

# Fortran 90 implementation of the Hartree-Fock approach within the CNDO/2 and INDO models

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## Abstract

Despite the tremendous advances made by the *ab initio* theory of electronic structure of atoms and molecules, its applications are still not possible for very large systems. Therefore, semi-empirical model Hamiltonians based on the zero-differential overlap (ZDO) approach such as the Pariser-Parr-Pople, CNDO, INDO, etc. provide attractive, and computationally tractable, alternatives to the *ab initio* treatment of large systems. In this paper we describe a Fortran 90 computer program developed by us, that uses CNDO/2 and INDO methods to solve Hartree-Fock(HF) equation for molecular systems. The INDO method can be used for the molecules containing the first-row atoms, while the CNDO/2 method is applicable to those containing both the first-, and the second-row, atoms. We have paid particular attention to computational efficiency while developing the code, and, therefore, it allows us to perform calculations on large molecules such as C<sub>60</sub> on small computers within a matter of seconds. Besides being able to compute the molecular orbitals and total energies, our code is also able to compute properties such as the electric dipole moment, Mulliken population analysis, and linear optical absorption spectrum of the system. We also demonstrate how the program can be used to compute the total energy per unit cell of a polymer. The applications presented in this paper include small organic and inorganic molecules, fullerene C<sub>60</sub>, and model polymeric systems, *viz.*, chains containing alternating boron and nitrogen atoms (BN chain), and carbon atoms (C chain).

*Key words:* Hartree-Fock method, self-consistent field approach

CNDO/INDO models, Molecular orbitals

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## **Program Summary**

*Title of program:* cindo.x

*Catalogue Identifier:*

*Program summary URL:*

*Program obtainable from:* CPC Program Library, Queen's University of Belfast, N. Ireland

*Distribution format:* tar.gz

*Computers :* PC's/Linux

*Linux Distribution:* Code was developed and tested on various recent versions of Fedora including Fedora 9 (kernel version 2.6.25-14)

*Programming language used:* Fortran 90

*Compilers used:* Program has been tested with Intel Fortran Compiler (non-commercial version 10.1) and gfortran compiler (gcc version 4.3.0) with optimization option -O.

*Libraries needed:* This program needs to link with LAPACK/BLAS libraries compiled with the same compiler as the program. For the Intel Fortran Compiler we used the ACML library version 3.6.0, while for gfortran compiler we used the libraries supplied with the Fedora distribution.

*Number of bytes in distributed program, including test data, etc.:* size of the tar file ..... bytes

*Number of lines in distributed program, including test data, etc.:* lines in the tar file .....

*Card punching code:* ASCII

*Nature of physical problem:* A good starting description of the electronic structure of extended many-electron systems such as molecules, clusters, and polymers, can be obtained using the Hartree-Fock (HF) method. Solution of HF equations within a fully *ab initio* formalism for large systems, however, is computationally quite expensive. For such systems, semi-empirical methods such as CNDO and INDO proposed by Pople and collaborators are quite attractive. The present program can solve the HF equations for both open- and closed-shell systems containing first- and second-row atoms using either the INDO model or the CNDO model.

*Method of Solution:* The single-particle HF orbitals are expressed as linear combinations of the Slater-type orbital (STO) basis set specified by Pople and coworkers. Then using the parameters prescribed for the CNDO/INDO methods, the HF integro-differential equations are transformed into a matrix eigenvalue problem. Thereby, its solutions are obtained in a self-consistent manner, using methods of computational linear algebra.

*Unusual features of the program:* None

## 1 Introduction

The linear combination of atomic orbitals (LCAO) method is one of the most common approaches for solving the Schrödinger equation for many-electron systems such as atoms, molecules, clusters, and solids. It consists of expressing the single-particle orbitals of the electrons of the system as a linear combination of a known basis set, and then solving the mean-field equations such as the Hartree-Fock (HF) or the Kohn-Sham equations. This converts these integro-differential equations into a matrix eigenvalue problem, which is subsequently solved using computational approaches from the linear algebra. If one intends to go beyond the mean-field to include the electron correlations effects, approaches such as the configuration-interaction (CI), coupled-cluster, or the Green's function based formalisms can be used. If  $N$  is the total number of basis functions used, the computational difficulty at the mean-field level scales roughly as  $N^4$ , which is the number of two-electron integrals needed to perform such calculations. For post mean-field correlated calculations, integrals need to be transformed from the basis-set atomic orbital (AO) representation to the molecular-orbital representation (MO), a process which scales as  $N^5$ , while subsequent solution of the corresponding equations can be even more time consuming[1]. Since  $N$  increases rapidly with the number of atoms (and hence electrons) in the system, therefore, for very large systems solution of even the mean-field equations can become computationally intractable. Therefore, it is always advisable to devise methods of electronic structure theory which aim at reducing the size of the basis set.

Using the zero-differential overlap (ZDO) approximation developed by Parr[2], Pople and coworkers developed a series of semi-empirical methods for computing the electronic structure of molecules such as the Pariser-Parr-Pople (PPP) model[3], the complete neglect of differential overlap (CNDO) method[4,5,6], and the intermediate neglect of differential overlap (INDO) method[7]. Of these, the PPP model is applicable only to  $\pi$ -conjugated systems, however, the CNDO and INDO models with suitable parametrization, are in principle, applicable to all molecular systems[8]. CNDO and INDO methods are a class of valence-electron models which utilize a minimal Slater-type orbital (STO) basis set for the representation of the valence orbitals[8]. Additionally, in the representation of the Hamiltonian, only one- and two-center integrals are retained, leading to a drastic reduction in the computational effort as compared to the *ab initio* calculations[8]. Therefore, the CNDO/INDO models share attractive feature of semi-empirical parametrization with the PPP model, and a spatial representation of the molecular orbital with the *ab initio* approaches[8]. And, unlike the PPP model, the CNDO/INDO methods can also be used for the geometry optimization of molecules[8]. Therefore, for large molecular systems and clusters, for which the applications of fully *ab initio* approaches can be computationally intractable, the CNDO/INDO methods provide an attrac-

tive alternative for the theoretical description of their electronic structure.

It is with possible applications to large molecules, clusters, and polymers in mind that we have developed the present computer program which implements the CNDO-2/INDO methods as formulated originally by Pople and coworkers[8]. As per the original formulation by Pople and coworkers[8], the INDO method can be used for the molecules containing the first-row atoms, while the CNDO/2 method is applicable to those containing both the first-, and the second-row, atoms. The fact that the code has been written in a modern programming language, *viz.*, Fortran 90, allows it to utilize dynamic memory allocation, thereby freeing it from various array limits, and resultant artificial restrictions on the size of the molecules. Thus our program can be used on a given computer until all its available memory is exhausted. The present computer program can perform restricted Hartree-Fock (RHF) calculations on closed-shell systems, and unrestricted-Hartree-Fock (UHF) calculations on open-shell systems. Additionally, it also allows one to compute properties such as the molecular dipole moment, Mulliken population analysis, and linear-optical absorption spectrum under the electric-dipole approximation. Apart from describing the computer program, we also present several of its applications which include various small molecules, fullerene C<sub>60</sub>, and polymeric chains consisting of carbon atoms (C-chain), and alternating boron and nitrogen atoms (BN-chain).

The remainder of the paper is organized as follows. In section 2 we briefly review the theory associated with the CNDO/INDO approaches. Next, in section 3 we discuss the general structure of our computer program, and also describe its constituent subroutines. In section 4 we briefly describe how to install the program on a given computer system, and to prepare the input files. Results of various example calculations using our program are presented and discussed in section 5. Finally, in section 6, we present our conclusions, as well as discuss possible future directions.

