITS
        DO 9 J = 1,3
 9      C(I,J) = C(I,J)/.529167D0
 10     CONTINUE
        IF(OPTION.EQ.CNDO) GO TO 6
 1      DO 5 I = 1,NATOMS
        IF(AN(I).LE.9) GO TO 4
 2      WRITE(3,3)
 3      FORMAT(5X,46HTHIS PROGRAM DOES NOT DO INDO CALCULATIONS FOR,
       151H MOLECULES CONTAINING ELEMENTS HIGHER THAN FLUORINE)
        STOP
 4      CONTINUE
 5      CONTINUE
 6      CONTINUE
        CALL COEFFT
        CALL INTGRL
        IF(OPNCLO.EQ.OPEN) GO TO 90
 80     CALL HUCKCL
        CALL SCFCLO
        CALL CPRINT
        GO TO 100
 90     CALL HUCKOP
        CALL SFCOPN
        CALL OPRINT
```

```
100   CONTINUE
20    FORMAT(20A4)
30    FORMAT(1H1,5X,20A4)
40    FORMAT(A4,1X,A4)
45    FORMAT(5X,A4,1X,A4)
50    FORMAT(3I4)
60    FORMAT(/5X,I4,18H ATOMS CHARGE = ,I4,18H MULTIPLICITY = ,I4/)
70  FORMAT(I4,3(3X,F12.7))
      CALL EXIT
      STOP
      END



      SUBROUTINE COEFFT
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/ARRAYS/S(80,80)Y(9135),Z(765),XX(2900)
      DO 1 I = 1,9135
1     Y(I) = 0.0D0
      DO 2 I = 1,765
2     Z(I) = 0.0D0
C     LOAD NON-ZERO Y COEFFICIENTS
      Y(7039) =      64.D0          Y(2842) =      16.D0
      Y(7040) =      64.D0          Y(2851) =     -16.D0
      Y(7049) =      64.D0          Y(2710) =      48.D0
      Y(7032) =     128.D0          Y(2719) =     -48.D0
      Y(7041) =     -64.D0          Y(2711) =      48.D0
      Y(7033) =    -128.D0          Y(2720) =     -96.D0
      Y(7042) =     128.D0          Y(2729) =      48.D0
      Y(7025) =      64.D0          Y(2703) =     -48.D0
      Y(7034) =     128.D0          Y(2712) =     -48.D0
      Y(7026) =      64.D0          Y(2721) =      96.D0
      Y(7035) =     -64.D0          Y(2704) =     -48.D0
      Y(7027) =     -64.D0          Y(2713) =      48.D0
      Y(6904) =     -96.D0          Y(2722) =      48.D0
      Y(6913) =      32.D0          Y(2731) =     -48.D0
      Y(6896) =    -192.D0          Y(2705) =      96.D0
      Y(6905) =     192.D0          Y(2714) =     -48.D0
      Y(6906) =     288.D0          Y(2723) =     -48.D0
      Y(6915) =     -96.D0          Y(2706) =      48.D0
      Y(6889) =     192.D0          Y(2715) =     -96.D0
      Y(6907) =    -192.D0          Y(2724) =      48.D0
      Y(6890) =      96.D0          Y(2707) =     -48.D0
      Y(6899) =    -288.D0          Y(2716) =      48.D0
      Y(6891) =    -192.D0          Y(5329) =      64.D0
      Y(6900) =     192.D0          Y(5322) =    -128.D0
      Y(6892) =     -32.D0          Y(5340) =     -64.D0
      Y(6901) =      96.D0          Y(5315) =      64.D0
      Y(2854) =     -16.D0          Y(5333) =     128.D0
      Y(2863) =      16.D0          Y(5326) =     -64.D0
      Y(2847) =      32.D0          Y(5185) =     -96.D0
      Y(2856) =     -16.D0          Y(5194) =      32.D0
      Y(2865) =     -16.D0          Y(5186) =      96.D0
      Y(2840) =     -16.D0          Y(5195) =      64.D0
      Y(2849) =     -16.D0          Y(5204) =      32.D0
      Y(2858) =      32.D0          Y(5178) =      96.D0
```

```
Y(5187) =      32.D0
Y(5196) =      64.D0
Y(5179) =      96.D0
Y(5188) =     -32.D0
Y(5197) =      32.D0
Y(5206) =     -96.D0
Y(5180) =     -64.D0
Y(5189) =     -32.D0
Y(5198) =     -96.D0
Y(5181) =     -32.D0
Y(5190) =     -64.D0
Y(5199) =      96.D0
Y(5182) =     -32.D0
Y(5191) =      96.D0
Y(4375) =    -144.D0
Y(4384) =      96.D0
Y(4393) =     -16.D0
Y(4368) =     144.D0
Y(4386) =     -48.D0
Y(4395) =      96.D0
Y(4370) =     -96.D0
Y(4379) =      48.D0
Y(4397) =    -144.D0
Y(4372) =      16.D0
Y(4381) =     -96.D0
Y(4390) =     144.D0
Y(1900) =     144.D0
Y(1909) =    -144.D0
Y(1893) =    -144.D0
Y(1920) =     144.D0
Y(1895) =     144.D0
Y(1922) =    -144.D0
Y(1906) =    -144.D0
Y(1915) =     144.D0
Y( 955) =     -16.D0
Y( 964) =      32.D0
Y( 973) =     -16.D0
Y( 948) =      16.D0
Y( 966) =     -48.D0
Y( 975) =      32.D0
Y( 950) =     -32.D0
Y( 959) =      48.D0
Y( 961) =     -32.D0
Y( 970) =      16.D0
Y(8155) =      64.D0
Y(8156) =     -64.D0
Y(8165) =     -64.D0
Y(8145) =     -64.D0
Y(8157) =      64.D0
Y(8149) =      64.D0
Y(8158) =      64.D0
Y(8150) =     -64.D0
Y(8020) =     -96.D0
Y(8029) =      32.D0
Y(8021) =     128.D0
Y(8013) =      96.D0
Y(8031) =     -96.D0
Y(8014) =    -128.D0
Y(8015) =     -32.D0
Y(8024) =      96.D0
Y(7084) =     -64.D0
Y(7076) =    -128.D0
Y(7085) =      64.D0
Y(7086) =     128.D0
Y(7069) =     128.D0
Y(7070) =      64.D0
Y(7079) =    -128.D0
Y(7071) =     -64.D0
Y(3205) =     -16.D0
Y(3214) =      16.D0
Y(3206) =      16.D0
Y(3215) =     -16.D0
Y(3198) =      16.D0
Y(3216) =     -16.D0
Y(3199) =     -16.D0
Y(3217) =      16.D0
Y(3200) =     -16.D0
Y(3209) =      16.D0
Y(3201) =      16.D0
Y(3210) =      16.D0
Y(7579) =      64.D0
Y(7580) =     -64.D0
Y(7572) =    -128.D0
Y(7573) =     128.D0
Y(7565) =      64.D0
Y(7566) =     -64.D0
Y(5680) =      64.D0
Y(5681) =     -64.D0
Y(5673) =     -64.D0
Y(5691) =     -64.D0
Y(5674) =      64.D0
Y(5692) =      64.D0
Y(5684) =      64.D0
Y(5685) =     -64.D0
Y(7435) =     -96.D0
Y(7444) =      32.D0
Y(7436) =     -96.D0
Y(7445) =     160.D0
Y(7428) =      96.D0
Y(7437) =     128.D0
Y(7446) =     -96.D0
Y(7429) =      96.D0
Y(7438) =    -128.D0
Y(7447) =     -96.D0
Y(7430) =    -160.D0
Y(7439) =      96.D0
Y(7431) =     -32.D0
Y(7440) =      96.D0
```

```
      Y(5545) =      -96.D0          Z(669) =       1.D0
      Y(5554) =       32.D0          Z(154) =      -1.D0
      Y(5546) =       32.D0          Z(156) =       5.D0
      Y(5555) =       32.D0          Z(158) =     -10.D0
      Y(5538) =       96.D0          Z(160) =      10.D0
      Y(5556) =       32.D0          Z(162) =      -5.D0
      Y(5539) =      -32.D0          Z(164) =       1.D0
      Y(5557) =      -96.D0          Z(222) =      -1.D0
      Y(5540) =      -32.D0          Z(223) =       1.D0
      Y(5549) =      -32.D0          Z(224) =       4.D0
      Y(5541) =      -32.D0          Z(225) =      -4.D0
      Y(5550) =       96.D0          Z(226) =      -6.D0
      Y(3070) =       48.D0          Z(227) =       6.D0
      Y(3079) =      -48.D0          Z(228) =       4.D0
      Y(3071) =      -48.D0          Z(229) =      -4.D0
      Y(3080) =       48.D0          Z(230) =      -1.D0
      Y(3063) =      -48.D0          Z(231) =       1.D0
      Y(3081) =       48.D0          Z(307) =      -1.D0
      Y(3064) =       48.D0          Z(308) =       2.D0
      Y(3082) =      -48.D0          Z(309) =       2.D0
      Y(3065) =       48.D0          Z(310) =      -6.D0
      Y(3074) =      -48.D0          Z(312) =       6.D0
      Y(3066) =      -48.D0          Z(313) =      -2.D0
      Y(3075) =       48.D0          Z(314) =      -2.D0
      Y(8200) =      -64.D0          Z(315) =       1.D0
      Y(8201) =       64.D0          Z(409) =      -1.D0
      Y(8193) =       64.D0          Z(410) =       3.D0
      Y(8194) =      -64.D0          Z(411) =      -1.D0
      Y(7615) =      -64.D0          Z(412) =      -5.D0
      Y(7616) =      -64.D0          Z(413) =       5.D0
      Y(7625) =       64.D0          Z(414) =       1.D0
      Y(7608) =       64.D0          Z(415) =      -3.D0
      Y(7617) =       64.D0          Z(416) =       1.D0
      Y(7609) =       64.D0          Z(528) =      -1.D0
      Y(7618) =      -64.D0          Z(529) =       4.D0
      Y(7610) =      -64.D0          Z(530) =      -5.D0
      Y(3250) =       16.D0          Z(532) =       5.D0
      Y(3259) =      -16.D0          Z(533) =      -4.D0
      Y(3243) =      -16.D0          Z(534) =       1.D0
      Y(3261) =       16.D0          Z(562) =      -1.D0
      Y(3245) =       16.D0          Z(563) =       2.D0
      Y(3254) =      -16.D0          Z(565) =      -2.D0
      Y(5725) =      -64.D0          Z(566) =       1.D0
      Y(5718) =       64.D0          Z(732) =      -1.D0
      Y(5736) =       64.D0          Z(733) =       1.D0
      Y(5729) =      -64.D0          Z(545) =       1.D0
C     LOAD NON-ZERO Z COEFFICIENTS
      Z(341) =       -1.D0          Z(546) =      -3.D0
      Z(343) =        3.D0          Z(547) =       2.D0
      Z(345) =       -3.D0          Z(548) =       2.D0
      Z(347) =        1.D0          Z(549) =      -3.D0
      Z(664) =       -1.D0          Z(550) =       1.D0
      Z(665) =        5.D0          Z(579) =       1.D0
      Z(666) =      -10.D0          Z(580) =      -1.D0
      Z(667) =       10.D0          Z(581) =      -1.D0
      Z(668) =       -5.D0          Z(582) =       1.D0
```

