CHAPTER FIVE

Molecular Orbital Calculations and Analysis

5.1 MO calculation program *MC*

The program *MC* of the *CAESAR* package performs MO calculations for molecules using the EHTB method. An input file, *filename.MI*, for *MC* has the structural information about a molecule to examine and the computational options. It is convenient to create this file by running the *NEWMI* program of *CAESAR* or by modifying an existing *filename.MI* file. The *MC* program produces output files *filename.MO*, *filename.ME*, *filename.MW* and *filename.MV*. The text file *filename.MO*, which records the input, output and the computational history, can be read by using any text editor. MO energies are stored in a text file *filename.ME*, gross populations of atomic orbitals in a text file *filename.MW*, and overlap populations between atoms in a text file *filename.MV*. The file *filename.ME* is used to obtain the total DOS plot and the Fermi level (i.e., the HOMO) as a function of the number of valence electrons. The file *filename.MW* is used to obtain PDOS plots, and the file *filename.MV* to obtain PDOP plots.

5.2 Creating an input file *filename.MI*

When the *NEWMI* program is launched, it opens the *New .MI File* dialog box (*Figure 5.1*), which facilitates the creation of a *filename.MI* file.

5.2.1 Basic parameter-setting for *filename.MI*

The *New .MI File* box has four input fields, *Memo*, *Charge*, *Atom Positions*, and *Details*. In this section, we discuss the first three of these items.

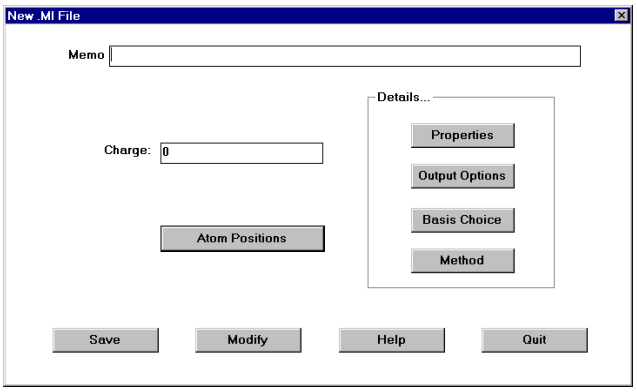


Figure 5.1. New .MI File dialog box.

•*Memo*

This is a text string to be used for writing a short comment about the molecule in question.

•*Charge*

This refers to the overall charge on the molecule. It does not affect MO's and their energies calculated by the EHTB method, but it determines the HOMO level corresponding to the total number of valence electrons on the molecule for its lowest possible spin state.

•*Atom Positions*

The program *Builder* (see Chapter 3) can be used to create a crystal structure containing the geometry of a molecule under examination and then edit the crystal structure to single out a molecule. The atom positions of this molecule are stored in a resulting *filename.CI* file the user saves. These atom positions can be copied into a *filename.MI* file. Alternatively, the atom positions of a *filename.MI* file can be specified either by typing their Cartesian coordinates or by using the Z-matrix method of geometry building. That is, the atom positions of a *filename.MI* file can be either in Cartesian coordinates or in Z-matrix format.

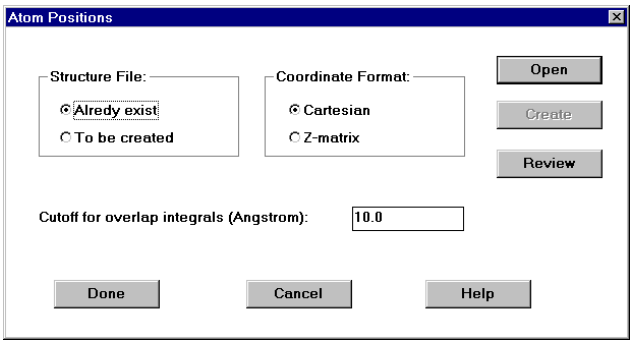
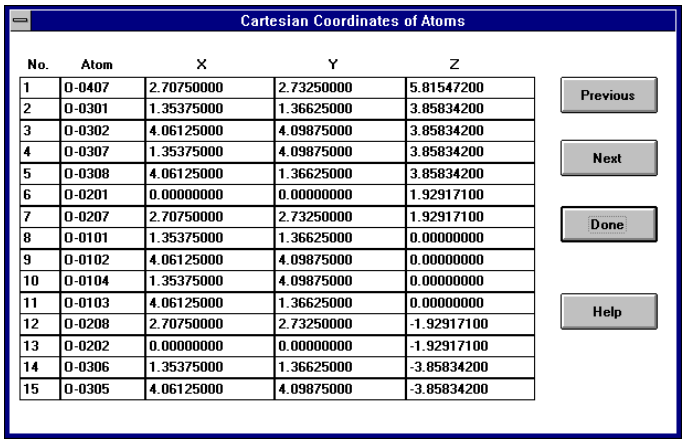


Figure 5.2. Atom Positions dialog box.