## 2 Theory

In this section we briefly review the theory associated with the CNDO/INDO methods. The detailed discussion on the topic can be found in the book by Pople and Beveridge[8]. Our discussion will be in the context of the UHF method, the corresponding RHF equations can be easily deduced from them. As per the assumptions of the UHF method, we assume that the  $i$ -th up- and down-spin orbitals are distinct, and are represented (say) as  $\psi_i^{(\alpha)}$  and  $\psi_i^{(\beta)}$ , respectively. We assume that these orbitals can be written as a linear

combination of a finite-basis set

$$\psi_i^{(\alpha)} = \sum_{\mu} C_{\mu i}^{(\alpha)} \phi_{\mu}, \quad (1)$$

where  $\phi_{\mu}$ 's represent the basis functions in question, and the determination of the unknown coefficients  $C_{\mu i}^{(\alpha)}$  amounts to the solution of the UHF equations. In the equation above, we have only stated the expressions for the up-spin orbitals, the case of the down-spin orbitals can be easily deduced. Assuming the Born-Oppenheimer Hamiltonian for the electrons of the system

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{A=1}^{N_n} \sum_{i=1}^{N_e} \frac{Z_A e^2}{R_{Ai}} + \sum_{i>j} \frac{e^2}{r_{ij}}, \quad (2)$$

where the first term represents the kinetic energy of  $N_e$  electrons of the system, the second term represents the interaction energy of those electrons with its  $N_n$  nuclei,  $Z_A$  represents the nuclear charge of the  $A$ -th nucleus,  $R_{Ai}$  denotes the distance between that nucleus and the  $i$ -th electron,  $r_{ij}$  represents the inter-electronic distance, while  $m$  and  $e$  are electronic mass and charge, respectively. We further assume that the total number of up-/down-spin electrons is  $N_{\alpha}/N_{\beta}$ , such that  $N_{\alpha} + N_{\beta} = N_e$ . Using the conjecture of Eq. 1 in conjunction with the Hamiltonian above, one obtains the so-called Pople-Nesbet equations

$$\sum_{\nu} (F_{\mu\nu}^{\alpha} - \epsilon_i^{\alpha} S_{\mu\nu}) C_{\nu i}^{(\alpha)} = 0, \quad (3)$$

where  $S_{\mu\nu}$  is the basis function overlap matrix,  $\epsilon_i^{\alpha}$  is the UHF eigenvalue of the  $i$ -th up-spin orbital,  $F_{\mu\nu}^{\alpha}$  is the Fock matrix for the up-spin electrons defined by

$$F_{\mu\nu}^{\alpha} = h_{\mu\nu} + \sum_{\lambda\sigma} [P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^{\alpha}(\mu\sigma|\lambda\nu)], \quad (4)$$

above  $h_{\mu\nu}$  represents the matrix elements of the one-electron part (kinetic energy and the electron-nucleus interaction) of the Hamiltonian of Eq. 2,  $(\mu\nu|\lambda\sigma)$  represents two-electron Coulomb repulsion integral in the Mulliken notation

$$(\mu\nu | \lambda\sigma) = \int \int d\tau_1 d\tau_2 \phi_{\mu}(1) \phi_{\nu}(1) r_{12}^{-1} \phi_{\lambda}(2) \phi_{\sigma}(2), \quad (5)$$

and  $P_{\lambda\sigma}^{\alpha}$  and  $P_{\lambda\sigma}$ , are the up-spin and total density matrix elements, respectively, defined as

$$P_{\lambda\sigma}^{\alpha} = \sum_{i=1}^{N_{\alpha}} C_{\lambda i}^{(\alpha)*} C_{\sigma i}^{(\alpha)}, \quad (6)$$

and

$$P_{\lambda\sigma} = P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta}. \quad (7)$$

Equations 4 through 7, define the UHF method without any approximations. Next we briefly describe the approximations involved in the CNDO/INDO methods, leading up to corresponding UHF equations[8]:

- (1) Only valence electrons are treated explicitly thus  $N_e = N_v$ , where  $N_v$  represents the number of valence electrons in the system.
- (2) A STO basis set centered on the individual atoms of the system is employed, with the basis functions of the form

$$\phi_{\mu}(r, \theta, \phi) = R_{nl}^{\mu}(r)Y_{lm}(\theta, \phi), \quad (8)$$

where  $n, l, m$  represent the principal, orbital, and magnetic quantum numbers associated with the  $\mu$ -th basis function,  $Y_{lm}(\theta, \phi)$  is the real spherical harmonic, and the radial part of the basis function is given by

$$R_{nl}^{\mu}(r) = (2\zeta_{\mu})^{n+1/2}(2n!)^{-1/2}r^{n-1} \exp(-\zeta_{\mu}r), \quad (9)$$

where  $\zeta_{\mu}$  is the orbital exponent associated with the  $\mu$ -th basis function, and is atom specific. In the CNDO method a minimal basis set is employed for the first row atoms, while an augmented basis set consisting also of  $d$ -type functions is employed for the second-row atoms. The present implementation of the INDO method, which is restricted only to the first-row atoms, uses a basis set identical to the CNDO method.

- (3) The effective one-electron matrix elements  $h_{\mu\nu}$  are called core integrals, and determined semi-empirically. Diagonal elements of the one-electron element  $h_{\mu\mu}$  are determined through various parameters such as electron affinity  $A_{\mu}$ , and ionization potential  $I_{\mu}$  of the atoms involved, while the off-diagonal elements ( $\mu \neq \nu$ ) are determined by

$$h_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu}, \quad (10)$$

where  $A$  and  $B$  denote the atoms on which basis functions  $\mu$  and  $\nu$  are located,  $\beta_{AB}^0$  is a semiempirical parameter dependent on  $A$  and  $B$ , and  $S_{\mu\nu}$  is the overlap matrix element for basis functions  $\mu$  and  $\nu$ .

- (4) For orbital orthonormalization purposes it is assumed that the basis set is orthonormal.
- (5) For the two-electron integrals  $(\mu\nu | \lambda\sigma)$ , following approximation is adopted

$$(\mu\nu | \lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu | \lambda\lambda), \quad (11)$$

and this set of integrals is further reduced by assuming

$$(\mu\mu | \lambda\lambda) = \gamma_{AB}, \quad (12)$$

where it is assumed that basis functions  $\mu$  and  $\lambda$  belong to atoms  $A$  and  $B$ , respectively. The value  $\gamma_{AB}$  is computed using the  $s$ -type orbitals located on  $A$  and  $B$ . Thus, all the two-electron integrals, apart from one- and two-center integrals, are ignored. As compared to the CNDO method, the following one-center integrals of the type  $(\mu\nu|\mu\nu)$  are assumed nonzero in the INDO method. The values of these integrals are determined semiempirically through the Slater-Condon parameters.

Once all the approximations listed above are implemented, the diagonal elements of the Fock matrix for the CNDO/2 model are given by

$$F_{\mu\mu}^{\alpha} = -\frac{1}{2}(I_{\mu} + A_{\mu}) + \sum_B (P_{BB} - Z_B)\gamma_{AB} - (P_{\mu\mu}^{\alpha} - 1/2)\gamma_{AA}, \quad (13)$$

while the off-diagonal elements for both the CNDO-2 and the INDO are

$$F_{\mu\nu}^{\alpha} = \beta_{AB}^0 S_{\mu\nu} - P_{\mu\nu}^{\alpha} \gamma_{AB}. \quad (14)$$

In the equations above,  $Z_B$  represents the effective nuclear charge of atom  $B$ , and  $P_{BB} = \sum_{\mu \in B} P_{\mu\mu}$  is the sum of those diagonal elements of the total density matrix which are centered on atom  $B$ . In the INDO method, however, one uses different expressions for the one-center diagonal and off-diagonal elements, given by

$$F_{\mu\mu}^{\alpha} = U_{\mu\mu} + \sum_{\lambda \in A} [P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - P_{\lambda\lambda}^{\alpha}(\mu\lambda|\mu\lambda)] + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB}, \quad (15)$$

and

$$F_{\mu\nu}^{\alpha} = (2P_{\mu\nu} - P_{\mu\nu}^{\alpha})(\mu\nu|\mu\nu) - P_{\mu\nu}^{\alpha}(\mu\mu|\nu\nu), \quad (16)$$

where  $\mu, \nu \in A$ . Above  $U_{\mu\mu}$ , and the one-center two electron integrals are obtained through  $I_{\mu}$ ,  $A_{\mu}$ , and various Slater-Condon parameters[7]. The two-center off-diagonal elements of the Fock matrix for the INDO model are obtained through 14. Once the Fock matrix is constructed, both for the CNDO/2 and INDO models, one solves the eigenvalue problem for the up-spin Fock matrix

$$\sum_{\nu} F_{\mu\nu}^{\alpha} C_{\nu i}^{(\alpha)} = \varepsilon_i^{\alpha} C_{\mu i}^{(\alpha)}, \quad (17)$$

as well as the down-spin Fock matrix, using the iterative diagonalization technique, to achieve selfconsistency. From the equations given above, it is easy

to deduce the expressions for  $F_{\mu\nu}^{\beta}$ , as well as the Fock matrix elements for the RHF case.