```
      Z(596)  =       -1.D0
      Z(598)  =        1.D0
      Z(443)  =       -1.D0
      Z(444)  =        1.D0
      Z(445)  =        2.D0
      Z(446)  =       -2.D0
      Z(447)  =       -1.D0
      Z(448)  =        1.D0
      Z(698)  =       -1.D0
      Z(699)  =        3.D0
      Z(700)  =       -3.D0
      Z(701)  =        1.D0
      Z(324)  =        1.D0
      Z(325)  =       -1.D0
      Z(326)  =       -3.D0
      Z(327)  =        3.D0
      Z(328)  =        3.D0
      Z(329)  =       -3.D0
      Z(330)  =       -1.D0
      Z(331)  =        1.D0
      Z(460)  =        1.D0
      Z(462)  =       -2.D0
      Z(464)  =        1.D0
      RETURN
      END


      SUBROUTINE INTGRL
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     ATOMIC INTEGRALS FOR CNDO CALCULATIONS
      COMMON/ARRAYS/S(80,80),Y(9,5,203),Z(17,45),XX(2900)
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON/GAB/XXX(400),GAMMA(35,35),T(9,9),PAIRS(9,9),TEMP(9,9)
     1,G1(3),G2(3),YYY(126)
      COMMON/AUXINT/A(17),B(17)
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      DIMENSION MU(18),NG(18),LG(9),MG(9),E(3)
      DIMENSION P(80,80)
      EQUIVALENCE (P(1),Y(1))
      DOUBLE PRECISION MU,NUM,K1,K2
      INTEGER AN,ULIM,ULK,ULL,CZ,U,CHARGE,ANL,ANK,OCCA,OCCB
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
C     DETERMINATION OF SIZE OF AO BASIS IN AND CORE CHARGE CZ
      N = 0
      DO 60 I = 1,NATOMS
      LLIM(I) = N+1
      K = 1
      IF(AN(I).LT.11) GO TO 20
   10 N = N+9
      CZ(I) = AN(I) - 10
      GO TO 50
   20 IF(AN(I).LT.3) GO TO 40
   30 N = N+4
      CZ(I) = AN(I) - 2
```

```
      GO TO 50
 40   N = N+1
      CZ(I) = AN(I)
 50   CONTINUE
      ULIM(I) = N
 60   CONTINUE
C     FILL U ARRAY --- U(J) IDENTIFIES THE ATOM TO WHICH ORBITAL J IS
C     ATTACHED E.G. ORBITAL 32 ATTACHED TO ATOM 7,ETC.
      DO 70 K = 1,NATOMS
      LLK = LLIM(K)
      ULK = ULIM(K)
      LIM = ULK + 1 - LLK
      DO 70 I = 1,LIM
      J = LLK +I - 1
 70   U(J) = K
C     ASSIGNMENT OF ORBITAL EXPONENTS TO ATOMS BY SLATER RULES
      MU(2)    = 1.7D0
      MU(1)    = 1.2D0
      NG(1)    = 1
      NG(1)    = 1
      DO 80 I = 3,10
      NG(I)    = 2
 80   MU(I)    = .325D0*FLOAT(I-1)
      DO 90 I  = 11,18
      NG(I)    = 3
 90   MU(I)    = (.650D0*FLOAT(I)-4.95D0)/3.D0
C     ASSIGNMENT OF ANGULAR MOMENTUM QUANTUM NOS. TO ATOMIC ORBITALS
      LG(1)    =  0
      LG(2)    =  1
      LG(3)    =  1
      LG(4)    =  1
      LG(5)    =  2
      LG(6)    =  2
      LG(7)    =  2
      LG(8)    =  2
      LG(9)    =  2
      MG(1)    =  0
      MG(2)    =  1
      MG(3)    = -1
      MG(4)    =  0
      MG(5)    =  0
      MG(6)    =  1
      MG(7)    = -1
      MG(8)    =  2
      MG(9)    = -2
C     STEPS THRU PAIRS OF ATOMS
      DO 320 K = 1,NATOMS
      DO 320 L = K,NATOMS
      DO 100 I = 1,3
      C1(I)    = C(K,I)
 100  C2(I)    = C(L,K)
C     CALCULATE UNIT VECTOR ALONG INTERATOM AXIS, E
      CALL RELVEC(R,E,C1,C2)
      LLK  =  LLIM(K)
      LLL  =  LLIM(L)
      ULK  =  ULIM(K)
```

```
      ULL    = ULIM(L)
      NORBK = ULK - LLK + 1
      NORBL = ULL - LLL + 1
      ANK    = AN(K)
      ANL    = AN(L)
C     LOOP THRU PAIRS OF BASIS FUNCTIONS, ONE ON EACH ATOM
      DO 200 I = 1,NORBK
      DO 200 J = 1,NORBL
      IF(K.EQ.L) GO TO 160
  110 IF(MC(I).NE.MC(J)) GO TO 150
  120 IF(MC(I).LT.0) GO TO 140
  130 PAIRS(I,J) = DSQRT((MU(ANK)*R)**(2*NC(ANK)+1)*(MU(ANL)*R)**(2*NC(AN
     1)+1)/(FACT(2*NC(ANK))*FACT(2*NC(ANL))))*(-1.D0)**(LC(J)+NC(J))
     2*SS(NC(ANK),LC(I),MC(I),NC(ANL),LC(J),MU(ANK)*R,MU(ANL)*R)
      GO TO 190
  140 PAIRS(I,J) = PAIRS(I-1,J-1)
      GO TO 190
  150 PAIRS(I,J) = 0.D0
      GO TO 190
  160 IF(I.EQ.J) GO TO 170
  180 PAIRS(I,J) = 0.D0
      GO TO 190
  170 PAIRS(I,J) = 1.0D0
  190 CONTINUE
  200 CONTINUE
      LCULK = LC(NORBK)
      LCULL = LC(NORBL)
      MAXL   = MAX0(LCULK,LCULL)
      IF(R.GT.0.000001D0) GO TO 220
  210 GO TO 250
C     ROTATE INTEGRALS FROM DIATOMIC BASIS TO MOLECULAR BASIS
  220 CALL HARMTR(T,MAXL,E)
      DO 230 I   = 1,NORBK
      DO 230 J   = 1,NORBL
      TEMP(I,J) = 0.D0
      DO 230 KK = 1,NORBL
      TEMP(I,J) = TEMP(I,J)+T(J,KK)*PAIRS(I,KK)
  230 CONTINUE
      DO 240 I    = 1,NORBK
      DO 240 J    = 1,NORBL
      PAIRS(I,J) = 0.D0
      DO 240 KK  = 1,NORBK
      PAIRS(I,J) = PAIRS(I,J)+T(I,KK)*TEMP(KK,J)
  240 CONTINUE
C     FILL S MATRIX
  250 CONTINUE
      DO 260 I = 1,NORBK
      LLKP      = LLK + I - 1
      DO 260 J = 1,NORBL
      LLLP      = LLL + J - 1
  260 S(LLKP,LLLP) = PAIRS(I,J)
C     COMPUTATION OF 1-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIO
      N1 = NC(ANK)
      N2 = NC(ANL)
      K1 = MU(ANK)
      K2 = MU(ANL)
      IF(K.NE.L) GO TO 290
```

```
 270   TERM1 = FACT(2*N1-1)/((2.D0*K2)**(2*N1))
       TERM2 = 0.D0
       LIM   = 2*N1
       DO 280 J = 1,LIM
       NUM = FLOAT(J)*(2.D0*K1)**(2*N1-J)*FACT(4*N1-J-1)
       DEN = FACT(2*N1-J)*2.D0*FLOAT(N1)*(2.D0*(K1+K2))**(4*N1-J)
       TERM2 = TERM1+NUM/DEN
 280   CONTINUE
       GO TO 310
C      COMPUTATION OF 2-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTI
 290   TERM1 = (R/2.D0)**(2*N2)*SS(0,0,0,2*N2-1,0,0.D0,2.D0*K2*R)
       TERM2 = 0.D0
       LIM = 2*N1
       DO 300 J =1,LIM
 300   TERM2 = TERM2*(FLOAT(J)*(2.D0*K1)**(2*N1-J)*(R/2.D0)**(2*
      1N1-J+2*N2))/(FACT(2*N1-J)*2.D0*FLOAT(N1)*SS(2*N1-J,0,0,2*N2-1,0
      2,2.D0*K1*R,2.D0*K2*R)
 310   GAMMA(K,L) = ((2.D0*K2)**(2*N2+1)/FACT*N2))*(TERM1-TERM2)
 320   CONTINUE
C      SYMMETRIZATION OF OVERLAP AND COULOMB INTEGRAL MATRICES
       DO 330 J = 1,N
 330   S(J,I) = S(I,J)
       DO 340 GAMMA(J,I) = GAMMA(I,J)
       WRITE(3,350)
 350   FORMAT(1H1,1X,23HOVERLAP INTEGRAL MATRIX)
       CALL MATOUT(N,1)
C      TRANSFER GAMMA TO 80X80 MATRIX P FOR PRINTING
       DO 360 I = 1,NATOMS
       DO 360 J = 1,NATOMS
 360   P(I,J) = GAMMA(I,J)
       WRITE(3,370)
 370   FORMAT(1X,23HCOULOMB INTEGRAL MATRIX)
       CALL MATOUT(NATOMS,2)
       RETURN
       END



       FUNCTION SS(NN1,LL1,MM,NN2,LL2,ALPHA,BETA)
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
       COMMON/ARRAYS/S(80,80),Y(9,5,203),Z(17,45),XX(2900)
       COMMON/AUXINT/A(17),B(17)
       INTEGER ULIM
       N1 = NN1
       L1 = LL1
       M  = MM
       N2 = NN2
       L2 = LL2
       P  = (ALPHA+BETA)/2.D0
       PT = (ALPHA-BETA)/2.D0
       X  = 0.D0
       M  = IABS(M)
C      REVERSE QUANTUM NUMBERS IF NECESSARY
       IF((L2.LT.L1).OR.((L2.EQ.L1).AND.(N2.LT.N1))) GO TO 20
 10    GO TO 30
 20    K  = N1
       N1 = N2
```