On clicking the *Atom Positions* button, the user can open the *Atom Positions* dialog box (*Figure 5.2*). There are three ways of specifying the atom positions of a molecule:



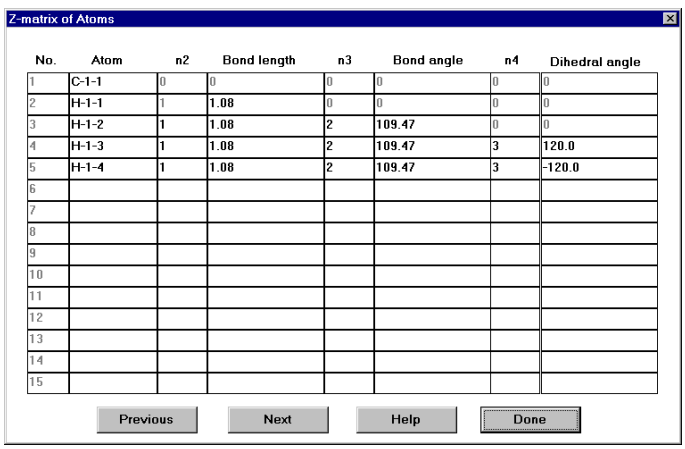
Cartesian Coordinates of Atoms

No.	Atom	X	Y	Z
1	O-0407	2.70750000	2.73250000	5.81547200
2	O-0301	1.35375000	1.36625000	3.85834200
3	O-0302	4.06125000	4.09875000	3.85834200
4	O-0307	1.35375000	4.09875000	3.85834200
5	O-0308	4.06125000	1.36625000	3.85834200
6	O-0201	0.00000000	0.00000000	1.92917100
7	O-0207	2.70750000	2.73250000	1.92917100
8	O-0101	1.35375000	1.36625000	0.00000000
9	O-0102	4.06125000	4.09875000	0.00000000
10	O-0104	1.35375000	4.09875000	0.00000000
11	O-0103	4.06125000	1.36625000	0.00000000
12	O-0208	2.70750000	2.73250000	-1.92917100
13	O-0202	0.00000000	0.00000000	-1.92917100
14	O-0306	1.35375000	1.36625000	-3.85834200
15	O-0305	4.06125000	4.09875000	-3.85834200

Previous
Next
Done
Help

Figure 5.3. Dialog box *Cartesian Coordinates of Atoms*.

(1) To specify the atom positions in terms of Cartesian coordinates, it is necessary to choose the *To be created* option from the *Structure File* field and the *Cartesian* option from the *Coordinate Format* field and then click the *Create* button. Then the *Cartesian Coordinates of Atoms* box opens (*Figure 5.3*). Then type the names and the (x, y, z) coordinates of atoms one by one. As discussed in Chapter 3, it is important to name each atom with a proper qualifier (in general, Sy-mm-nn, as C-1-1, C-2-1, etc.). The *Previous* and *Next* buttons enable one to move pages. Click the *Done* button to return to the *Atom Positions* dialog box.



Z-matrix of Atoms

No.	Atom	n2	Bond length	n3	Bond angle	n4	Dihedral angle
1	C-1-1	0	0	0	0	0	0
2	H-1-1	1	1.08	0	0	0	0
3	H-1-2	1	1.08	2	109.47	0	0
4	H-1-3	1	1.08	2	109.47	3	120.0
5	H-1-4	1	1.08	2	109.47	3	-120.0
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

Previous Next Help Done

Figure 5.4. Dialog box *Direct Space Setting*.

(2) In cases when a structure should be constructed using the Z-matrix method, choose the *To be created* option from the *Structure File* field and the *Z-matrix* option from the *Coordinate Format* field and then click the *Create* button. Then the *Z-matrix of Atoms* dialog box opens (*Figure 5.4*). For a molecule with N atoms, one should define N cards defining these real atoms and may also include additional cards defining dummy atoms. The latter are introduced for ease of structure building and are automatically deleted at the end of calculating the coordinates of the real atoms. All real and dummy atoms are defined with the following format:

ATOM n2 r n3 θ *n4* ϕ

The *ATOM* for a dummy atom is ?. In the Z-matrix method, what is important is the atom connectivity, *ATOM-n2-n3-n4*, where the integers *n2*, *n3* and *n4* are the sequential numbers of the atoms (real or dummy) already defined prior to the atom being defined. Let the sequence number of *ATOM* be *n1*. In Chapter 3, the Z-matrix method was discussed in terms of an A1-A2-A3-A4 atoms connection. The atoms A1, A2, A3 and A4 are identified by their sequence numbers *n1*, *n2*, *n3* and *n4*, respectively, so that the atom connectivity is *n1-n2-n3-n4*. *r* is the length of the *n1-n2* bond in Å, θ is the *n1-n2-n3* bond angle in degrees, and ϕ is the dihedral angle in degrees between the *n1-n2* and *n3-n4* bonds using the *n2-n3* bond as the rotational axis. The first atom is placed at the origin so that only *ATOM* needs to be defined. The second atom is placed on the z-axis so that only *ATOM*, *n2* and *r* need to be specified (by definition, *n2* = 1). The third atom is placed on the xz-plane so that only *ATOM*, *n2*, *r*, *n3* and θ need to be defined. From the fourth atom on, all parameters should be specified. After completing the Z-matrix of the atoms, click the *Done* button to return to the *Atom Positions* box.

