Input Prepartion Guide for the Program ppp.x

October 6, 2009

All the input data is written in the free format to minimize errors. Therefore, before each important input card, there is a compulsory comment line to make the input self explanatory. It is irrelevant as to what is written in the comment lines, but, by writing something meaningful, one can keep the input process transparent. We do require that all the ASCII input cards (not the ones in the comment lines) should be in uppercase letters. To distinguish comment lines from the input, in this guide we precede each comment line with the character '#", although in actual input files, that is seldom done. We encourage the user to compare the explanation provided here with the actual input files provided in the Examples subdirectory. Next, we explain the preparation of input files card by card.

1. The input file starts with a title. Thus, the first is for a title of the calculations. A user can provide a relevant title so as to provide an idea about the calculation or system at the first glance.

   # Title

2. As the purpose of our code is to perform calculations using various semi-empirical model Hamiltonians, the first input card is an ASCII card describing the model Hamiltonians to be used for the calculations. Options are: P-P-P, Hubbard, extended Hubbard, and Hückel.

   (a) For a system using P-P-P model, the input card may read:

   # The Hamiltonian to be used
   PPP

   (b) For a system using Hubbard model, the input card may read:

   # The Hamiltonian to be used
   HUBBARD

   (c) For a system using extended Hubbard model, the input card may read:

   # The Hamiltonian to be used
   EXTHUB

   (d) For a system using Hückel model, the input card may read:

   # The Hamiltonian to be used
   HUECKEL

3. If P-P-P model Hamiltonian is to be used, one can use various parameterizations. Thus, our second card is also an ASCII card, stating which parameterization is to use. Options are: Ohno, Mataga-Nishimoto, and exponential parameterizations.

   (a) For Ohno parameterization, the input card may read:

   # Parameterization for the P-P-P Hamiltonian
   OHNO

   (b) For Mataga-Nishimoto parameterization, the input card may read:

   # Parameterization for the P-P-P Hamiltonian
   MATNIS

   (c) For exponential parameterization, the input card may read:

   # Parameterization for the P-P-P Hamiltonian
   EXP

4. The long-range Coulomb potentials in case of Ohno parametrization can be parameterized using different sets of parameters, such as standard parameters or screened parameters. If standard parameters is given as input card, the program automatically takes U=11.13d0, r_0=1.2785884d0, and $\kappa_{i,j}$=1.d0, while in case of screened parameters it takes U, r_0, and $\kappa_{i,j}$ as 8.d0, 1.2785884d0, and 2.d0, respectively. However, one can also directly give the parameters. If the user opts for Hubbard or extended Hubbard model, then parameters should be provided explicitly.
   If Ohno paramterization is set as an option then the next card will be an ASCII, mentioning the parameters to use.

   (a) For standard parameters, the input card may read:

   # Parameters for the Ohno parameterization in the P-P-P Hamiltonian
   STANDARD

   (b) For screened parameters, the input card may read:

   # Parameters for the Ohno parameterization in the P-P-P Hamiltonian
   SCREENED

   (c) For other parameters, the input card may read:

   # Parameters for the Ohno parameterization in the P-P-P Hamiltonian
   PARA
   11.d0,1.28d0,1.d0

   If the user wants to use other than Ohno parameterization such as Mataga-Nishimoto or exponential then one needs to just provide the values of U

2

and r_0. For example,

Parameters for the Mataga-Nishimoto or exponential parameterization
in the P-P-P Hamiltonian
11.d0, 1.28d0

If one is using Hubbard model, the value for U should be given directly.

11.d0

In case of extended Hubbard model calculations, the value for U and V (nearest neighbours potential) should also be given directly.

11.d0,3.d0

5. Next card will read the electric charge (ionicity) on the system. The magnitude of the nuclear charges have been defined as unity (= 1). For the neutral system the ionicity will be zero, and so on.

For example, in case of *trans*-polyacetylene, the card will read as follows

#Charge on the system
0

In order to handle a singly ionized cation the input is:

#Charge on the system
1

while for a singly ionized anion, the input will be:

#Charge on the system
-1

6. As our code has been framed to handle mainly molecules and polymers, the next input card will read the total number of atoms in the unit cell, after the comment line.