```
      N2 = K
      K = L1
      L1 = L2
      L2 = K
      PT = -PT
 30   CONTINUE
      K = MOD((N1+N2-L1-L2),2
C     FIND A AND B INTEGRALS
      CALL AINTGS(P,N1+N2)
      CALL BINTGS(PT,N1+N2)
      IF((L1.GT.0).OR.(L2.GT.0)) GO TO 60
C     BEGIN SECTION USED FOR OVERLAP INTEGRALS INVOLVING S FUNCTIONS
C     FIND Z TABLE NUMBER
 40   L = (90-17*N1+N1**2-2*N2)/2
      ULIM = N1+N2
      LLIM = 0
      DO 50 I = LLIM,ULIM
      NNI1 = N1+N2-I+1
 50   X = X+Z(I+1,L)*A(I+1)*B(NNI1)/2.D0
      SS = X
      GO TO 80
C     BEGIN SECTION USED FOR OVERLAP INVOLVING NON-S FUNCTIONS
C     FIND Y TABLE NUBMER L
 60   L = (5-M)*(24-10*M+M**2)*(83-30*M+3*M**2)/120+
     1(30-9*L1+L1**2-2*N1)*(28-9*L1+L1**2-2*N1)8+
     2(30-9*L2+L2**2-2*N2)/2
      LLIM = 0
      DO 70 I = LLIM,8
      IIII = 2*J+MOD(K+I,2)+1
 70   X = X+Y(I+1,J+1,L)*A(I+1*B(IIII)
      SS = X*(FACT(M+1)/8.D0)**2*DSQRT(FLOAT(2*L1+1)*FACT(L1-M)*
     1FLOAT(2*L2+1)*FACT(L2-M)/(4.D0*FACT(L1+M)*FACT(L2+M)))
 80   CONTINUE
      RETURN
      END



      SUBROUTINE HARMTR(T,MAXL,E)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION T(9,9),E(3)
      COST = E(3)
      IF((1.D0-COST**2).GT.0.0000000001) GO TO 20
 10   SINT = 0.D0
      GO TO 30
 20   SINT = DSQRT(1.D0-COST**2)
 30   CONTINUE
      IF(SINT.GT.0.000001D0) GO TO 50
 40   COSP = 1.D0
      SINP =0.D0
      GO TO 70
 50   COSP = E(1)/SINT
 60   SINP = E(2)/SINT
 70   CONTINUE
      DO 80 I = 1,9
      DO 80 J = 1,9
 80   T(I,J) = 0.D0
```

```
      T(1,1) = 1.D0
      IF(MAXL.GT.1) GO TO 100
 90   IF(MAXL.GT.0) GO TO 100
      GO TO 120
 100  COS2T = COST**2-SINT**2
      SIN2T = 2.D0*SINT*COST
      COS2P = COSP**2-SINP**2
      SIN2P = 2.D0*SINP*COSP
C     TRANSFER MATRIX ELEMENTS FOR D FUNCTIONS
      SQRT3 =  DSQRT(3.D0)
      T(5,5) = (3.D0*COST**2-1.D0)/2.D0
      T(5,6) = -SQRT3*SIN2T/2.D0
      T(5,8) = SQRT3*SINT**2/2.D0
      T(6,5) = SQRT3*SIN2T*COSP/2.D0
      T(6,6) = COS2T*COSP
      T(6,7) = -COST*SINP
      T(6,8) = -T(6,5)/SQRT3
      T(6,9) = SINT*SINP
      T(7,5) = SQRT3*SIN2T*SINP/2.D0
      T(7,6) = COS2T*SINP
      T(7,7) = COST*COSP
      T(7,8) = -T(7,5)/SQRT3
      T(7,9) = -SINT*COSP
      T(8,5) = SQRT3*SINT**2*COS2P/2.D0
      T(8,6) = SIN2T*COS2P/2.D0
      T(8,7) = -SINT*SIN2P
      T(8,8) = (1.D0+COST**2)*COS2P/2.D0
      T(8,9) = -COST*SIN2P
      T(9,5) = SQRT3*SINT**2*SIN2P/2.D0
      T(9,6) = SIN2T*SIN2P/2.D0
      T(9,7) = SINT*COS2P
      T(9,8) = (1.D0+COST**2)*SN2P/2.D0
      T(9,9) = COST*COS2P
 110  CONTINUE
C     TRANSFORMATION MATRIX ELEMENTS FOR P FUNCTIONS
      T(2,2) = COST*COSP
      T(2,3) = -SINP
      T(2,4) = SINT*COSP
      T(2,2) = COST*SINP
      T(2,3) = COSP
      T(2,4) = SINT*SINP
      T(4,2) = -SINT
      T(4,4) = COST
 120  CONTINUE
      RETURN
      END



      SUBROUTINE RELVEC(R,E,C1,C2)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION E(3),C1(3),C2(3)
      X = 0.D0
      DO 10 I = 1,3
      E(I) = C2(I)-C1(I)
      X = X+E(I)**2
 10   CONTINUE
```

```
      R = DSQRT(X)
      DO 40 I = 1,3
      IF(R.GT..000001D0) GO TO 30
20    GO TO 40
30    E(I) = E(I)/R
40    CONTINUE
      RETURN
      END



      FUNCTION FACT(N)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      PRODT = 1.D0
20    DO 30 I = 1,N
30    PRODT = PRODT*FLOAT(I)
40    FACT = PRODT
      RETURN
      END



      SUBROUTINE BINTGS(X,K)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     FILLS ARRAY OF B-INTEGRALS. NOTE THAT B(I) IS B(I-1) IN THE
C     USUAL NOTATION
C     FOR X.GT.3                      EXPONENTIAL FORMULA IS USED
C     FOR 2.LT.X.LT.3 AND K.LE.10 EXPONENTIAL FORMULA IS USED
C     FOR 2.LT.X.LE.3 AND K.GT.10 15 TERM SERIES IS USED
C     FOR 1.LT.E.2 AND K.LE.7      EXPONENTIAL FORMULA IS USED
C     FOR 1.LT.E.2 AND K.GT.7      12 TERM SERIES IS USED
C     FOR .5.LT.X.LE.1 AND K.LE.5 EXPONENTIAL FORMULA  IS USED
C     FOR .5.LT.X.LE.1 AND K.GT.5 7 TERM SERIES IS USED
C     FOR X.LE.5                       6 TERM SERIES IS USED
C     ***************************************************************
      COMMON/AUXINT/A(17),B(17)
      I0 = 0
      ABSX = DABS(X)
      IF(ABSX.GT.3.D0) GO TO 120
10    IF(ABSX.GT.2.D0) GO TO 20
40    IF(ABSX.GT.1.D0) GO TO 50
70    IF(ABSX.GT..5D0) GO TO 80
100   IF(ABSX.GT..000001D0) GO TO 110
      GO TO 170
110   LAST = 6
      GO TO 140
80    IF(K.LE.5) GO TO 120
90    LAST = 7
      GO TO 140
50    IF(K.LE.7) GO TO 120
60    LAST = 12
      GO TO 140
20    IF(K.LE.10) GO TO 120
30    LAST = 15
      GO TO 140
120   EXPX = DEXP(X)
      EXPMX = 1.D0/EXPX
```

```
      B(1) = (EXPX-EXPMX)/X
      DO 130 I = 1,K
130   B(I+1) = (FLOAT()*B(I)+(-1.D0)**(M+I+1))/(FACT(M)*FLOAT(M+I+1))
      GO TO 190
140   DO 160 I = 10,K
      Y = 0.D0
      DO 150 M = 10,LAST
150   Y = Y+(-X)**M*(1.D0-(-1.D0)**(M+I+1))/(FACT(M)*FLOAT(M+I+1))
160   B(I+1) = Y
      GO TO 190
170   DO 180 I = 10,K
180   B(I+1) = (1.D0-(-1.D0)**(I+1))/FLOAT(I+1)
190   CONTINUE
      RETURN
      END



      SUBROUTINE AINTGS(X,K)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/AUXINT/A(17),B(17)
      A(1) = DEXP(-X)/X
      DO 10 I =1,K
10    A(I+1) = (A(I)*FLOAT(I)+DEXP(-X))/X
      RETURN
      END



      SUBROUTINE MATOUT(N,MATOP)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/ARRAYS/A(80,80,3)
      DO 80 M = 1,N,11
      K = M+10
      IF(K.LE.N) GO TO 30
20    K = N
30    CONTINUE
      WRITE(3,40) (J,J = M,K)
40    FORMAT(//,7X,11(4X,I2,3X),//)
      DO 60 I = 1,N
      WRITE(3,50) I,(A(I,J,MATOP),J = M,K)
50    FORMAT(1X,I2,4X,50(F9.4))
60    CONTINUE
      WRITE(3,70)
70    FORMAT(//)
80    CONTINUE
      RETURN
      END
```

```
      SUBROUTINE HUCKEL
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     EXTENDED HUCKEL THEORY FOR CLOSED SHELLS
C     OVERLAPS ARE IN MATRIX A,COULOMB INTEGRALS(GAMMA) ARE IN MATR
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35)NELECS,OCCA,OCCB
      COMMON/GAB/XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      DIMENSION ENEG(18,3),BETA0(18)
      DIMENSION G1(18),F2(18)
      INTEGER CHARGE OCCA,OCCB,UL,AN,CZ,U,ULIM,ANI
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      G1(3) = .092012          D0
      G1(4) = .1407            D0
      G1(5) = .199265          D0
      G1(6) = .267708          D0
      G1(7) = .346029          D0
      G1(8) = .43423           D0
      G1(9) = .532305          D0
      F2(3) = .049865          D0
      F2(4) = .089125          D0
      F2(5) = .13041           D0
      F2(6) = .17372           D0
      F2(7) = .219055          D0
      F2(8) = .266415          D0
      F2(9) = .31580           D0
      ENEG(1,1) = 7.1761       D0
      ENEG(3,1) = 3.1055       D0
      ENEG(3,2) = 1.258        D0
      ENEG(4,1) = 5.94557    D0
      ENEG(4,2) = 2.563        D0
      ENEG(5,1) = 9.95407      D0
      ENEG(5,2) = 4.001        D0
      ENEG(6,1) = 14.051       D0
      ENEG(6,2) = 5.572        D0
      ENEG(7,1) = 19.31637     D0
      ENEG(7,2) = 7.275        D0
      ENEG(8,1) = 25.39017     D0
      ENEG(8,2) = 9.111        D0
      ENEG(9,1) = 32.2724      D0
      ENEG(9,2) = 11.08        D0
      ENEG(11,1) = 2.804       D0
      ENEG(11,2) = 1.302       D0
      ENEG(11,3) = 0.150       D0
      ENEG(12,1) = 5.1254      D0
      ENEG(12,2) = 2.0516      D0
      ENEG(12,3) = 0.16195     D0
      ENEG(13,1) = 7.7706      D0
      ENEG(13,2) = 2.9951      D0
      ENEG(13,3) = 0.22425     D0
      ENEG(14,1) = 10.0327     D0
      ENEG(14,2) = 4.1325      D0
      ENEG(14,3) = 0.337       D0
      ENEG(15,1) = 14.0327     D0
      ENEG(15,2) = 5.4638      D0
      ENEG(15,3) = 0.500       D0
```