### 3 Description of the Program

Our computer code consists of the main program, and various subroutines and modules, all of which have been written in Fortran 90 language. Additionally, the program must link to the LAPACK/BLAS library, whose diagonalization routines are used by our program. In the following we briefly describe the main program, and each subroutine.

#### 3.1 Main program CINDO

This is the main program of our package which reads input data such as atomic numbers of the atoms constituting the system, and their positions, from the input file. The program also calculates the number of valence electrons of the system under consideration, and the total number of basis functions needed. It dynamically allocates various arrays, and then calls other subroutines to accomplish the remainder of the calculations. Because of the dynamical array allocation, the user need not worry about various array sizes, as the program will automatically terminate when it exhausts all the available memory on the computer.

#### 3.2 Subroutine BASEGEN

This subroutine generates various arrays containing information to the basis functions used in the calculations. This includes quantities such as principal quantum number ( $n$ ), orbital angular momentum ( $l$ ), magnetic quantum number ( $m$ ), orbital exponent ( $\zeta_{\mu}$ ) associated with each STO type basis function defined in Eqs. 8 and 9. Additionally, it also stores some semi-empirical data associated with the Hamiltonian such the  $\beta_{\mu\nu}^0$ , and various Slater-Condon parameters. This routine is called from the main program CINDO.

#### 3.3 Subroutine FACTCAL

The primary task of this subroutine is to generate the factorials of various integers. The factorials thus generated are stored in global arrays accessible

via the `MODULE factorials`. This subroutine is also called from the main program `CINDO`.

### 3.4 Subroutine `ASSOC_LEGNDRE`

This subroutine initializes the expansion coefficients which define associated Legendre polynomials of various degrees, needed to represent the angular part of the basis functions. The data is stored in global arrays through `MODULE legendre`. This subroutine is also called from the main program.

### 3.5 function `SS`

A very important quantity used in computing Hamiltonian matrix elements is the so-called reduced overlap integral between two basis functions (labeled  $a$ , and  $b$ ) [8]

$$s(n_a, l_a, m, n_b, l_b, \alpha, \beta) = \int_1^\infty \int_{-1}^1 (\mu + \nu)^{n_a} (\mu - \nu)^{n_b} \exp[-\frac{1}{2}(\alpha + \beta)\mu] \times \exp[-\frac{1}{2}(\alpha - \beta)\nu] T(\mu, \nu) d\mu d\nu, \quad (18)$$

where

$$T(\mu, \nu) = D(l_a, l_b, m) \sum_u^{l_a-m} \sum_v^{l_b-m} C_{l_a m u} C_{l_b m u} (\mu^2 - 1)^m (1 - \nu^2)^m \times (1 + \mu\nu)^u (1 - \mu\nu)^v (\mu + \nu)^{-m-u} (\mu - \nu)^{-m-v}. \quad (19)$$

Above  $(n_a, l_a, m)$  and  $(n_b, l_b, m)$  are the quantum numbers of two basis functions,  $C_{l_a m u}$ ,  $D(l_a, l_b, m)$  etc. are coefficients associated with the angular part of the basis functions, and  $\alpha = \zeta_a R$ , and  $\beta = \zeta_b R$ , where  $\zeta_a$ ,  $\zeta_b$  are the basis function exponents, and  $R$  is the distance between the atoms on which basis functions are located. If we define the so-called  $Y_{ij\lambda}$  coefficients defined through the relation

$$\sum_u^{l_a-m} \sum_v^{l_b-m} C_{l_a m u} C_{l_b m u} (\mu^2 - 1)^m (1 - \nu^2)^m \times (1 + \mu\nu)^u (1 - \mu\nu)^v (\mu + \nu)^{n_a-m-u} (\mu - \nu)^{n_b-m-v} = \sum_{i,j=0} Y_{ij\lambda} \mu^i \nu^j, \quad (20)$$

we obtain the expression

$$s(n_a, l_a, m, n_b, l_b, \alpha, \beta) = D(l_a, l_b, m) \sum_{i,j} Y_{ij\lambda} A_i[\frac{1}{2}(\alpha + \beta)] B_j[\frac{1}{2}(\alpha - \beta)], \quad (21)$$

where

$$A_k(\rho) = \int_1^{\infty} x^k \exp(-\rho x) dx, \quad (22)$$

and

$$B_k(\rho) = \int_{-1}^1 x^k \exp(-\rho x) dx. \quad (23)$$

For the  $s$  functions ( $l_a = l_b = m = 0$ ), the reduced overlap integrals (cf. Eq. 18) can be written as

$$\begin{aligned} s(n_a, 0, 0, n_b, 0, \alpha, \beta) &= \frac{1}{2} \int_1^{\infty} \int_{-1}^1 (\mu + \nu)^{n_a} (\mu - \nu)^{n_b} \exp[-\frac{1}{2}(\alpha + \beta)\mu] \\ &\quad \times \exp[-\frac{1}{2}(\alpha - \beta)\nu] d\mu d\nu. \end{aligned} \quad (24)$$

If we define the so-called  $Z_{k\lambda}$  coefficients through

$$(\mu + \nu)^{n_a} (\mu - \nu)^{n_b} = \sum_{k=0}^{n_a+n_b} Z_{k\lambda} \mu^k \nu^{(n_a+n_b-k)}, \quad (25)$$

we obtain

$$s(n_a, 0, 0, n_b, 0, \alpha, \beta) = \frac{1}{2} \sum_{k=0}^{n_a+n_b} Z_{k\lambda} A_k[\frac{1}{2}(\alpha + \beta)] B_{n_a+n_b-k}[\frac{1}{2}(\alpha - \beta)]. \quad (26)$$

The task of this REAL(kind=8) function is to compute the reduced overlap integral as defined in Eqs. 21 and 26, for a given pair of basis functions  $a$  and  $b$ . The input to this routine is all the basis function related information such as their quantum numbers, orbital exponents, and the distance between them. It performs these calculations by calling subroutines GETYCOEF, GETZCOEF, AINT, and BINT which described below.

### 3.6 Subroutine *GETYCOEF*

The task of this subroutine is to compute these  $Y_{ij\lambda}$  coefficients, for a given set of  $n_a, n_b, l_a, l_b$ , and  $m$  as defined in Eq. 20. It achieves this goal by calling subroutines *BINOMIAL* and *POL2MUL* described below.

### 3.7 Subroutine *GETZCOEF*

The task of this subroutine is to compute the  $Z_{k\lambda}$  coefficients, defined in Eq. 25, for a given pair of  $s$ -type basis functions. As in case of subroutine *GETYCOEF*, this routine also computes for these coefficients by calling routines *BINOMIAL* and *POL2MUL*.

### 3.8 Subroutine *BINOMIAL*

Using the binomial expansion, expression  $(ax^m y^n + bx^p y^q)^l$  can be expanded as

$$(ax^m y^n + bx^p y^q)^l = \sum_{i,j} c_{ij} x^i y^j, \quad (27)$$

where  $i, j, m, n, p, q$ , and  $l$ , are integers,  $x$ , and  $y$  are variables, and  $a, b$ , and  $c_{ij}$ 's are constants. This subroutine computes these expansion coefficients  $c_{ij}$ 's for a given set of input values of  $a, b, m, n, p, q$ , and  $l$ . It is called both from routines *GETZCOEF* and *GETYCOEF*.