For example, if we are handling a system having two number of atoms in the unit cell, then the card will read

Total number of atoms in the unit cell
2

7. Next card deals with the Cartesian coordinates of the different atoms in the unit cell, to be provided in the units of Å. We have two options to facilitate this: (a) Automatic generation through various keywords, (b) by explicitly providing coordinates of each atom. First we will describe the

keywords involved in the automatic generation of coordinates followed by one example illustrating their use.

Give the coordinates of the atoms involved in the system

(a) For example, for the benzene ring oriented in parallel direction to the conventional orientation, in the xy-plane, the input card may read:

BEN-XY
 In case of ring lying in yz- or zx-plane, one should give card as 'BEN-YZ'

or 'BEN-ZX', respectively.

The next card will specify the center of the benzene ring. For example input,

-3.2725,0.575907,0.0
implies that the phenyl ring is centered at the point (-3.2725,0.575907,0.0), in Cartesian coordinates .

The next card must specify the bond length of the hexagon constituting the phenyl ring and whether we need to rotate this ring with respect to some axis. For example input,

1.4,0
implies that the bond length is 1.4 Å and no rotations need to be performed on the ring.

If instead this input is like:

1.4,2
3,-90.d0
2,30.d0
which implies that the C–C bond length in the ring is 1.4 Å, which will undergo two susequent rotations. First rotation is a clockwise one by 90° about the z-axis, followed by second counter clockwise rotation by 30° about the y-axis. For example, in an entry of the type 3, -90.d0, first number denotes the axis of the rotation, while the second number denotes the angle of the rotation.

(b) For a benzene ring oriented in perpendicular direction to the conventional orientation, in the xy-plane, the keyword will be:

BENP-XY

and rest of the input will be identical to the case of BEN-XY, discussed above.

4

(c) For generating a bond (a unit consisting of two atoms seperated by a distance) whose location is specified by the coordinates of the bond center, the input card is:

BOND

Next to this card, the user should specify origin, bond length and number of rotations to be performed on the bond because by default the bond is assumed to be along the x-axis. Rotations, if desired, are performed keeping the center fixed. Positive angles imply counter-clockwise rotations, while the negative angles denote clockwise rotations. For example input,

1.0,0.0,0.0
1.33,1
3,-60.d0
will initially generate a bond centered at the Cartesian coordinates (1.0, 0.0, 0.0) of length 1.33 Åalong the x-axis, then subsequently it will be rotated with respect to the z-axis by 60° angle (clockwise).

(d) For generating a bond whose first atom lies at the user specified location (as against the center lying at the user specified location in case of the BOND keyword), an alternative input card called LINE is provided:

LINE

rest of the inputs are identical to those needed with the keyword BOND.

(e) Keyword ATOM is provided to generate a single atomic site located at the user specified coordinates. The input:

ATOM
0.0,0.0,0.0
will generate an atomic site located at the origin.

(f) A keyword C60 is provided to generate the atomic coordinates of a bond alternating fullerene C_{60}. For example the input,

C60
1.45,1.35
1.0,1.0,1.0
will generate the coordinated of 60 carbon atoms consituting a fullerene molecule center located at point (1.0,1.0,1.0), with single and double bond lengths, 1.45 Åand 1.35 Årespectively.

(g) If one does not want to use the above mentioned keywords and stright away wants to provide Cartesian coordinates of all the atoms located in the system, keyword COORD should be used. For example input,

5

COORD
0.0,0.0,0.0
1.4,0.0,0.0
0.0,1.4,0.0
1.4,1.4,0.0
will generate a system with four atoms located at positions (0.0,0.0,0.0),
(1.4,0.0,0.0), (0.0,1.4,0.0), and (1.4,1.4,0.0).

(h) In all the cases the end of the inputs for the atomic coordinates generation is signalled by the keyword ENDA.

ENDA

Next we provide couple of examples of coordinate inputs which will illustrate the use of these keywords. The first example specifies the generation of the atomic coordinates of a unit cell of the polymer phenyl disubstituted polyacetylene (PDPA), considered in several of our papers (*e.g.*, P. Sony and A. Shukla, Phys. Rev. B 71 (2005) 165204.). This input illustrates the use of the some of the keywords discussed above.