```
      ENEG(16,1) = 17.6496      D0
      ENEG(16,2) = 6.989        D0
      ENEG(16,3) = 0.71325      D0
      ENEG(17,1) = 21.5906      D0
      ENEG(17,2) = 8.7081       D0
      ENEG(17,3) = 0.97695      D0
      BETA0(1) = -9.            D0
      BETA0(3) = -9.            D0
      BETA0(4) = -13.           D0
      BETA0(5) = -17.           D0
      BETA0(6) = -21.           D0
      BETA0(7) = -25.           D0
      BETA0(8) = -31.           D0
      BETA0(9) = -39.           D0
      BETA0(11) = -7.7203       D0
      BETA0(12) = -9.4471       D0
      BETA0(13) = -11.3011      D0
      BETA0(14) = -13.065       D0
      BETA0(15) = -15.070       D0
      BETA0(16) = -18.150       D0
      BETA0(17) = -22.330       D0
C     FIND NELECS AND FILL H CORE(DIAGONAL) WITH (I+A)/2
      NELECS = 0
      DO 60 I = 1,NATOMS
      NELECS = NELECS+CZ(I)
      LL = LLIM(I)
      UL = ULIM(I)
      ANI = AN(I)
      L = 0
      DO 50 J = LL,UL
      L = L+1
      IF(L.EQ.1) GO TO 10
 20   IF(L.LT.5) GO TO 40
 30   A(J,J) = -ENEG(ANI,3)/27.21D0
      GO TO 50
 40   A(J,J) = -ENEG(ANI,2)/27.21D0
      GO TO 50
 10   A(J,J) = -ENEG(ANI,1)/27.21D0
 50   CONTINUE
 60   CONTINUE
      NELECS = NELECS-CHARGE
      OCCCA = NELECS/2
C     FORM HUCKEL HAMILTONIAN IN A (OFF DIAGONAL TWO CENTER TERMS)
      DO 90 I = 2,N
      K = U(I)
      L = AN(K)
      UL = I-1
      DO 90 J = 1,UL
      KK = U(J)
      LL = AN(KK)
      IF((L.GT.9).OR.(LL.GT.9)) GO TO 70
 80   A(I,J) = A(I,J)*BETA0(L)+BETA0(LL)/54.42D0
      A(J,I) = A(I,J)
      GO TO 90
 70   A(I,J) = 0.75D0*A(I,J)*(BETA0(L)+BETA0(LL))/54.42D0
      A(J,I) = A(I,J)
```

```
 90     CONTINUE
        DO 100 I = 1,N
 100    Q(I) = A(I,I)
        RHO = 1.D-6
        CALL EIGN(N,RHO)
C       EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
        DO 140 I = 1,N
        DO 120 J = 1,N
 110    XXX(J) = XXX(J)+2.D0*B(I,K)*B(J,K)
 120    CONTINUE
        DO 130 J = I,N
 130    B(I,J) = XXX(J)
 140    CONTINUE
        DO 150 I = 1,N
        DO 150 J = 1,N
 150    B(J,I) = B(I,J)
C       ADD V(AB) TO HCORE---CNDO
        DO 170 I = 1,N
        J = U(I)
        Q(I) = Q(I)+0.5D0*G(J,J)
        DO 160 K = 1,NATOMS
 160    Q(I) = Q(I)-FLOAT(CZ(K))*G(J,K)
 170    CONTINUE
C       EXIT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED
        IF(OPTION.EQ.CNDO) GO TO 290
C       INDO MODIFICATION(CORRECTION TO U(I,I))
 180    DO 280 I = 1,NATOMS
        K = AN(I)
        J = LLIM(I)
        IF((K.GT.1).AND.(K.LT.10)) GO TO 190
        GO TO 280
 190    IF(K.LE.3) GO TO 210
 200    Q(J) = Q(J)+(FLOAT((CZ(I))-1.5D0)*G1(K)/6.D0
 210    IF(K.EQ.3) GO TO 220
 230    IF(K.EQ.4) GO TO 240
 250    TEMP = G1(K)/3.D0+(FLOAT(CZ(I))-2.5D0)*2.D0*F2(K)/25.D0
        GO TO 260
 240    TEMP = G1(K)/4.D0
        GO TO 260
 220    TEMP = G1(K)/12.D0
 260    CONTINUE
        DO 270 L = 1,3
 270    Q(J+L) = Q(J+L)+TEMP
 280    CONTINUE
 290    CONTINUE
        DO 310 I = 1,N
        DO 300 J = 1,N
 300    A(J,I) = A(I,J)
 310    A(I,I) = Q(I)
        WRITE(3,320)
 320    FORMAT(1X,18H CORE HAMILTONIAN/)
        RETURN
        END
```

```
 90     CONTINUE
        DO 100 I = 1,N
 100    Q(I) = A(I,I)
        RHO = 1.D-6
        CALL EIGN(N,RHO)
C       EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
        DO 140 I = 1,N
        DO 120 J = 1,N
 110    XXX(J) = XXX(J)+2.D0*B(I,K)*B(J,K)
 120    CONTINUE
        DO 130 J = I,N
 130    B(I,J) = XXX(J)
 140    CONTINUE
        DO 150 I = 1,N
        DO 150 J = 1,N
 150    B(J,I) = B(I,J)
C       ADD V(AB) TO HCORE---CNDO
        DO 170 I = 1,N
        J = U(I)
        Q(I) = Q(I)+0.5D0*G(J,J)
        DO 160 K = 1,NATOMS
 160    Q(I) = Q(I)-FLOAT(CZ(K))*G(J,K)
 170    CONTINUE
C       EXIT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED
        IF(OPTION.EQ.CNDO) GO TO 290
C       INDO MODIFICATION(CORRECTION TO U(I,I))
 180    DO 280 I = 1,NATOMS
        K = AN(I)
        J = LLIM(I)
        IF((K.GT.1).AND.(K.LT.10)) GO TO 190
        GO TO 280
 190    IF(K.LE.3) GO TO 210
 200    Q(J) = Q(J)+(FLOAT((CZ(I))-1.5D0)*G1(K)/6.D0
 210    IF(K.EQ.3) GO TO 220
 230    IF(K.EQ.4) GO TO 240
 250    TEMP = G1(K)/3.D0+(FLOAT(CZ(I))-2.5D0)*2.D0*F2(K)/25.D0
        GO TO 260
 240    TEMP = G1(K)/4.D0
        GO TO 260
 220    TEMP = G1(K)/12.D0
 260    CONTINUE
        DO 270 L = 1,3
 270    Q(J+L) = Q(J+L)+TEMP
 280    CONTINUE
 290    CONTINUE
        DO 310 I = 1,N
        DO 300 J = 1,N
 300    A(J,I) = A(I,J)
 310    A(I,I) = Q(I)
        WRITE(3,320)
 320    FORMAT(1X,18H CORE HAMILTONIAN/)
        RETURN
        END
```

```
      SUBROUTINE SCFCLO
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     CNDO/INDO CLOSED SHELL SCF SEGMENT
C     GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND
C     UPPER TRIANGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B
C     OPTIONS CNDO OR INDO
      COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
      COMMON/GAB/XXX(400),G(35,35)Q(80),YYY(80)ENERGY,XXY(214)
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON/INFO1/CZ(35),U(80),ULIM(35)LLIM(35)NELECS,OCCA,OCCB
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z
      DIMENSION G1(18),F2(18)
      G1(3) = .092012D0
      G1(4) = .1407   D0
      G1(5) = .199265D0
      G1(6) = .267708D0
      G1(7) =  .346029D0
      G1(8) = .43423   D0
      G1(9) = .532305D0
      F2(3) = .049865D0
      F2(4) = .089125D0
      F2(5) = .13041   D0
      F2(6) = .17372   D0
      F2(7) = .219055D0
      F2(8) = .266415D0
      F2(9) = .31580   D0
      Z = 0
      IT = 25
      RHO = 1.D-6
 10   CONTINUE
      Z = Z+1
      ENERGY = 0.D0
C     TRANSFER CORE HAMILTONIAN TO LOWER TRIANGLE OF A
      DO 20 I = 1,N
      A(I,I) = Q(I)
      DO 20 J = 1,N
 20   A(J,I) = A(I,J)
      DO 30 I = 1,N
      II = U(I)
      A(I,I) = A(I,I)-B(I,I)*G(II,II)*0.5D0
      DO 30 K = 1,N
      JJ = U(K)
 30   A(I,I) = A(I,I)+B(K,K)*G(II,JJ)
      NM = N-1
      DO 40 I = 1,NM
      II = U(I)
      LL = I+1
      DO 40 J = LL,N
      JJ = U(J)
 40   A(J,I) = A(J,I)-B(J,I)*G(II,JJ)*0.5D0
C     INDO MODIFICATION
      IF(OPTION.EQ.CNDO) GO TO 90
 50   DO 80 II = 1,NATOMS
      K = AN(II)
```

```
      I = LLIM(II)
      IF(K.EQ.1) GO TO 80
 60   PAA = B(I,I)+B(I+1,I+1)+B(I+2,I+2)+B(I+3,I+3)
      A(I,I) = A(I,I)-(PAA-B(I,I))*G1(K)/6.D0
      DO 70 J = 1,3
      A(I+J,I+J) = A(I+J,I+J)-B(I,I)*G1(K)/6.D0-(PAA-B(I,I))*7.D0*
     1F2(K)/50.D0+B(I+J,I+J)*11.D0*F2(K)/50.D0
 70   A(I+J,I) = A(I+J,I)+B(I,I+J)*G1(K)/2.D0
      I1 = I+1
      I2 = I+2
      I3 = I+3
      A(I2,I1) = A(I2,I1)+B(I2,I1)*11.D0*F2(K)/50.D0
      A(I3,I1) = A(I3,I1)+B(I3,I1)*11.D0*F2(K)/50.D0
      A(I3,I2) = A(I3,I2)+B(I3,I2)*11.D0*F2(K)/50.D0
 80   CONTINUE
 90   CONTINUE
      DO 100 I = 1,N
 100  ENERGY = ENERGY+0.5D0*B(I,I)*A(I,I)+Q(I))
      DO 105 I = 1,NM
      LL = I+1
      DO 105 J = LL,N
 105  ENERGY = ENERGY+B(I,J)*(A(I,J)+A(J,I))
      WRITE(3,110) ENERGY
 110  FORMAT(//,10X,22H ELECTRONIC ENERGY   , F16.10)
      IF(DABS(ENERGY-OLDENG).GE..000001D0) GO TO 150
 120  Z = 26
 130  WRITE(3,140)
 140  FORMAT(5X,18H ENERGY SATISFIED /)
      GO TO 170
 150 CONTINUE
 160  OLDENG = ENERGY
 170  CONTINUE
      IF(Z.LE.IT) GO TO 210
C     SYMMETRIZE F FOR PRINTING (MATRIX A)
 180  DO 190 I = 1,N
      DO 190 J = 1,N
 190  A(I,J) = A(J,I)
      WRITE(3,200)
 200  FORMAT(1X,27H HARTREE-FOCK ENERGY MATRIX)
      CALL SCFOUT(0,1)
 210  CONTINUE
      CALL EIGN(N,RHO)
      IF(Z.LE.IT) GO TO 240
 220  WRITE(3,230)
 230  FORMAT(1X,28HEIGENVALUES AND EIGENVECTORS)
      CALL SCFOUT(1,2)
 240  CONTINUE
C     EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)
      DO 280 I = 1,N
      DO 260 J = 1,N
      XXX(J) = 0.0D0
      DO 250 K = 1,OCCA
 250  XXX(J) = XXX(J)+B(I,K)*B(J,K)*2.D0
 260  CONTINUE
      DO 270 J = I,N
 270  B(I,J) = XXX(J)
```