### 3.9 Subroutine *POL2MUL*

This subroutine computes the coefficients of the product polynomial when two polynomial of the type  $\sum_{i,j} a_{ij} x^i y^j$  are multiplied, *i.e.*,

$$\sum_{i,j} c_{ij} x^i y^j = \left( \sum_{k,l} a_{kl} x^k y^l \right) \left( \sum_{l,m} b_{lm} x^l y^m \right). \quad (28)$$

The input to this routine are coefficients  $a_{kl}$  and  $b_{kl}$ , while the output consists of  $c_{ij}$ . The arrays meant for storing these coefficients are allocated dynamically.

### 3.10 Subroutine AINT

The value of the integral  $A_k(\rho)$ , defined in Eq. 22, can be shown to be

$$A_k(\rho) = \exp(-\rho) \sum_{\mu=1}^{k+1} \frac{k!}{\rho^\mu (k - \mu + 1)!}. \quad (29)$$

Subroutine AINT uses this series to compute the value of  $A_k(\rho)$ , for a given value of  $k$  and  $\rho$ .

### 3.11 Subroutine BINT

The purpose of this subroutine is to compute integral  $B_k(\rho)$ , defined in Eq. 23, for a given value of  $k$  and  $\rho$ . We use the following recursion relation to perform the task

$$B_{k+1}(\rho) = -A_{k+1}(\rho) + \frac{(-1)^{k+1} \exp(\rho)}{\rho} + (k+1) \left( \frac{(A_k(\rho) + B_k(\rho))}{\rho} \right). \quad (30)$$

Thus first a call is made to the routine AINT to compute all the  $A_k(\rho)$  's needed. Subsequently, the  $B_k(\rho)$ 's are generated using the recursion relation of Eq. 30.

### 3.12 Subroutine REDOVINT

This is a very important subroutine which evaluates overlap matrix elements  $S_{\mu\nu}$  among the basis functions. It evaluates the reduced overlap integrals described above for each pair of basis functions, by calling the function SS, using a coordinate system in which the atoms corresponding to the basis function pair are located along the  $z$ -axis. Then by a call to the subroutine TRANS described below, it obtains the actual overlap integrals by transforming the reduced integrals from the special coordinate system, to the actual molecular coordinate system. The upper-triangle of the overlap matrix is stored in a one-dimensional array.

### 3.13 Subroutine *TRANS xmgrace*

The formulas for reduced overlap integrals (Eqs. 18 and 24) assume that the atoms on which the basis functions are centered are a distance  $R$  apart from each other along the  $z$ -axis. But in practice, the molecules may have any kind of orientation. Therefore, we need to transform the reduced overlap integrals computed using these formulas, to the real orientation of the molecule. This is achieved through a transformation matrix which depends upon angular momenta of the basis functions, as well as on the angles by which the  $z$ -axis should be rotated to align it with the real orientation of the atoms involving the two basis functions. The task of this subroutine is to construct this transformation matrix, and then apply it to obtain the overlap integrals with respect to the molecular frame.

### 3.14 Subroutine *COUL\_INT*

This subroutine calculates the Coulomb integrals  $\gamma_{AB}$  (*cf.* Eq. 12) needed for the construction of the Fock matrix. It can be shown that these integrals are proportional to the reduced overlap integrals discussed above. Therefore, this routine computes these integrals by calling the function *SS*, and stores the values (one per atom pair) in a two-dimensional array.

### 3.15 Subroutine *CORE\_INT*

The aim of this subroutine is to compute the one-electron part of Fock matrix, referred to as core integrals, and discussed in section 2. The calculation of off-diagonal elements involves the use of the overlap matrix elements  $S_{\mu\nu}$  computed in the routine *REDOVINT*, discussed earlier. The semiempirical data needed for computing these matrix elements is also passed to this routine through arguments. The upper-triangle of the one-electron part of the Fock matrix, along with the extended Hückel Hamiltonian, are finally stored in separate one-dimension arrays, and constitute the output of this routine.

### 3.16 Subroutine *DIPINT*

The aim of this subroutine is to compute matrix elements of dipole operator over the basis set. This subroutine is called only if the linear-optical absorption, or permanent electric dipole calculations are desired. Standard formulas are

utilized to compute these matrix elements, and it is called from the main program CINDO.

### 3.17 Subroutine *SCF\_RHF*

This subroutine solves the RHF equations for the system under consideration in a self-consistent manner, using the iterative diagonalization procedure. The arrays which are needed during the calculations are allocated before the calculations begins, and are deallocated upon completion. Before the first iteration, extended Hückel Hamiltonian is diagonalized to obtain a set of starting orbitals. Subsequently, the Fock matrix corresponding to those orbitals is constructed and diagonalized. The process is repeated until the self-consistency is achieved. During the self-consistency iterations, subroutine DSPEVX from the LAPACK/BLAS library is used to obtain the occupied eigenvalues and eigenvectors. Obtaining only the occupied eigenpairs, as against the entire spectrum, leads to considerable savings of CPU time for large systems. However, if the entire spectrum of eigenvalues and eigenvectors is needed, say, to perform optical absorption calculations, the Fock matrix is diagonalized using the routine DSPEV from the LAPACK/BLAS library, upon completion of the self-consistency iterations. Because the entire spectrum is obtained only after self-consistency has been achieved, it does not strain the computational resources too much. Apart from computing the RHF total energy, this subroutine also calculates the total binding energy of the system, and, if needed, performs Mulliken population analysis as well.

### 3.18 Subroutine *SCF\_UHF*

This subroutine is exactly the same in its logic and structure as the previously described *SCF\_RHF*, except that the task of this routine is to solve the UHF equation for the system under consideration. Different Fock matrices for the up- and the down-spin are constructed and diagonalized in each iteration, until the self-consistency is achieved. Similar to the case of routine *SCF\_RHF*, during the iterations only the occupied eigenvalues and eigenvectors are computed using the routine DSPEVX. The iterations are stopped once the total UHF energy of the system converges to within a user defined threshold.

### 3.19 Subroutine *PROPERTY*

This is a driver subroutine whose task is to read the converged SCF orbitals written onto the disk by the SCF routines, and then call other subroutines

meant for computing various properties of the system under investigation. It is called from the main program CINDO after the SCF calculations, provided the user has opted for one of the property calculations such as the permanent electric dipole moment of the molecule, or its optical absorption spectrum.

### 3.20 Subroutine *DIPIND*

This subroutine transforms the dipole matrix elements from the basis-set AO representation to the SCF MO representation, by means of a two-index transformation. Therefore, it uses the dipole matrix elements computed in *DIPINT*, and the SCF MOs as inputs. The transformed dipole matrix elements, which constitute the output of this routine, are used in the calculation of linear optical absorption spectrum of the molecule. This subroutine is called from the routine *PROPERTY* described above, if the user has opted for the optical absorption calculations.

### 3.21 Subroutine *DIPMOM\_RHF*

This subroutine calculates the total net electric dipole moment component of the molecule under investigation for restricted Hartree-Fock case. It is called from the routine *PROPERTY* if the user has opted for the dipole moment calculation. It uses dipole matrix elements calculated in the subroutine *DIPINT* and the SCF MOs as input, and computes the permanent dipole moment of the system using a straightforward formula.

### 3.22 Subroutine *DIPMOM\_UHF*

The purpose and logic of this routine is the same as *DIPMOM\_RHF*, except that it is used for the case when UHF calculations have been performed. This routine is also called from the subroutine *PROPERTY*.

### 3.23 Subroutine *SPECTRUM*

This is an important subroutine which calculates the linear optical absorption of the system, under electric-dipole approximation, assuming a Lorentzian line shape and a constant line width for all the levels. Thus, if this calculation is opted, in the input file the user needs to provide the line width, along with the range of frequencies over which the spectrum needs to be computed.