BEN-XY
-0.577485,3.289479,0.0
1.4,2
3,-90.d0
2,30.d0
BOND
0.0,0.0,0.0
1.35,1
3,-31.18125
BEN-XY
0.577485,-3.289479,0.0
1.4,2
3,-90.d0
2,30.d0
ENDA

The next example illustrates a case of a benzene ring centered at (-2.4248,1.4000,0.0000), where atomic coordinates are provided directly.

COORD
2.42480 -2.80000 0.00000
-3.63720 -2.10000 0.00000
-3.63720 -0.70000 0.00000
-2.42480 0.00000 0.00000
-1.21240 -0.70000 0.00000

-1.21240 -2.10000 0.00000
ENDA

8. The next card is again an ASCII card, which will contain information regarding the type of calculations one wants to perform.

   # Type of Calculations

   (a) For example, if one wants to do restricted Hartree-Fock calculations, then the input card should be:

   RHF

   (b) In case of unrestricted Hartree-Fock calculations, the input card will be:

   UHF

   For the UHF card above additional input specifying the number of up spin (nalpha) and down spins (nbeta) electrons is essential

   #Number of up and down spin electrons
   7, 6
   The input above implies that the system contains 13 electrons in all, 7 of which are of up spin and remaining 6 of down spin.

   (c) If followed by RHF calculations one wants to perform a single CI calculation, the corresponding input card is:

   SCI

   The following example illustrates a situation where both RHF and SCI calculations are performed.

   #TYPE OF CALCULATION
   RHF
   #SCI CALCULATIONS TO BE PERFORMED
   SCI

   (d) The input card OPTICS should be used when one wants to perform calculations of linear optical absorption on the given system. At present this card cannot be used with a UHF calculation. Keyword OPTICS is to be followed by $d\omega, \omega_{min}, \omega_{max}, \Gamma, scale$, where $d\omega$, represents the frequency step, $\omega_{min}/\omega_{max}$ represent minimum/maximum range of frequencies for which the spectrum is to be computed, while Γ is the line width of the

excited states, and *scale* is a number which can be used to convert the energy unit from the default eVs to a unit of user's choice. If the energy unit of eVs is to be used then this number can be given to be 1.0, 0.0, or any negative number. For single particle calculations such as Hückel model or RHF one needs to specify that from how many reference states we want to compute the linear absorption spectrum. Thus, one can compute both the ground state, as well as excited state absorptions. For excited states absorption, at present we are restricted to only those excited states which can be obtained by single excitations from the ground state. The input format is:

#OPTICS TO BE PERFORMED
OPTICS
#Read the number of dipole moment components needed and line-width parameters
3 # dimensions
1,2,3 # directions
0.1, 0.0, 10.0, 0.01, 1.0 # Γ, ω_{min},ω_{max}, $d\omega$, scale
#From how many states one wants to compute linear absorption, '0' implies ground state
1 # no. of states from which absorption will be computed
0 # this implies that absorption is computed from the ground state

If the state from which absorption is to be computed is not the ground state but an excited state (*i.e.*, not '0', but '1'), then we need to specify the orbitals in which holes and electrons exists to characterize the excited state in question. The input will be:

#From how many states one wants to compute linear absorption, '0' implies ground state
1 # no. of states from which absorption will be computed
1 # this implies that absorption is computed from the excited state
4, 5 # excited state has a hole in orbital 4 and an electron in orbital 5

The above inputs specifies the linear absorption calculations in which all the three Cartesian components of the transition dipole will be used and the spectrum will be computed in the range from 0.0 to 10.0 eV in the steps of 0.01 eV with a linewidth of 0.1 eV for the Hückel model or RHF calcualtions. In the first case the absorption is from the ground state and in the second case it is from an excited state.