```
  280   CONTINUE
        DO 290 I = 1,N
        DO 290 J = 1,N
  290   B(J,I) = B(I,J)
        IF(Z.LE.IT) GO TO 10
  300   CONTINUE
        RETURN
        END



        SUBROUTINE CPRINT
        IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C       CNDO-INDO SCF CLOSED SHELL - PRINTOUT SEGMENT
        COMMON/ARRAYS/A(80,80),B(80,80),D(80,80)
        COMMON/GAB/XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)
        COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
        COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
        COMMON/PERTBL/EL(18)
        COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
        INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
        INTEGER CHARGE,AN,U,ULIM,EL,OCCA,OCCB,UL,CZ,ANI
        DIMENSION DPM(3),DM(3),DMSP(3),DMPD(3)
        DIMENSION ATENG(18)
        IF(OPTION.EQ.CNDO) GO TO 20
        ATENG(1) = -0.6387302462     D0
        ATENG(3) = -.2321972405      D0
        ATENG(4) = -1.1219620354     D0
        ATENG(5) = -2.8725750048     D0
        ATENG(6) = -5.9349548261     D0
        ATENG(7) = -10.6731741251    D0
        ATENG(8) = -17.2920850650    D0
        ATENG(9) = -26.2574377875 D0
        GO TO 30
  20    CONTINUE
        ATENG(1)  = -0.6387302462     D0
        ATENG(3)  = -.92321972405     D0
        ATENG(4)  = -1.1454120355     D0
        ATENG(5)  = -2.9774239048     D0
        ATENG(6)  = -6.1649936261     D0
        ATENG(7)  = -11.0768746252    D0
        ATENG(8)  = -18.0819658651    D0
        ATENG(9)  = -27.5491302880    D0
        ATENG(11) = -.1977009568      D0
        ATENG(12) = -.8671913833      D0
        ATENG(13) = -2.0364557744     D0
        ATENG(14) = -3.8979034686     D0
        ATENG(15) = -6.7966009163     D0
        ATENG(16) = -10.7658174341    D0
        ATENG(17) = -16.0467017940    D0
  30    CONTINUE
        K = NATOMS-1
        WRITE(3,40)
  40    FORMAT(1X,15H DENSITY MATRIX)
        CALL SCFOUT(0,2)
        DO 50 I = 1,K
```

```
      L = I+1
      DO 50 J = L,NATOMS
      RAD = DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2
     1            +(C(I,3)-C(J,3))**2)
50    ENERGY = ENERGY+(FLOAT(CZ(I))*FLOAT(CZ(J)))/RAD
      WRITE(3,60) ENERGY
60    FORMAT(//,10X,16H TOTAL ENERGY = F16.10)
      DO 70 I = 1,NATOMS
      ANI = AN(I)
70    ENERGY = ENERGY-TENG(ANI)
      WRITE(3,80) ENERGY
80    FORMAT(//,10X,16HBINDING ENERGY= ,F16.10,5H A.U.)
      DO 110 I = 1,NATOMS
      TCHG = 0.D0
      LL = LLIM(I)
      UL = ULIM(I)
      DO 90 J = LL,UL
90    TCHG = TCHG+B(J,J)
      ANI = AN(I)
      WRITE(3,100) I,EL(ANI),TCHG
100   FORMAT(I3,A4,8X,F7.4)
      XXX(I) = TCHG
110   CONTINUE
      DO 120 I = 1,3
      DM(I) = 0.0D0
      DMSP(I) = 0.0D0
120   DMPD(I) = 0.0D0
      DO 200 J = 1,NATOMS
      IF(AN(J).LT.3) GO TO 180
130   IF(AN(J).LT.11) GO TO 140
160   SLTR1 = (.65D0*FLOAT(AN(J))-495D0)/3.D0
      FACTOR = 2.5416D0D0/(DSQRT(5.D0)*SLTR1)
      INDEX = LLIM(J)
      DO 170 K = 1,3
170   DMSP(K) = DMSP(K)-B(INDEX,INDEX+K)*10.27175D0/SLTR1
      DMPD(1) = DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+5)
     1    +B(INDEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))
      DMPD(2) = DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+,INDEX+6)
     1    +B(INDEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))
      DMPD(3) = DMPD(3)-FACTOR-*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)
     1    +2.D0/DSQRT(3.D0)*B(INDEX+3,INDEX+4))
      GO TO 180
140   INDEX = LLIM(J)
      DO 150 K = 1,3
150   DMSP(K) = DMSP(K)-B(INDEX,INDEX+K)*7.33697D0/
     1(.325D0*FLOAT(AN(J-1)))
180   DO 190 I = 1,3
190   DM(I) = DM(I)+(FLOAT(CZ(J))-XXX(J))*C(J,I)*2.5416D0
200   CONTINUE
      DO 210 I = 1,3
210   DPM(I) = DM(I)+DMSP(I)
      WRITE(3,220)
220   FORMAT(//,20X,16H DIPOLE MOMENTS,/)
      WRITE(3,230)
230   FORMAT(5X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)
      WRITE(3,240)DM(1),DM(2),DM(3)
240   FORMAT(5X,10H DENSITIES,3(1X,F9.5))
```

```
      WRITE(3,250)DMSP(1),DMSP(2),DMSP(3)
  250 FORMAT(5X,4H S,P,6X,3(1X,F9.5))
      WRITE(3,260)DMPD(1),DMPD(2),DMPD(3)
  260 FORMAT(5X,4H P,D,6X,3(1X,F9.5))
      WRITE(3,270)DPM(1),DPM(2),DPM(3)
  270 FORMAT(5X,6H TOTAL,4X,3(1X,F9.5),/)
      DP = DSQRT(DPM(1)**2+DPM(2)**2+DPM(3)**2
      WRITE(3,280)DP
  280 FORMAT(3X,15H DIPOLE MOMENT=,F9.5,7H DEBYES,//)
      RETURN
      END



      SUBROUTINE HUCKOP
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     EXTENDED HUCKEL THEORY O FOR OPEN SHELLS
C     OVERLAP IN A, GAMMA MATRIX IS IN G
C     AN INTIAL F MATRIX IS FORMED FROM (I+A)/2 AND S(U,V)*(1/2)*
C     (BETA0A+BETA0B). THIS F MATRIX IS USED TO GENERATE AN INITIAL
C     DENSITY MATRIX. AT THIS POINT, ADDITIONAL INTEGRALS AND COR-
C     RECTIONS ARE ADDED TO THE F MATRIX TO FORM EITHER THE CNDO OR
C     COR HAMILTONIAN. THESE ADDITIONS ARE THE INTEGRALS V(AB) FOR CNI
C     AND CORRECTIONS TO U(I,I) FOR INDO.
      COMMON/ARRAYS/A(80,80),B(80,80),Q(80,80)
      COMMON/GAB/XXX(400),G(35,35),FDIAG(80),PDIAG(80),ENERGY,YYY(214)
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      DIMENSION ENEG(18,3),BETA0(18)
      DIMENSION G1(18),F2(18)
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER CHARGE,OCCA,OCCB,UL,AN,CZ,U,ULIM,ANI
      G1(3)   = .092012       D0
      G1(4)   = .1407         D0
      G1(5)   = .199265       D0
      G1(6)   = .267708       D0
      G1(7)   = .346029       D0
      G1(8)   = .43423        D0
      G1(9)   = .532305       D0
      F2(3)   = .049865       D0
      F2(4)   = .089125       D0
      F2(5)   = .13041        D0
      F2(6)   = .17372        D0
      F2(7)   = .219055       D0
      F2(8)   = .266415       D0
      F2(9)   = .31580        D0
      ENEG(1,1) = 7.1761      D0
      ENEG(3,1) = 3.1055      D0
      ENEG(3,2) = 1.258       D0
      ENEG(4,1) = 5.94557     D0
      ENEG(4,2) = 2.563       D0
      ENEG(5,1) = 9.59407     D0
      ENEG(5,2) = 4.001       D0
      ENEG(6,1) = 14.051      D0
      ENEG(6,2) = 5.572       D0
      ENEG(7,1) = 19.31637D0
```

```
      ENEG(7,2) = 7.275       D0
      ENEG(8,1) = 25.39017D0
      ENEG(8,2) = 9.111       D0
      ENEG(9,1) = 32.2724     D0
      ENEG(9,2) = 11.08       D0
      ENEG(11,1) = 2.804      D0
      ENEG(11,2) = 1.302      D0
      ENEG(11,3) = 0.150      D0
      ENEG(12,1) = 5.1254     D0
      ENEG(12,2) = 2.0516     D0
      ENEG(12,3) = 0.16195D0
      ENEG(13,1) = 7.7708     D0
      ENEG(13,2) = 2.9951     D0
      ENEG(13,3) = 0.22455D0
      ENEG(14,1) = 10.0327D0
      ENEG(14,2) = 4.1325     D0
      ENEG(14,3) = 0.337      D0
      ENEG(15,1) = 14.0327D0
      ENEG(15,2) = 5.4638     D0
      ENEG(15,3) = 0.500      D0
      ENEG(16,1) = 17.6496D0
      ENEG(16,2) = 6.989      D0
      ENEG(16,3) = 0.71325D0
      ENEG(17,1) = 21.5906D0
      ENEG(17,2) = 8.7081     D0
      ENEG(17,3) = 0.97695D0
      BETA0(1)  = -9.         D0
      BETA0(3)  = -9.         D0
      BETA0(4)  = -13         D0
      BETA0(5)  = -17.        D0
      BETA0(6)  = -21.        D0
      BETA0(7)  = -25.        D0
      BETA0(8)  = -31.        D0
      BETA0(9)  = -39         D0
      BETA0(11) = -7.7203     D0
      BETA0(12) = -9.4471     D0
      BETA0(13) = -11.3011D0
      BETA0(14) = -13.065     D0
      BETA0(15) = -15.070     D0
      BETA0(16) = -18.150     D0
      BETA0(17) = -22.330     D0
C     FIND NELECS AND FILL H CORE(DIAGONAL) WITH (I+A)/2
      NELECS = 0
      DO 60 I = 1,NATOMS
      NELECS = NELECS+CZ(I)
      LL = LLIM(I)
      UL = ULIM(I)
      ANI = AN(I)
      L = 0
      DO 50 J = LL,UL
      L = L+1
      IF(L.EQ.1) GO TO 10
   20 IF(L.LT.5) GO TO 40
   30 A(J,J) = -ENEG(ANI,3)/27.21D0
      GO TO 50
   40 A(J,J) = -ENEG(ANI,2)/27.21D0
```