Additionally, the routine uses the dipole matrix elements over the MOs as computed in routine DIPIND, along with the RHF single-particle energies. The computed spectrum is written in an ASCII file 'spectrum.dat', which can be readily used for plotting using programs such as gnuplot[9] or xmgrace[10]. This subroutine is also called from the routine PROPERTY, if the user has opted for linear absorption spectrum calculations.

### 3.24 *Orbital and Charge Density Plotting Subroutines*

For the purpose of orbital visualization, our code offers several options to the user for plotting the MOs, and the corresponding charge density. It is accomplished through four subroutines, PLOT\_1D\_RHF, PLOT\_2D\_RHF, PLOT\_1D\_UHF, and PLOT\_2D\_UHF.

The task of subroutine PLOT\_1D\_RHF is to compute and print out the numerical values of RHF MOs, or their charge densities, on a one-dimensional grid of points, whose direction and range is provided by the user. Output of this program is written in an ASCII file called 'orbplot.dat', and can be readily used for plotting by gnuplot[9] and xmgrace[10]. This routine is called from the routine PROPERTY, if the user has opted for it. To compute the numerical values of RHF MOs (or their charge densities) at different points in space, it uses the numerical values of basis functions computed at those points, by calling function BASFUNC.

When a user is interested in obtaining a two-dimensional plot of the RHF orbitals/charge densities in the Cartesian planes, subroutine PLOT\_2D\_RHF is called from the routine PROPERTY. The structure of this routine is also similar to that of PLOT\_1D\_RHF, except that for this case the orbital/density values are printed out with respect to the two cartesian coordinates of the plane. This routine also uses function BASFUNC to compute the numerical values of the orbitals/densities, and the output is also written in the file 'orbplot.dat'. In order to facilitate contour plots of charge densities, the option of making logarithmic plots is also available.

In case of open-shell UHF calculations, the corresponding plots of the up- and down-spin MOs are obtained through calls to subroutines PLOT\_1D\_UHF and PLOT\_2D\_UHF, and the output is again written in the file 'orbplot.dat'.

### 3.25 *Function BASFUNC*

It is a REAL(kind=8) function whose aim is to calculate the numerical value of a given basis function, at a particular point in space. Therefore, the input

to this function consists of the coordinates of the point in space with respect to the location of the basis function,  $(n, l, m)$  quantum numbers of the basis function, and its exponent  $\zeta$ . This function is called from all the orbital/density plotting subroutines described above.

## 4 Installation, input files, output files

We believe that the installation and execution of the program, as well as preparation of suitable input files is fairly straightforward. Therefore, we will not discuss these topics in detail here. Instead, we refer the reader to the README file for details related to the installation and execution of the program. Additionally, the file 'input\_prep.pdf' explains how to prepare a sample input file. Several sample input and output files corresponding to various example runs are also provided with the package.

## 5 Results and Discussions

In this section, we present and discuss the numerical applications of our results. First we present the results on a number of molecules. Next, we apply our method to obtain the ground states of model polymeric systems C chain and BN chain. Finally, we present the results of our calculations of optical absorption in Buckminster fullerene  $C_{60}$ . Wherever possible, we compare our results to those published by other authors.

### 5.1 Molecular Systems

In this section we present the results of our calculations on a variety of molecules, including fullerene  $C_{60}$ . The aim of these calculations is to compare our results with those published by other authors[8], and also with the CNDO/INDO calculations performed using Gaussian 03[11], in order to check the correctness of our program.

In table 1 we compare the total HF energies of several molecules computed by our program, to those computed using Gaussian 03[11]. We used the bond length of 0.74 Å for the  $H_2$  molecule as used also by Surjan[12]. For water molecule we used the geometry from Schaeffer *et al.* [13], for formic acid from Schwartz *et al.*[14], for borazane from Palke[15], and for fluoropropene from the work of Scarzafava *et al.*[16]. For  $C_{60}$ , we considered a dimerized configuration with the  $I_h$  symmetry group and bond lengths 1.449 Å and 1.397 Å optimized

Table 1

Comparison of the total Hartree-Fock energies ( $E_{HF}$ ) of several molecules obtained using both the CNDO/2 and the INDO methods using our program, to those computed using Gaussian 03[11]. All results are in atomic units. S/E inside the parentheses imply staggered/eclipsed configurations. For the molecular geometries utilized in these calculations, refer to the text.

Molecule	$E_{HF}$ (This work)		$E_{HF}$ (Gaussian03)	
	CNDO/2	INDO	CNDO/2	INDO
H <sub>2</sub>	-1.474625	-1.474625	-1.474625	-1.474625
H <sub>2</sub> O	-19.868052	-19.013606	-19.868052	-19.013606
<i>cis</i> -HCOOH	-45.305164	-43.364618	-45.305163	-43.364618
<i>trans</i> -HCOOH	-45.301984	-43.360996	-45.301984	-43.360996
Borazane (E)	-20.169898	-19.567825	-20.169897	-19.567824
Borazane (S)	-20.172764	-19.570726	-20.172763	-19.570730
<i>cis</i> -fluoropropene (E)	-52.763845	-50.693901	-52.763845	-50.693901
<i>cis</i> -fluoropropene (S)	-52.762138	-50.692238	-52.762138	-50.692238
<i>trans</i> -fluoropropene (E)	-52.761824	-50.692176	-52.761823	-50.692175
<i>trans</i> -fluoropropene (S)	-52.759748	-50.690019	-52.759748	-50.690019
C <sub>60</sub>	-427.624631	-412.293447	-427.624631	-412.293447

by Shibuya and Yoshitani [17]. The Cartesian coordinates for the carbon atoms of C<sub>60</sub> were generated using the computer program developed by Dharamvir and Jindal[18]. Thus, for all the cases illustrated in the table, the agreement on the total HF energies between our calculations and those obtained using Gaussian 03[11] is excellent both for the CNDO/2 and the INDO methods.

Next we turn our attention to the comparison of results for geometry optimization of a few closed- and open-shell molecules. In table 2 we compare the bond lengths optimized by our program to those reported by Pople *et al.*[8] for several closed- and open-shell diatomic molecules. Again the agreement obtained between the two sets of calculations is excellent both for the CNDO/2 and the INDO calculations.

Finally, in table 3 we compare the molecular dipole moments and Mulliken populations of several heteronuclear diatomic molecules obtained by our code with those reported by Pople *et al.* [8]. Both for the CNDO/2 and the INDO calculations the agreement between our results and those of Pople *et al.* [8] is virtually exact. Thus, excellent agreement between our results with those of other authors, not just for HF total energy, but also for other properties, testifies to the essential correctness of our computer program.

Table 2

Comparison of geometries optimized by our code to those reported by Pople *et al.*[8], for several small molecules. Calculations for all the molecules with doublet or triplet ground states were performed using the UHF method.

Molecule	State	Equilibrium Length (Å)			
		This work		Pople <i>et al.</i> [8]	
		CNDO/2	INDO	CNDO/2	INDO
Li <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.179	2.134	2.179	2.134
B <sub>2</sub>	<sup>3</sup> Π <sub>g</sub>	1.278	1.278	1.278	1.278
C <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.146	1.148	1.146	1.148
N <sub>2</sub> <sup>+</sup>	<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	1.127	1.129	1.127	1.129
N <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.140	1.147	1.140	1.147
O <sub>2</sub> <sup>+</sup>	<sup>2</sup> Π <sub>g</sub>	1.095	1.100	1.095	1.100
O <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	1.132	1.140	1.132	1.140
NH	<sup>3</sup> Σ <sup>-</sup>	1.061	1.069	1.061	1.070
OH	<sup>2</sup> Π <sub>i</sub>	1.026	1.033	1.026	1.033
BeH	<sup>2</sup> Σ <sup>+</sup>	1.324	1.324	1.324	1.323
LiH	<sup>1</sup> Σ <sup>+</sup>	1.573	1.572	1.573	1.572
BN	<sup>3</sup> Σ <sup>+</sup>	1.269	1.269	1.268	1.269
LiF	<sup>1</sup> Σ <sup>+</sup>	2.161	2.162	2.161	2.162
HF	<sup>1</sup> Σ <sup>+</sup>	1.000	1.005	1.000	1.006
BF	<sup>1</sup> Σ <sup>+</sup>	1.404	1.408	1.404	1.408

## 5.2 Calculations on Lithium Clusters

In this section we discuss the optimized geometries of small lithium clusters computed using our program. The number of computational studies of the electronic structure of small lithium clusters by other authors is too numerous to list here. We will mainly refer to the *ab initio* works of Ray *et al.*[20], Boustani *et al.*[21], Jones *et al.*[22], and Wheeler *et al.*[23] who studied clusters similar to the ones studied by us. Detailed computational studies of several large atomic clusters containing various atoms are in progress in our group, and will be published later.