If optical absorption spectrum is to be computed for an SCI calculations then the input will be like:

#TYPE OF CALCULATION

RHF
#SCI CALCULATIONS TO BE PERFORMED
SCI
#OPTICS TO BE PERFORMED
OPTICS
#GIVE THE NUMBER OF DIPOLE MOMENTS
3 #dimensions
1 2 3 #directions
0.1 0.0 20.0 0.01 1.0 # Γ, ω_{min},ω_{max}, $d\omega$, scale
#Read the number of states and the states from which absorption is to
be computed
1 # no. of states from which absorption will be computed
1 # this implies that absorption is computed from the excited state, '0'
will imply the absorption from the ground state

The absorption spectrum in all the cases is written in a file spec001.dat,
which can plotted using graphical programs such as gnuplot or xmgrace.

(e) If one wants to perform nonlinear optical (NLO) susceptibility calcula-
tions within a single particle model such as Hückel model or RHF model,
the occupied and unoccupied orbital energies, as well as dipole matrix el-
ements among them are needed. This data in turn can be provided to a
seperate computer program meant for calculating various NLO suscepti-
bilities. By invoking the NLO card, the user can get the above mentioned
data written in a seperate file called NLO001.DAT. We had written a
seperate program (not provided with this package) meant for computing
these NLO susceptibilities for which file NLO001.DAT served as an input.
The input in such a case will be:

#NON LINEAR OPTICS TO BE PERFORMED
NLO
#Read the components of dipole moments
2 # dimensions
1,2 # directions

In order to reduce the size of dipole matrix elements, one can delete the
outermost occupied and virtual orbitals choosing the card 'ORBDEL'.

Delete occupied and valence orbitals
ORBDEL
1,10 # delete occupied orbitals from 1 to 10
21,30 # delete virtual orbitals from 21 to 30

As this is an essential card, so if in case no orbital has to be deleted, then
give the input card:

NOORBDEL

(f) Orbital charge density analysis can be done by giving input cards as:

ORBDEN
0,2 #providing the density flag and no. of sites.
7,8 #site numbers for which the charge density is desired

If '0' is assigned to the density flag, then only the specified sites will be analyzed. While if it is assigned a value '1', the sites given along with their periodic copies will be analyzed.

(g) The band structure calculations can be performed using the Hückel model Hamiltonian. To opt for the band structure calculations, the input cards will be:

BAND
-1.0,1.0,0.01 #lower limit and upper limit of the k-values (crystal momentum), and the differential step

(h) If the user wants to perform post HF correlated calculations such as FCI, QCI, or MRSDCI, etc., using some other computer program, various files containing the data such as one- and two-electron integrals will be required. The card CIPREP serves as the flag to the program to prepare these files, which are written in the binary format. Thus, the input card will be given as:

CIPREP

In case of UHF calculations one needs to specify first that which type of orbitals will be used for the correlation treatment. For this a flag is provided, whose value is assigned '1' for using the alpha-type orbitals, and '2' for the beta-type orbitals.

1

If RHF calculations are to be performed then the above line should be skipped.

User can also freeze the occupied orbitals and delete the virtual orbitals,

thus, can perform correlated calculations choosing a specified set of occupied and virtual orbitals. The input for this can be like this:

12,0 # no. of occupied orbitals to be frozen (1st twelve orbitals will be freezed), flag for freezing
11,0 # no. of virtual orbitals to be deleted, flag for deletion
23,33 # from 23rd to 33rd orbital are to be deleted.

If the electric dipole integrals are needed along with the CIPREP option (possibly with the aim of performing optical properties calculations at the correlated level), card DIPINT should be used.

Dipole moment calculation
DIPINT
#How many components of dipole moments
2 # dimensions
1,2 # directions
 If no dipole integral calculation is desired, the input should be:

Dipole moment calculation
NODIPINT

(i) The orbitals can be printed in the ASCII format in the output file by using the card:

#To print the orbitals
PRORB

However, this card should be used with caution because, for large systems, the orbital related data can be huge.

(j) In order to calculate dielectric response properties or electro-absorption spectrum, one needs to solve the HF equation in the presence of a finite external electric field. The input card for such calculations will be:

#Calculations to be performed in the presence of finite electric field
EFIELD
0.001 0.0 0.0 #components of electric field in x, y, and z-directions, respectively.

The numbers specifying the components of the external electric field above are in the units of V/Å.