```
      GO TO 50
 10   A(J,J) = -ENEG(ANI,1)/27.21D0
 50   CONTINUE
 60   CONTINUE
      NELECS = NELECS-CHARGE
      OCCA = (NELECS+MULTIP-1)/2
      OCCB = (NELECS-MULTIP+1)/2
C     FORM HUCKEL HAMILTONIAN IN A(OFF DIAGONAL TWO CENTER TERMS)
      DO 90 I = 2,N
      K = U(I)
      L = AN(K)
      UL = I-1
      DO 90 J = 1,UL
      KK = U(J)
      LL = AN(KK)
      IF((L.GT.9).OR.(LL.GT.9) GO TO 70
 80   A(I,J) = A(I,J)*(BETA0(L)+BETA0(LL))/54.42D0
      A(J,I) = A(I,J)
      GO TO 90
 90   CONTINUE
      DO 100 I = 1,N
      DO 100 J = 1,N
 100  Q(I,J) = A(I,J)
      RHO = 1.D-6
      CALL EIGN(N,RHO)
      DO 110 I = 1,N
      PDIAG(I) = 0.0D0
      DO 110 J = 1,N
      A(I,J) = B(I,J)
 110  B(I,J) = 0.0D0
      DO 160 I = 1,N
      DO 120 K = 1,OCCA
 120  B(I,I) = B(I,I)+A(I,K)*A(J,K)
      DO 130 K = 1,OCCB
 130  PDIAG(I) = PDIAG(I)+A(I,K)*A(I,K)
      LL = I+1
      DO 160 J = LL,N
      DO 140 K = 1,OCCB
 140  B(I,J) = B(I,J)+A(I,K)
      DO 150 K = 1,OCCA
 150  B(J,I) = B(J,I)+A(I,K)*A(J,K)
 160  CONTINUE
C     ADD V(AB) TO H CORE--CNDO
      DO 180 I = 1,N
      J = U(I)
      Q(I,I) = Q(I,I)+0.5D0*G(J,J)
      DO 170 K = 1,NATOMS
 170  Q(I,I) = Q(I,I)-FLOAT(CZ(K))*G(J,K)
 180  CONTINUE
C     EXIT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED
      IF(OPTION.EQ.CNDO) GO TO 300
C     INDO MODIFICATION (CORRECTION TO U(I,I))
 190  DO 290 I = 1,NATOMS
      K = AN(I)
      J = LLIM(I)
      IF((K.GT.1).AND.(K.LT.10)) GO TO 200
      GO TO 290
```

```
  200   IF(K.LT.3) GO TO 220
  210   Q(J,J) = Q(J,J)+(FLOAT(CZ(I))-1.5D0)*G1(K)/6.D0
  220   IF(K.EQ.3) GO TO 230
  240   IF(K.EQ.4) GO TO 250
  260   TEMP = G1(K)/3.D0+(FLOAT(CZ(I))-2.5D0)*2.D0*F2(K)/25.D0
        GO TO 270
  250   TEMP = G1(K)/4.D0
        GO TO 270
  230   TEMP = G1(K)/12.D0
  270   CONTINUE
        DO 280 L = 1,3
  280   Q(J+L,J+L) = Q(J+L,J+L)+TEMP
  290   CONTINUE
  300   CONTINUE
        WRITE(3,310)
  310   FORMAT(1X,18H CORE HAMILTONIAN//)
        CALL SCFOUT(0,3)
        RETURN
        END



        SUBROUTINE SCFOPN
        IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C       CNDO/INDO OPEN SHELL SEGMENT
C       GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q,
C       INITIAL DENSITY MATRICES IN B
C       OPTION    CNDO OR INDO
C       AND THE APPROPRIATE CORE HAMILTONIAN, THE TWO ELECTRON INTEGRA
C       ARE ADDED TO THE F MATRIX (A) IN TWO PARTS-FIRST THE CNDO GAMM
C       ARE ADDED AND THEN THE IDO CORRECTIONS TO THE ONE-CENTER INTEG
C       THE PROCEDURE IS THAT F(ALPHA) AND F(BETA) ARE FORMED, THEN
C       THE ELECTRONIC ENERGY IS COMPUTED. EIGN IS CALLED TO DIAGONALIZ
C       THE TWO F MATRICES AND THE ALPHA AND BETA BONDORDERS ARE FORM
C       THESE ARE USED TO FORM NEW F MATRICES AND THE CYCLE IS REPEATE
C       UNTIL THE ENERGY CONVERGES TO THE DESIRED VALUE(0.000001 IN THIS
C       PROGRAM).
C       AN UPPER LIMIT OF 25 CYCLES IS INCLUDED (IT)
        COMMON/ARRAYS/A(80,80),B(80,80),Q(80,80)
        COMMON/GAB/XXX(400),G(35,35),FDIAG(80),PDIAG(80),ENERGY,YYY(214)
        COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
        COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
        COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
        DIMENSION G1(18),F2(18)
        INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
        INTEGER CHARGE,OCCA,OCCB,UL,AN,CZ,U,ULIM,Z
        G1(3) = .092012D0
        G1(4) = .1407     D0
        G1(5) = .199265D0
        G1(6) = .267708D0
        G1(7) = .346029D0
        G1(8) = .43423    D0
        G1(9) = .532305D0
        F2(3) = .049865D0
        F2(4) = .08925    D0
        F2(5) = .13041    D0
```

```
      F2(6) = .17372   D0
      F2(7) = .219055D0
      F2(8) = .266415D0
      F2(9) = .31580   D0
C     INITIALIZIE COUNTER Z AND BEGIN SCF CYCLE AT 10
      Z = 0
      IT = 25
      RHO = 1.D-6
 10   CONTINUE
      Z = Z+1
      ENERGY = 0.D0
C     TRANSFER CORE HAMILTONIAN TO A
      DO 20 I = 1,N
      FDIAG(I) = Q(I,I)
      DO 20 J = 1,N
 20   A(I,J) = Q(I,J)
      DO 30 I = 1,N
      II = U(I)
      A(I,I) = A(I,I)-B(I,I)*G(II,II)
      FDIAG(I) = FDIAG(I)-PDIAG(I)*G(II,II)
      DO 30 K = 1,N
      JJ = U(K)
      A(I,I) = A(I,I) + (PDIAG(K)+B(K,K))*G(II,JJ)
 30   FDIAG(I) = FDIAG(I)+(PDIAG(K)+B(K,K))*G(II,JJ)
      NM = N-1
      DO 50 I = 1,NM
      II = U(I)
      LL = I+1
      DO 40 J = LL,N
      JJ = U(J)
      A(I,J) = A(I,J)-B(I,J)*G(II,JJ)
 40   A(J,I) = A(I,J)-B(J,I)*G(II,JJ)
 50   CONTINUE
C     INDO MODIFICATION
      IF(OPTION.EQ.CNDO) GO TO 100
 60   DO 90 II = 1,NATOMS
      K = AN(II)
      I = LLIM(II)
      IF(K.EQ.1) GO TO 90
 70   PAA = B(I,I)+B(I+1,I+1)+B(I+2,I+2)+B(I+3,I+3)
      PAB = PDIAG(I+1)+PDIAG(I+2)+PDIAG(I+3)
      A(I,I) = A(I,I)-(PAA-(B(I,I))*G1(K)/3.D0
      FDIAG(I) = FDIAG(I)-(PAB-PDIAG(I))*G1(K)/3.D0
      DO 80 J = 1,3
      A(I+J,I+J) = A(I+J,I+J)+(B(I+J,I+J)-(PAA-B(I,I)))*F2(K)/5.D0-B(I,I)
     1*G1(K)/3.D0+(6.D0*PDIAG(I+J)-2.D0*(PAB-PDIAG(I)))*F2(K)/25.D0
      FDIAG(I+J) = FDIAG(I+J)+(PDIAG(I+J)-(PAB-PDIAG(I)))*F2(K)5.D0
     1-FDIAG(I)*G1(K)/3.D0+(6.D0*B(I+J,I+J)-2.D0-(PAA-B(I,I)))
     2*F2(K)/25.D0
      A(I,I+J) = A(I,I+J)+(B(I+J,I)+2.D0*B(I+J,I))*G1(K)/3.D0
      A(I+J,I) = A(I+J,I)+(B(I+J,I)+2.D0*B(I,I+J))*G1(K)/3.D0
      DO 80 L = 1,3
      IF(J.EQ.L) GO TO 80
 75   A(I+L,I+J) = A(I+L,I+J)+(5.D0*B(I+L,I+J)+6.D0*B(I+J,I+L))
     1*F2(K)/25.D0
 80   CONTINUE
```

```
 90    CONTINUE
 100   CONTINUE
       DO 110 I = 1,N
 110   ENERGY = ENERGY+0.5D0*((A(I,I)+Q(I,I))*B(I,I)+(FDIAG(I)+Q(I,I))
      1*PDIAG(I))
       DO 115 I = 1,NM
       LL = I+1
       DO 115 J = LL,N
 115   ENERGY = ENERGY+((A(I,J)+Q(I,J))*B(I,J)+(A(J,I)+Q(J,I))*B(J,I))
       WRITE(3,120) ENERGY
 120   FORMAT(//,10X,22H ELECTRONIC ENERGY     ,F16.10)
       IF(DABS(ENERGY-OLDENG).GE.1.D-6) GO TO 160
 130   Z = 26
 140   WRITE(3,150)
 150   FORMAT(5X,18H ENERGY SATISFIED/)
       GO TO 180
 160   CONTINUE
 170   OLDENG = ENERGY
 180   CONTINUE
       IF(Z.LE.IT) GO TO 240
C      TRANSFER F(ALPHA) TO Q FOR PRINTING
 190   DO 200 I = 1,N
       DO 200 J = I,N
       Q(I,J) = A(J,I)
 200   Q(J,I) = A(J,I)
       WRITE(3,210)
 210   FORMAT(1X,42H HARTREE-FOCK ENERGY MATRIX FOR ALPHA SPIN//)
C      TRANSFER F(BETA) TO Q FOR PRINTING
       DO 220 I = 1,N
       Q(I,I) = FDIAG(I)
       LL = I+1
       DO 220 J = LL,N
 220   Q(J,I) = A(I,J)
       WRITE(3,230)
 230   FORMAT(1X,41H HARTREE-FOCK ENERGY MATRIX FOR BETA SPIN//)
       CALL SCFOUT(0,3)
 240   CONTINUE
       CALL EIGN(N,RHO)
       IF(Z.LE.IT) GO TO 270
 250   WRITE(3,260)
 260   FORMAT(1X,43HEIGENVALUES AND EIGENVECTORS FOR ALPHA SPIN//)
       CALL SCFOUT(1,2)
 270   CONTINUE
C      TRANSFER F(BETA) TO LOWER HALF OF A
       DO 280 I = 1,N
       A(I,I) = FDIAG(I)
       K = I+1
       DO 280 J = K,N
       A(J,I) =A(I,J)
 280   A(I,J) = 0.0D0
C      FORM ALPHA BONDORDERS IN TOP HALF OF A AND IN FDIAG-TEMPORARY
       DO 300 I = 1,N
       LL = I+1
       DO 290 K = 1,OCCA
 290   FDIAG(I) = FDIAG(I)+B(I,K)*B(I,K)
       DO 300 J = LL,N
       DO 300 K = 1,OCCA
```