Table 3

Comparison of computed electric dipole moments and Mulliken populations of heteronuclear diatomic molecules with the work of Pople *et al.*[8] The first number in each category is the CNDO/2 result, while the second number represents the INDO result.

Molecule	Electric Dipole Moment (Debye)		Mulliken Population	
	This work	Pople <i>et al.</i> [8]	This work	Pople <i>et al.</i> [8]
NH	1.76/1.69	1.76/1.68	0.08/0.09	0.08/0.09
OH	1.78/1.80	1.78/1.79	0.16/0.18	0.17/0.18
BeH	0.67/0.65	0.67/0.64	0.14/0.14	0.14/0.14
LiH	6.16/6.20	6.16/6.20	0.27/0.29	0.27/0.29
BN	0.36/0.50	0.36/0.50	0.05/0.03	0.05/0.03
LiF	7.91/7.87	7.90/7.86	0.56/0.58	0.56/0.58
HF	1.86/1.99	1.86/1.98	0.23/0.27	0.23/0.27
BF	1.31/0.87	1.31/0.86	0.15/0.15	0.15/0.15

### 5.2.1 $Li_2$

Results of our calculations on the optimized geometry of lithium dimer for the closed-shell ground state were presented in Table 2. As is obvious from the table that our optimized bond lengths of 2.179 Å (CNDO) and 2.134 Å (INDO) for  $Li_2$  are in perfect agreement with similar calculations performed by Pople *et al.*[8]. As far as the comparison with the experiments is concerned, both these results are significantly smaller than the measured value of 2.672 Å [19]. Therefore, it will be of considerable interest whether, or not, the inclusion of electron correlation effects will improve the results.

### 5.2.2 $Li_3$

Geometrical configurations for a triatomic cluster can be broadly classified as: (a) linear, and (b) triangular. For homonuclear systems such as  $Li_3$ , the possible triangular geometries can be further subclassified into: (i) equilateral triangle, (ii) isosceles triangle, and (iii) a triangle with unequal arms. Of course, the equilateral triangle geometry ( $D_{3h}$ ) is expected to undergo Jahn-Teller distortion to a lower symmetry configuration. Indeed, several density-functional theory (DFT) and *ab initio* correlated calculations have indicated that the isosceles triangle geometry ( $C_{2v}$ ) is the most stable configuration for  $Li_3$  [20,21,22,23]. Our calculations were performed on the doublet ground state using the UHF method, and the results are summarized in table 4. We found that equilateral triangular configuration is energetically more favorable as compared to the Jahn-Teller distorted isosceles triangles, as well as equidis-

Structure	CNDO Results		INDO Results	
	Bond Length (Å)	$E_{HF}$ (a.u.)	Bond Length (Å)	$E_{HF}$ (a.u.)
Linear	1.461	-1.8870412	1.457	-1.8819986
$D_{3h}$	1.932	-2.0133753	1.919	-2.0066737

Table 4

Optimized CNDO and INDO geometries of  $\text{Li}_3$ , and corresponding HF energies ( $E_{HF}$ ). Calculations were performed on the doublet ground states using the UHF method.

Structure	CNDO Results		INDO Results	
	Bond Length (Å)	$E_{HF}$ (a.u.)	Bond Length (Å)	$E_{HF}$ (a.u.)
Linear	1.186	-2.9683366	1.185	-2.9590571
Square	1.617	-3.3083610	1.612	-3.2976927

Table 5

Optimized geometries of  $\text{Li}_4$  clusters of various shapes obtained by CNDO and INDO methods, and corresponding HF energies ( $E_{HF}$ ). Calculations were performed on the closed-shell ground state.

tant linear configuration, both for CNDO and INDO models. Optimized INDO and CNDO geometries are in very good agreement with each other. The potential energy surface of the triangular configuration shows interesting features for both the models. We find that if the equal arms of the triangle are longer or shorter than the optimized bond lengths of the  $D_{3h}$  geometry presented in table 4, the system does exhibit Jahn-Teller instability. For bond lengths longer than those of the  $D_{3h}$  geometry, the distorted triangle has an angle less than  $60^\circ$  between the equal arms, while for bond lengths smaller than the optimized values, the corresponding angle is more than  $60^\circ$ . However, the global minimum was found for the  $D_{3h}$  geometry described in table 4. As far as the *ab initio* correlated and the DFT calculations are concerned, most of them report the length of equal arms of the  $C_{2v}$  geometry close to 2.8 Å, and the angle between them in excess of  $70^\circ$ [20,21,22,23]. Therefore, it will be interesting whether the inclusion of electron correlation effects will improve the agreement between CNDO/INDO models and the *ab initio* results.

### 5.2.3 $\text{Li}_4$

For  $\text{Li}_4$  clusters various geometries, ranging from linear to tetrahedral are possible as investigated, *e.g.*, by Ray *et al.*[20]. However, as reported by various authors, a rhombus structure is energetically most favorable. As a demonstration of our code we compute the relative stability of three possible structures of this system namely, linear, square, and rhombus.

Results of our calculations are summarized in table 5. We found that, of the three possible structures considered, the square structure had the minimum energy. The rhombus shaped structures have lower energy than the square structure for bond lengths in excess of 2.1 Å. However, the energies of those structures was found to be higher than those of square structures reported in table 5. This result is similar to what we obtained for Li<sub>3</sub> for which the equilateral triangular structure was found to be more stable than the isosceles triangular structure, both within the CNDO and INDO models. Our result for Li<sub>4</sub> disagrees with those obtained by correlated *ab initio*, and DFT calculations[20,21,22,23] which predict the lowest energy for the rhombus structure with its acute angle close to 50°. Additionally, all *ab initio* calculations predict bond lengths significantly larger than obtained here. Therefore, it is of considerable interest to explore whether the inclusion of electron-correlation effects will bring our results in better agreement with the *ab initio* ones.

### 5.3 Ground state of polymers

Our code can be used to study both the ground and excited state properties of oligomers of various polymers because they are nothing but finite molecules, ranging in size from small to large. However, in this section we demonstrate that our code can also be used to obtain the ground state energy/cell, in the bulk limit, for one-dimensional periodic systems such as polymers. Thus, it can be used, *e.g.*, for the purpose of ground-state geometry optimization of polymers, which is what we demonstrate next.