(k) After specifying all the methods which are to be used during the calculations, the end of this input is specified by the following card:

#End Method Card
ENDM

9. Next card provides the total number of unit cells and should be a positive integer. For example, for generating an oligomer with eight units (unit cell coordinate input is specified above), the input will read:

#Total number of units
8

10. If the number of units cells specified in the previous card is greater than one, translational vector needs to be provided as of the type below:
2.4253866 0.0 0.0

11. Atomic operations such as atom deletion can also be used while generating a given molecule. This operation is useful when for a system containing more than one unit cell, periodic copies lead to more atoms in the system than what is needed. For example, for oligomers of polymers such as PPV and polyacenes, this is usually the case.

For the case of naphthalene atom numbers 11 and 12 need to be deleted (*cf.* example input files acene2.dat).

#If any atomic operations (such as atom deletion) need to be performed
DELATOM
2 # number of atoms to be deleted
11, 12 # atom numbers 11 and 12 are deleted

#If no atom is to be deleted, the input card should be given as:
NODELATOM

12. The convergence threshold set by the user to achieve convergence in total energy in the units of eV, will be given as:

#Convergence threshold
1.D-8

13. The maximum number of iterations allowed to achieve convergence can be given as follows:

Maximum iterations allowed
100

14. Sometimes, because of the oscillatory nature of total energy during the SCF iterations it becomes difficult to achieve convergence. However, in those cases one usually utilizes the techniques of Fock matrix mixing (which is also popularly called damping). This can be invoked by the keyword DAMP to be followed by the input value of parameter $xdamp$, which denotes the fractional amount of damping used in the formula explained below.

$F^{(i)} = xdamp \, F^{(i)} + (1 - xdamp) \, F^{(i-1)}$

where $F^{(i)}$ is the Fock matrix in the i-th iteration, where $0 \leqq xdamp \leqq 1$.

For example, if one intends to use 50% mixing the input will read:

#DAMPING WILL BE USED
DAMP
0.5

if in case no Fock matrix mixing is required, then the input file reads,

NO DAMPING TO BE USED
NODAMP

15. Next input consists of data related to the hopping matrix elements. The input differs slightly for finite systems as compared to the case when band structure for an infinite polymer is desired within the Hückel model. For finite systems one has the option of explicitly providing the hopping matrix elements or for their automatic generation by attaching a given hopping value with a certain bond distance. Below we provide examples to illustrate all the three cases.

First we present the example input associated with the band structure calcualtion of the polymer PPP, within the Hückel model (*cf.* example file ppp_band.dat)

#Read the no. of unique intracell and intercell hopping matrix elements
1 1 #number of unique intracell and intercell hoppings
-2.4,6 # value of intracell hopping and number of site pairs connected by it

13

2,1
3,1
4,2
5,3
6,4
6,5
-2.23,1 # value of intercell hopping and its connectivity
6,1,1 # site pair which is connected by it, followed by the primitive vector of the cell

Next we present the example of a bond alternated polyene oligomer, made up of identical double bonds (*cf.* example file tpa10.dat or tpa11.dat).

#HOPPING PARAMETERS
#Number of unique hoppings
2
-2.568,1 # intracell double bond hopping and number of site pairs connected by it
2,1 #intracell sites connected by above hopping
-2.232,1 # intercell single bond hopping and number of site pairs connected by it
3,2 #intercell sites connected by above hopping

In the next example we illustrate the automatic hopping generation option through the keyword HOPGEN, meant for finite systems which can simplify this task tremendously (*cf.* example file trigonal_zigzag_benzo6_uhf.dat).

#HOPPING PARAMETERS
#HOPGEN
1 #no. of unique hopping values
1.40 #bond length corresponding to the value of hopping
-2.40 #value of hopping

16. The final card specifies whether or not we want to provide nonzero values for site energies. In case we want to provide a nonzero value, it is done through the keyword SITE, explained as below:

#Site energies to be read
SITE
4 #Number of nonzero site energies/cell
3, 0.1 #site 3 is assigned the energy 0.1
4, 0.3 #site 4 is assigned the energy 0.3
5, -0.2 #site 5 is assigned the energy -0.2

6, -0.1 #site 6 is assigned the energy -0.1

However, if no nonzero site energies are to be assigned the following data suffices:

#Whether site energies are to be read
NO SITE