```
 300   A(I,J) = A(I,J)+B(I,K)*B(J,K)
       CALL EIGN(N,RHO)
       IF(Z.LE.IT) GO TO 330
 310   WRITE(3,320)
 320   FORMAT(1X,43HEIGENVALUES AND EIGENVECTORS FOR BETA SPIN//)
       CALL SCFOUT(1,2)
 330   CONTINUE
C      FORM BETA BONDORDERS IN LOWER HALF OF A AND IN PDIAG)
       DO 350 I = 1,N
       LL = I+1
       PDIAG(I) = 0.0D0
       DO 340 K = 1,OCCB
 340   PDIAG(I) PDIAG(I)+B(I,K)*B(I,K)
       DO 350 J = LL,N
       A(J,I) = 0.0D0
       DO 350 K = 1,OCCB
 350   A(J,I) = A(J,I)+B(I,K)*B(J,K)
C      TRANSFER BONDORDERS FROM A TO B
       DO 370 I = 1,N

       DO 360 J = 1,N
 360   B(I,J) = A(J,I)
 370   B(I,I) = FDIAG(I)
       IF(Z.LE.IT) GO TO 10
 380   CONTINUE
       RETURN
       END



       SUBROUTINE OPRINT
       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C      CNDO-INDO OPEN SHELL PRINT OUT SEGMENT
       COMMON/ARRAYS/A(80,80),B(80,80),Q(80,80)
       COMMON/GAB/XXX(400),G(35,35),FDIAG(80),PDIAG(80),ENERGY,YYY(214)
       COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
       COMMON/INFO1/CZ(35),U(80),ULIM(35)LLIM(35),NELECS,OCCA,OCCB
       COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
       COMMON/PERTBL/EL(18)
       DIMENSION CISO(10)
       DIMENSION DPM(3),DM(3),DMSP(3),DMPD(3)
       DIMENSION ATENG(18)
       INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
       INTEGER CHARGE,AN,U,ULIM,EL,OCCA,OCCB,UL,CZ,ANI
       IF(OPTION.EQ.CNDO) GO TO 20
       ATENG(1)  = -0.6387302462    D0
       ATENG(3)  = -.2321972405     D0
       ATENG(4)  = -1.1219620354    D0
       ATENG(5)  = -2.8725750048    D0
       ATENG(6)  = -5.9394548261    D0
       ATENG(7)  = -10.6731741251D0
       ATENG(8)  = -17.2920850650D0
       ATENG(9)  = -26.2574377875D0
       GO TO 30
 20    CONTINUE
       ATENG(1)  = -0.6387302462    D0
```

```
      ATENG(3)  = -.2321972405     D0
      ATENG(4)  = -1.1454120355    D0
      ATENG(5)  = -2.9774239048    D0
      ATENG(6)  = -6.1649936261    D0
      ATENG(7)  = -11.0768746252D0
      ATENG(8)  = -18.0819658651D0
      ATENG(9)  = -27.5491302880D0
      ATENG(11) = -.1977009568     D0
      ATENG(12) = -.8671913833     D0
      ATENG(13) = -2.0364557744    D0
      ATENG(14) = -3.8979034686    D0
      ATENG(15) = -6.7966009163    D0
      ATENG(16) = -10.7658174341D0
      ATENG(17) = -16.0467017940D0
 30   CONTINUE
      K = NATOMS-1
C     BONDORDER HALF MATRICES ARE NOW BEING STORED IN FULL MATRICES F
C     PRINTING--ALPHA IN B AND BETA IN A
      DO 40 I = 1,N
      A(I,I) = PDIAG(I)
      LL = I+1
      DO 40 J = LL,N
      A(I,J) = B(I,J)
      A(J,I) = B(I,J)
 40   B(I,J) = B(J,I)
      WRITE(3,50)
 50   FORMAT(1X,23H ALPHA BONDORDER MATRIX//)
      CALL SCFOUT(0,2)
      WRITE(3,60)
 60   FORMAT(1X,22H BETA BONDORDER MATRIX//)
      CALL SCFOUT(0,1)
 70   CONTINUE
      DO 80 I = 1,N
      DO 80 J = 1,N
      B(I,J) = A(I,J)+B(I,J)
 80   A(I,J) = B(I,J)-2.D0*A(I,J)
      WRITE(3,90)
 90   FORMAT(1X,25H SCF TOTAL DENSITY MATRIX//)
      CALL SCFOUT(0,2)
      WRITE(3,100)
 100  FORMAT(1X,24H SCF SPIN DENSITY MATRIX//)
      CALL SCFOUT(0,1)
      DO 110 I = 1,K
      RAD = DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,3))**2
     1                                +(C(I,3)-C(J,3))**2)
 110  ENERGY = ENERGY+(FLOAT(CZ(I))*FLOAT(CZ(J)))/RAD
      WRITE(3,120) ENERGY
 120  FORMAT(//10X,16H TOTAL ENERGY = F16.10)
      DO 130 I = 1,NATOMS
      ANI = AN(I)
 130  ENERGY = ENERGY-ATENG(ANI)
      WRITE(3,140) ENERGY
 140  FORMAT(//10X,BINDING ENERGY= ,F16.10,5H A.U.)
      CISO(1) = 539.8635D0
      CISO(6) = 820.0959D0
      CISO(7) = 379.3557D0
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      CISO(8) = 888.6855D0
      CISO(9) = 44829.2 D0
      WRITE(3,150)
150   FORMAT(15X,7HVALENCE,10X,9HS ORBITAL,10X,9HHYPERFINE)
      WRITE(3,160)
160   FORMAT(10X,55H*ELECTRON DENSITY* *SPIN DENSITY* *COUPLING CONST/
     1NT*)
      WRITE(3,170)
170   FORMAT(80X)
      DO 200 I = 1,NATOMS
      TCHG = 0.D0
      LL = LLIM(I)
      UL = ULIM(I)
      ANI = AN(I)
      HFC = CISO(ANI)*A(LL,LL)
      IF(OPTION.EQ.INDO) GO TO 2
1     HFC = 0.0
2     CONTINUE
      DO 180 J = LL,UL
180   TCHG = TCHG+B(J,J)
      WRITE(3,190) I,EL(ANI),TCHG,A(LL,LL),HFC
190   FORMAT(I3,A4,8X,F7.4,10X,F7.4,12X,F9.4)
      XXX(I) = TCHG
200   CONTINUE
      DO 210 I = 1,3
      DM(I) = 0.0D0
      DMSP(I) = 0.0D0
      DMPD(I) = 0.0D0
      DO 290 J = 1,NATOMS
      IF(AN(J).LT.3) GO TO 270
220   IF(AN(J).LT.11) GO TO 230
250   SLTR1 = (.65D0*FLOAT(AN(J))-4.95D0)/3.D0
      FACTOR = 2.5416D0*7.D0/(DSQRT(5.D0)*SLTR1)
      INDEX = LLIM(J)
      DO 260 K = 1,3
260   DMSP(K) = DMSP(K)-B(INDEX,INDEX+K)*1027175D0/SLTR1
      DMPD(1)     =     DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+
     1    +B(INDEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))
      DMPD(2) = DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+,INDEX+6)
     1    +B(INDEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))
      DMPD(3) = DMPD(3)-FACTOR-*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)
     1         +2.D0/DSQRT(3.D0)*B(INDEX+3,INDEX+4))
      GO TO 270
230   INDEX = LLIM(J)
      DO 240 K = 1,3
240   DMSP(K) = DMSP(K)-B(INDEX,INDEX+K)*7.33697D0/
     1(.325D0*FLOAT(AN(J)-1))
270   DO 280 I = 1,3
280   DM(2) = DM(I)+(FLOAT(CZ(J))-XXX(J))*C(J,I)*2.5416D0
290   CONTINUE
      DO 300 I = 1,3
300   DPM(I) = DPM(I)+DMSP(I)+DMPD(I)
      WRITE(3,310)
310   FORMAT(//,20X,16H DIOLE MOMENTS,/)
      WRITE(3,320)
320   FORMAT(5X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)
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      WRITE(3,330)DM(1),DM(2),DM(3)
  330 FORMAT(5X,10H DENSITIES,3(1X,F9.5))
      WRITE(3,340)DMSP(1),DMSP(2),DMSP(3)
  340 FORMAT(5X,4H S,P,6X,3(1X,F9.5))
      WRITE(3,350)DMPD(1),DMPD(2),DMPD(3)
  350 FORMAT(5X,4H P,D,6X,3(1X,F9.5))
      WRITE(3,360)DPM(1),DPM(2),DPM(3)
  360 FORMAT(5X,6H TOTAL,4X,3(1X,F9.5),/)
      DP = DSQRT(DPM(1)**2+DPM(2)**2+DPM(3)**2)
      WRITE(3,370)DP
  370 FORMAT(3X,15H DIPOLE MOMENT=,F9.5,//)
      RETURN
      END