The energy per unit cell of a one-dimensional periodic system can be obtained using the formula

$$E_{cell} = \lim_{n \rightarrow \infty} \Delta E(n) = \lim_{n \rightarrow \infty} (E(n+1) - E(n)), \quad (31)$$

where  $E(n+1)/E(n)$  represent the total energies of oligomers containing  $n+1/n$  unit cells. Thus, using this formula, for sufficiently large value of  $n$ , one can obtain the energy/cell of a polymer in the bulk limit, from oligomer based calculations. In what follows we show that value of  $E_{cell}$  converges quite rapidly with respect to  $n$ , even for polymers which have metallic ground states. For the purpose of illustration we consider two model polymers namely chains consisting of: (a) carbon atoms (henceforth C-chain), and (b) alternating boron and nitrogen atoms (henceforth BN-chain). A C-chain consisting of uniformly spaced atoms will be metallic, which, as per Peierls theorem[24], is not allowed. Therefore, such a system is expected to dimerize leading to an insulating ground state[24]. On the other hand Peierls theorem is not applicable to the BN-chain, which is a band insulator and isoelectronic with the C-chain for

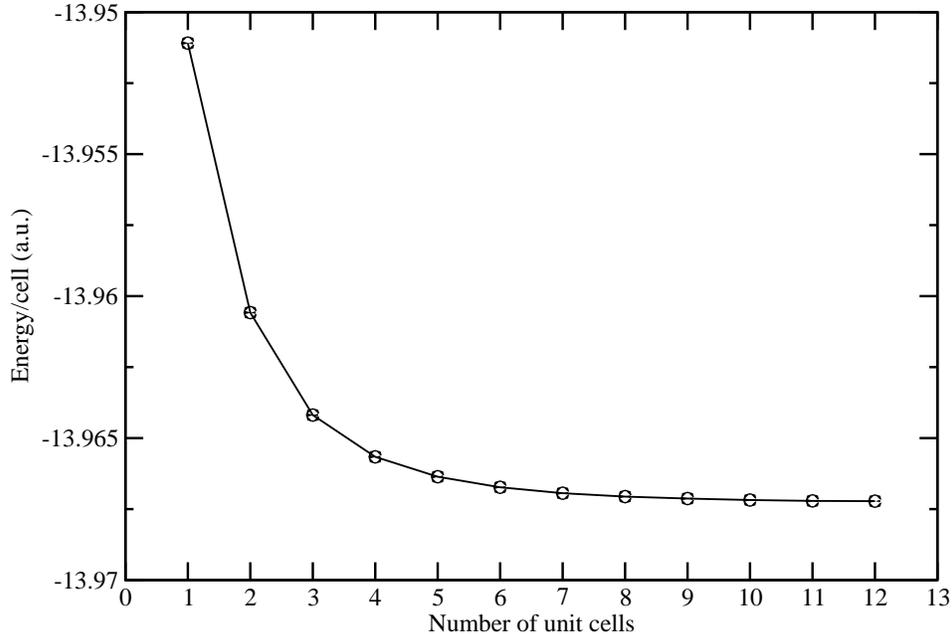


Figure 1. Energy per two-atom unit cell, of an undimerized C-chain, plotted as a function of the number of unit cells. The C-C bond length was taken to be  $1.297\text{\AA}$ .

a two-atom unit cell. In an earlier work from our group, we had studied the ground state geometry of C- and BN-chains using a fully *ab initio* methodology both at the RHF and the correlated levels, and concluded that C-chain does indeed exhibit dimerization, while the BN chain prefers the uniform geometry[25]. We explore the ground state geometries of these two systems using our code. In order to take care of the dangling bonds, we terminate the ends of oligomers of uniform C-chain and the BN chain with two hydrogen atoms on the each end. The dimerized C-chain consisting of alternating single and triple bonds, on the other hand, is terminated by one hydrogen atom on the each end.

First we examine the convergence of  $E_{cell}$  obtained using Eq. 31 with respect to the number of unit cells  $n$ . In Figs. 1 and 2 we plot  $\Delta E(n)$  as a function of  $n$ , for uniform C- and BN-chains, respectively. In both the cases convergence with respect to  $n$ , for the two-atom unit cells, is quite rapid, and for  $n = 10$  the bulk limit has been achieved to reasonable accuracy. This is quite remarkable because the C-chain considered for this calculation is metallic because of uniformly placed atoms. The convergence is even more rapid for C-chains with dimerized geometry.

Table 6

Comparison of our CNDO/2 and INDO geometries for uniform C-chain, and the BN chain, with our earlier *ab initio* RHF results[25].

Calculation	Bond Length ( $\text{\AA}$ )	
	C-Chain	BN-Chain
This Work (CNDO/2)	1.297	1.360
This Work (INDO)	1.300	1.362

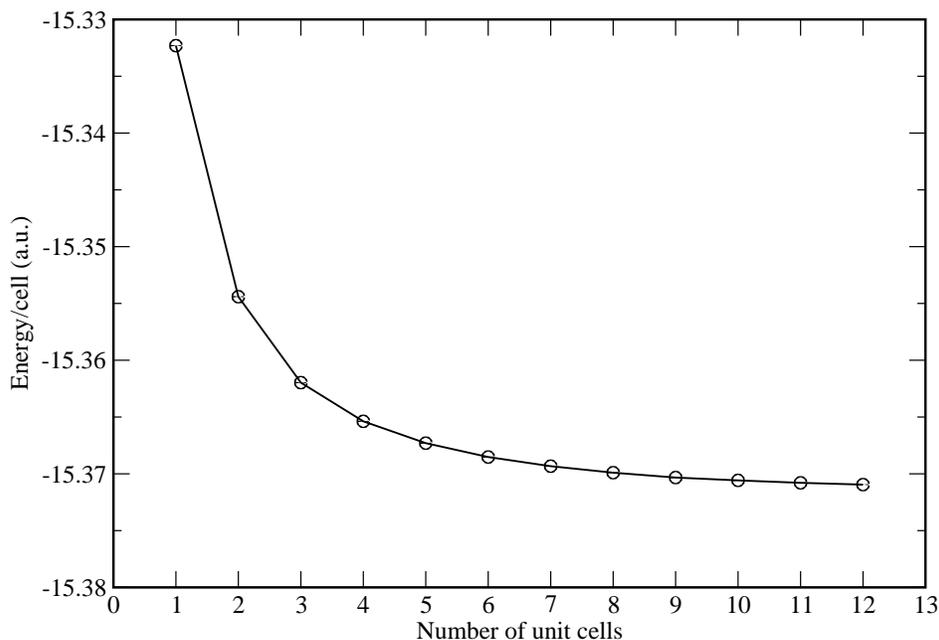


Figure 2. Energy per unit cell of boron-nitrogen chain, plotted as a function of the number of unit cells. The B-N bond length was taken to be  $1.360\text{\AA}$ .

Results of our calculations are summarized in tables 6 and 7. From these tables, the following trends are obvious: (a) CNDO/2 and INDO optimized geometries in all the cases are in good agreement with each other, and (b) optimized bond lengths obtained here are slightly larger than those obtained using the *ab initio* RHF method[25].

Additionally, the condensation energy per atom of the C-chain, defined as the difference in  $E_{cell}$  per atom of the optimized geometries in the uniform and dimerized configurations, are obtained to be 11.1 mHartrees/atom (CNDO/2), and 11.3 mHartrees/atom (INDO). These numbers are in reasonable agreement with the corresponding *ab initio* RHF value of 7.8 mHartrees/atom[25].

Table 7

Comparison of our CNDO/2 and INDO geometries obtained for the dimerized C-chain, with our earlier *ab initio* RHF results[25]

Calculation	$r_{single}(\text{\AA})$	$r_{triple}(\text{\AA})$
This work (CNDO/2)	1.390	1.231
This work (INDO)	1.390	1.227
Abdurahman <i>et al.</i> [25]	1.360	1.174

#### 5.4 Optical Absorption in Fullerene C<sub>60</sub>

Since the discovery of the C<sub>60</sub> in 1985[26], the field of the electronic structure and optical properties of fullerenes has become one of the foremost research topics these days[27]. Therefore, as the last application of our code in this paper, we present the results of linear optical absorption calculations in C<sub>60</sub>, at the RHF level. For these calculations we utilized the same geometry of Shibuya and Yoshitani[17], as was used for total energy calculations presented in section 5.1. In the CNDO/INDO models, with four basis functions per carbon atom, C<sub>60</sub> has 120 occupied and 120 unoccupied orbitals, with the ground state being a closed shell with the  $A_g$  symmetry. The HOMO/LUMO exhibit nearly  $\pi/\pi^*$  character, with a five-fold degenerate HOMO ( $h_u$ ) and a three-fold degenerate LUMO ( $t_{1u}$ ). Our HOMO-LUMO gap of 9.23 eV for the INDO calculations is in perfect agreement with that reported by Shibuya and Yoshitani[17].