      SUBROUTINE EIGN(NN,RHO)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     RHO = UPPER LIMIT FOR OFF-DIAGONAL ELEMENT
C     NN = SIZE OF MATRIX
C     A = F MATRIX (ONLY LOWER TRIANGLE IS USED + THIS IS DESTROYED)
C     EIG = RETURNED EIGENVALUES IN ALGEBRAIC ASCENDING ORDER
C     VEC = RETURNED EIGENVECTORS IN COLUMNS
      COMMON/ARRAYS/A(80,80),VEC(80,80),X(80,80)
      COMMON/GAB/GAMMA(80),BETA(80),BETASQ(80),EIG(80),W(80),XYZ(1600)
C     THE FOLLOWING DIMENSIONED VARIABLES ARE EQUIVALENCED
      DIMENSION P(80),Q(80)
      EQUIVALENCE (P(1),BETA(1)),(Q(1),BETA(1))
      DIMENSION IPOSV(80),IVPOS(80),IORD(80)
      EQUIVALENCE (IPOSV(1),GAMMA(1)),(IVPOS(1),BETA(1)),
     1(IORD(1),BETASQ(1))
      RHSQ = RHO*RHO
      N = NN
      IF(N.EQ.0) GO TO 640
   10 N1 = N-1
      N2 = N-2
      GAMMA(1) = A(1,1)
      IF(N2) 200,190,40
   40 DO 180 NR = 1,N2
      B = A(NR+1,NR)
      S = 0.D0
      DO 50 I = NR,N2
   50 S = S+A(I+2,NR)**2
C     PREPARE FOR POSSIBLE BYPASS OF TRANSFORMATION
      AN(NR+1,NR) = 0.D0
      IF(S) 170,170,60
   60 S = S+B*B
      SGN = +1.D0
      IF(B) 70,80,80
   70 SGN = -1.D0
   80 SQRTS = DSQRT(S)
      D = SGN/(SQRTS+SQRTS)
      TEMP = DSQRT(.5D0+B*D)
      W(NR) = TEMP
      A(NR+1,NR) = TEMP
```

```
      D = D/TEMP
      B = SGN*SQRTS
C     D IS FRACTOR OF PROBABILITY. NOW COMPUTE AND SAVE W VECTOR.
C     EXTRA SINGLY SUBSCRIPTED W VECTOR USED FOR SPEED.
      DO 90 I = NR,N2
      TEMP = D*A(I+2,NR)
      W(I+1) = TEMP
 90   A(I+2,NR) = TEMP
C     PREMULTIPLY VECTOR W BY MATRIX A TO OBTAIN P VECTOR.
C     SIMULTANEOUSLY ACCUMULATE DOT PRODUCT WP,(THE SCALAR K)
      WTAW = 0.D0
      DO 140 I = NR,N1
      SUM = 0.D0
      DO 100 J = NR,I
 100  SUM = SUM+A(I+1,J+1)*W(J)
      I1 = I+1
      IF(N1-I1) 130,110,110
 110  DO 120 J = I1,N1
 120  SUM = SUM+A(J+1,I+1)*W(J)
 130  P(I) = SUM
 140  WTAW = WTAW+SUM*W(I)
C     P VECTOR AND SCALAR K NOW STORED. NEXT COMPUTE Q VECTOR
      DO 150 I = NR,N1
 150  Q(I) = P(I)-WTAW*W(I)
C     NOW FORM PAP MATRIX, REQUIRED PART
      DO 160 J = NR,N1
      QJ = Q(J)
      WJ = W(J)
      DO 160 I = J,N1
 160  A(I+1,J+1) = A(I+1,J+1)-2.D0*(W(I)*QJ+WJ*Q(I))
 170  BETA(NR) = B
      BETASQ(NR) = B*B
 180  GAMMA(NR+1) = A(NR+1,NR+1)
 190  B = A(N,N-1)
      BETA(N-1) = B
      BETASQ(N-1) = B*B
      GAMMA(N) = A(N,N)
 200  BETASQ(N) = 0.D0
C     ADJOIN AN IDENTITY MATRIX TO BE POSTMULTIPLIED BY ROTATIONS.
      DO 220 I = 1,N
      DO 210 J = 1,N
 210  VEC(I,J) = 0.D0
 220  VEC(I,I) = 1.D0
      M = N
      SUM = 0.D0
      NPAS = 1
      GO TO 350
 230  SUM = SUM+SHIFT
      COSA = 1.D0
      G = GAMMA(1)-SHIFT
      PP = G
      PPBS = PP*PP+BETASQ(1)
      PPBR = DSQRT(PPBS)
      DO 230 J = 1,M
      COSAP = COSA
      IF(PPBS.ST.1.D-12) GO TO 250
```

```
 240   SINA = 0.D0
       SINA2 = 0.D0
       COSA = 1.D0
       GO TO 290
 250   SINA = BETA(J)/PPBR
       SINA2 = BETASQ(J)PPBS
       COSA = PP/PPBR
C      POSTMULTIPLY BY P-TRANSPOSE MATRIX
       NT = J+NPAS
       IF(NT.LT.N) GO TO 270
 260   NT = N
 270   DO 280 I = 1,NT
       TEMP = COSA*VEC(I,J)+SINA*VEC(I,J+1)
       VEC(I,J+1) = SINA*VEC(I,J)+COSA*VEC(I,J+1)
 280   VEC(I,J) = TEMP
 290   DIA = GAMMA(J+1)-SHIFT
       U = SINA2*(G+DIA)
       GAMMA(J) = G+U
       G = DIA-U
       PP = DIA*COSA-SINA*COSAP*BETA(J)
       IF(J.NE.M) GO TO 310
 300   BETA(J) = SINA*PP
       BETASQ(J) = SINA2*PP*PP
       GO TO 330
 310   PPBS = PP*PP+BETASQ(J+1)
       PPBR = DSQRT(PPBS)
       BETA(J) = SINA*PPBR
 320   BETASQ(J) = SINA2*PPBS
 330   GAMMA(M+1) = G
C      TEST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT
       NPAS = NPAS+1
       IF(BETASQ(M).GT.RHOSQ) GO TO 370
 340   EIG(M+1) = GAMMA(M+1)+SUM
 350   BETA(M) = 0.D0
       M = M-1
       IF(M.EQ.0) GO TO 400
 360   IF(BETASQ(M).LE.RHOSQ) GO TO 340
C      TAKE ROOT OF CORNER 2 BY 2 NEAREST TO LOWER DIAGONAL IN VALUE
C      AS ESTIMATE EIGENVALUE TO USE FOR SHIFT
 370   A2 = GAMMA(M+1)
       R2 = 0.5D0*A2
       R1 = 0.5D0*GAMMA(M)
       R12 = R1+R2
       DIF = R1-R2
       TEMP = DSQRT((DIF*DIF+BETASQ(M))
       R1 = R12+TEMP
       R2 = R12-TEMP
       DIF = DABS(A2-R1)-DABS(A2-R2)
       IF(DIF.LE.0.D0) GO TO 390
 380   SHIFT = R2
       GO TO 230
 390   SHIFT = R1
       GO TO 230
 400   EIG(1) = GAMMA(1)+SUM
C      INITIALIZE AUXILIARY TABLES REQUIRED FOR REARRANGIMG THE VECTORS
       DO 410 J = 1,N
       IPOSV(J) = J
```

```
      IVPOS(J) = J
  410 IORD(J) = J
C     USE A TRANSPOSITION SORT TO ORDER THE EIGENVALUES
      M = N
      GO TO 450
  420 DO 440 J = 1,M
      IF(EIG(J).LE.EIG(J+1)) GO TO 440
  430 TEMP = EIG(J)
      EIG(J) = EIG(J+1)
      EIG(J+1) = TEMP
      ITEMP = IORD(J)
      IORD(J) = IORD(J+1)
      IORD(J+1) = ITEMP
  440 CONTINUE
  450 M = M-1
      IF(M.NE.0) GO TO 420
  460 IF(N1.EQ.0) GO TO 510
  470 DO 500 L = 1,1
      NV = IORD(L)
      NP = IPOSV(NV)
      IF(NP.EQ.N) GO TO 500
  480 LV = IVPOS(L)
      IVPOS(NP) = LV
      DO 490 I = 1,N
      TEMP = VEC(I,L)
      VEC(I,L) = VEC(I,NP)
  490 VEC(I,NP) = TEMP
  500 CONTINUE
  510 CONTINUE
C     BACK TRANSFORM THE VECTORS THE TRIPLE DIAGONAL MATRIX
      DO 570 NRR = 1,N
      K = N1
  520 K = K-1
      IF(K.LE.0) GO TO 560
  530 SUM = 0.D0
      DO 540 I = K,N1
  540 SUM = SUM+VEC(I+1,NRR)*A(I+1,K)
      SUM = SUM+SUM
      DO 550 I = K,N1
  550 VEC(I+1,NRR) = VEC(I+1,NRR)-SUM*A(I+1,K)
      GO TO 520
  560 CONTINUE
  570 CONTINUE
  640 RETURN
      END


      SUBROUTINE SCFOUT(OP,MOP)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIG
C     MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO
C     PRINTED. IF OP = 0 THE EIGENVALUES ARE NOT PRINTED
      COMMON/ARRAYS/A(80,80,3)
      COMMON/GAB/XXX(2000)
      COMMON/INFO/NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON/ORB/ORB(9)
```

```
      COMMON/PERTBL/EL(18)
      INTEGER OP,AN,ANII,CZ,U,ORB,ULIM,EL,CHARGE,OCCA,OCCB
      DO 120 M = 1,N,11
      K = M+10
      IF(K.LE.N) GO TO 30
20    K = N
30    CONTINUE
      WRITE(3,100)
      IF(OP.EQ.1) GO TO 40
      GO TO 50
40    CALL EIGOUT(M,K)
50    CONTINUE
      WRITE(3,60) (I,I=M,K)
60    FORMAT(13X,50I9)
      DO 110 I = 1,N
      II = U(I)
      ANII = AN(II)
      L = I-LLIM(I)+1
70    WRITE(3,80) I,II,EL(ANII),ORB(L),(A(I,J,MOP),J=M,K)
80    FORMAT(1X,I2,I3,A4,1X,A4,50(F9.5))
      IF(I.EQ.ULIM(II)) GO TO 90
      GO TO 100
90    WRITE(3,100)
100   FORMAT(1X)
110   CONTINUE
120   CONTINUE
      WRITE(3,100)
      RETURN
      END


      SUBROUTINE EIGOUT(M,K)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C     THIS ROUTINE IS CALLED IN SCFOUT TO PRINT THE EIGENVALUES M TO K
      COMMON/GAB/XXX(240),EPSILN(80),YYY(1680)
      WRITE(3,10) (EPSILN(I),I=M,K)
10    FORMAT(//,15H EIGENVALUES---,20(F9.4),//)
      RETURN
      END


      BLOCK DATA
      COMMON/ORB/ORB(9)
      COMMON/PERTBL/EL(18)
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER ORB,EL
      DATA CNDO/4HCNDO/
      DATA INDO/4HINDO/
      DATA OPEN/4HOPEN/
      DATA CLOSED/'CLSD'/
      DATA ORB /' S',' PX',' PY',' PZ',' DZ2',' DXZ',' DYZ','DX-Y',
     1'DXY'/
      DATA EL /' H',' HE',' LI',' BE',' B',' C',' N',' O',
     1' F',' NE',' NA',' MG',' AL',' SI',' P',' S',' CL',
     2'AR'/
      END
```