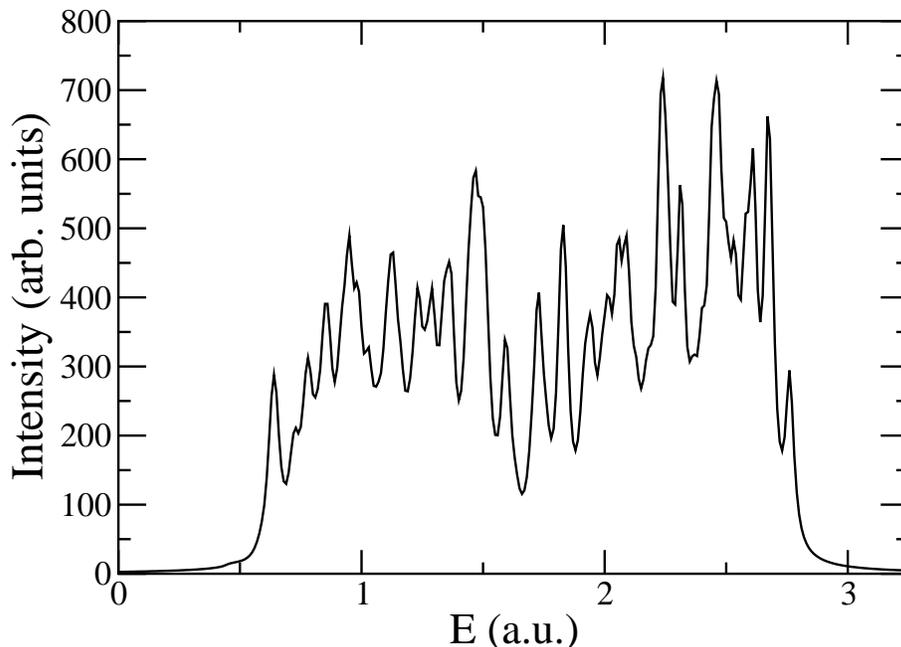


Figure 3. Linear absorption spectrum of  $C_{60}$ , obtained from RHF calculations using the INDO model, plotted as a function of the photon energy (in atomic units). A line width of 0.02 a.u. was assumed.

Next we present the linear optical absorption spectrum of  $C_{60}$  computed by the INDO method under the electric-dipole approximation, in Fig. 3. Because the HOMO and LUMO orbitals have the same inversion symmetry (*ungerade*), the HOMO $\rightarrow$ LUMO transition is dipole forbidden leading to negligible absorption intensity in the low-energy regions, in complete agreement with the experiments[27]. We have intentionally plotted the spectrum with a relatively small line width to emphasize the fact that a number of transitions among various orbitals contribute to the linear absorption. Qualitative features of our computed spectrum, namely the occurrence of two broad bands with a number of subpeaks in the spectrum, are in good agreement with other theoretical calculations[28]. As far as the quantitative comparison with the experiments is concerned, it is a well-known fact that the HF method overestimates the energy gaps significantly. Therefore, in future works we intend to carry out various levels of CI calculations to investigate the influence of electron-correlation effects on the linear absorption in  $C_{60}$ .

## 6 Conclusions and Future Directions

In this paper we have described our Fortran 90 program which solves the HF equations for both the closed- and open-shell molecular systems using the semiempirical CNDO/2 and INDO models. To demonstrate the correctness of

our approach, we presented numerous test calculations on molecular systems for which CNDO/INDO results are known, and obtained essentially exact agreement. Additionally, we presented results on systems such as clusters, fullerene, and polymers to demonstrate the wide utility of our present program. The reason behind developing the present program is twofold: (a) to develop a code in a modern language such as Fortran 90 which can carry out dynamic array allocation and thus free the user from specifying and changing array sizes, and (b) to provide an open software which will be widely available to users which they can use and modify as per their needs. One could write programs to perform a change of basis on the Hamiltonian matrix elements from the basis set AO representation to the MO representation, and use the transformed Hamiltonian to perform correlated CI calculations. Additionally, one could also introduce an electric-field in the Hamiltonian to perform finite-field calculations to compute quantities such as static polarizabilities of various orders.

The present version of our code is restricted to first-row atoms using the INDO method and up to the second-row elements using the CNDO/2 approach. It will be extremely desirable to extend these methods to elements further in the periodic table, preferably up to the transition metals. However, there are several versions of these models available for heavier elements such as the s-p-d INDO, ZINDO, and other methods[29]. Therefore, one could implement these methods in the present code which will allow the user to perform both INDO and CNDO/2 calculations on elements of second-row and beyond.

Work along those directions is continuing in our group, and results will be published as and when they become available.

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## References

- [1] See, *e.g.*, F. Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons Ltd. (1999).
- [2] R. G. Parr, *J. Chem. Phys* 20 (1952) 239.

- [3] R. Pariser and R. G. Parr, *J. Chem. Phys.* 21 (1953) 466; *ibid.* (1953) 767; J. A. Pople, *Trans. Faraday Soc.* 49 (1953) 1375.
- [4] J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys.* 43 (1965) S129.
- [5] J.A. Pople and G.A. Segal, *J. Chem. Phys.* 43 (1965) S136.
- [6] J.A. Pople and G.A. Segal, *J. Chem. Phys.* 44 (1966) 3289.
- [7] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.* 47 (1967) 2026.
- [8] For a review, see, *e.g.*, J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill Publications, 1970.
- [9] Gnuplot is a public domain command-line driven interactive data and function plotting utility available at URL <http://www.gnuplot.info>.
- [10] Xmgrace is a two-dimensional plotting tool for X Window based systems available at URL <http://plasma-gate.weizmann.ac.il/Grace>.
- [11] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [12] P. R. Surjan, *Phy. Rev.A* 30 (1984) 43.
- [13] H. F. Schaeffer and C. F. Bender, *J. Chem. Phys.* 55 (1971) 1720.
- [14] M. E. Schwartz, E. F. Hayes, and S. Rothenberg, *J. Chem. Phys.* 52, 2011 (1970).
- [15] W. E. Palke, *J. Chem. Phys.* 56 (1972) 5308.
- [16] E. Scarzafava and L. C. Allen, *J. Am. Chem. Soc.* 93 (1971) 311.
- [17] T. Shibuya and M. Yoshitani, *Chem. Phys. Lett.* 137 (1987) 13.
- [18] K. Dharamvir and V. K. Jindal (unpublished).
- [19] G. Herzberg, *Diatomic Molecules*, D. Van Nostrand Company, Inc., Princeton, N.J. (1950).
- [20] A. K. Ray, J. L. Fry, and C. W. White, *J. Phys. B: At. Mol. Phys.* 18 (1985) 381.

- [21] I. Boustani, W. Pewestorf, P. Fantucci, V. Bonačić-Koutecký and J. Koutecký, Phys. Rev. B 35 (1987) 9437.
- [22] R. O. Jones, A. I. Lichtenstein, and J. Hutter, J. Chem. Phys. 106 (1996) 4566.
- [23] S. E. Wheeler, K. W. Sattlemeyer, P. v. R. Schleyer, and H. F. Schaefer III, J. Chem. Phys. 120 (2004) 4683.
- [24] R. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955), p.108.
- [25] A. Abdurahman, A. Shukla, and M. Dolg, Phys. Rev B 65 (2002) 115106.
- [26] H.W. Kroto, J.R. Heath, S.C. O' Brien, R.F. Curl and R.E. Smalley, Nature 318 (1985) 162.
- [27] For a review, see, *e.g.*, G. Orlandi and F. Negri, Photochem. Photobiol. Sci., 1(2002) 289.
- [28] See, *e.g.*, Z. Shuai and J. L. Brédas, Phys. Rev. B 46 (1992) 16135; ref.[27].
- [29] See, *e.g.*, H. L. Hase and A. Schweig, Theoret. Chim. Acta 31 (1973) 215; V. Santhanam and J. Sobhanadri, Pramāna 24 (1985) 737; W. P. Anderson, T. R. Cundari, and M. C. Zerner, Theoret. Chim. Acta 39 (1991) 31; L.-H. Lu, K.-C. Sun, and C. Chen, J. Mol. Struct. (Theochem) 392 (1997) 305.