(3) If the *filename.CI* file for a molecule under consideration already exists, choose the *Already exist* option of the *Structure File* field and click the *Open* button. This opens the *Open* dialog box, which allows the user to locate the *filename.CI* file. Once the user confirms the action of copying the atom positions of this file into a *filename.MI* file being made, then the *Cartesian Coordinates of Atoms* box opens to show the structural information copied into the *filename.MI* file. The user may edit the contents of this box, if necessary.

5.2.2 Advanced parameter-setting for *filename.MI*

In this section we describe the use of the four options of the *Details...* field in *Figure 5.1*, i.e., *Properties*, *Output Options*, *Basis Choices*, and *Method*. The *MC* program sets default values for these computational options. The functions of the four buttons are as follows:

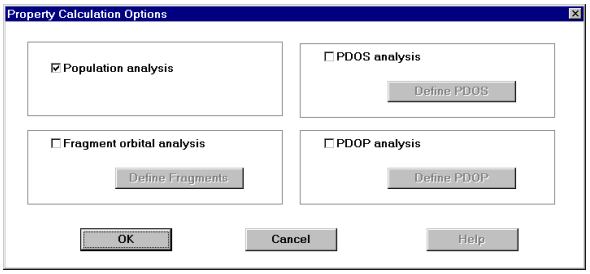


Figure 5.5. Property Calculation Options dialog box.

•*Properties*

The *Properties* button opens the *Property Calculation Options* dialog box (*Figure 5.5*). If the *Population analysis* option is checked, the *MC* program calculates the gross and overlap populations of a molecule. The default is to perform these calculations. Population analysis requires the occupation numbers of the MO's. In the EHTB method they are determined by the total number of valence electrons in a molecule assuming that the molecule adopts the lowest possible spin state.

To perform fragment orbital analysis, check the *Fragment orbital analysis* option. This activates the *Define Fragments* button. When clicked, this button opens the *Define Fragments* dialog box (*Figure 5.6*), which allows one to define fragments of a molecule by choosing the atoms belonging to each fragment from the *Atom List* of the dialog box.

To carry out a PDOS analysis, check the *PDOS analysis* option. This activates the *Define PDOS* button. When clicked, this button opens the *Define Projected Density of States* dialog box (*Figure 5.7*). To define a PDOS, it is necessary to first highlight the atomic orbitals making up the

PDOS from the *AO List* and the *Atom List* fields and then click the *Select* button to send the information to the *AOs in PDOS* field. This procedure may be repeated to define up to five PDOS plots.

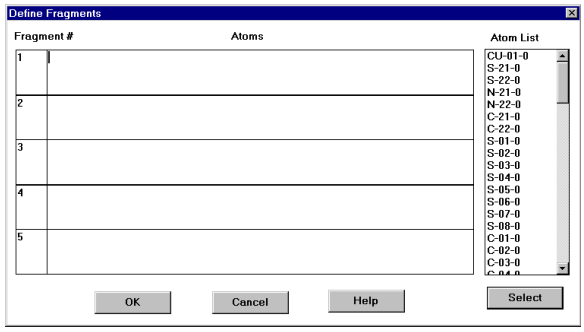


Figure 5.6. Define Fragments dialog box.

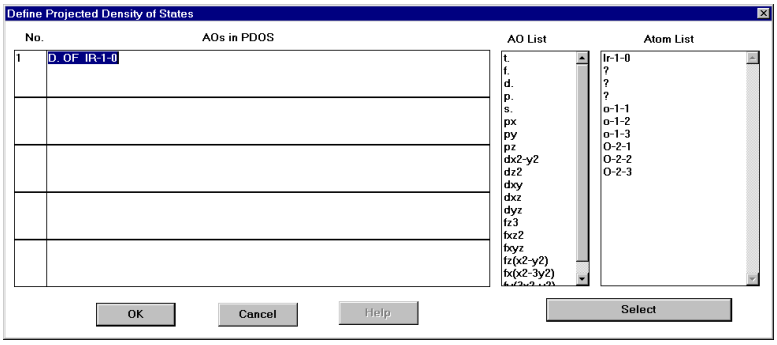


Figure 5.7. Define Projected Density of States dialog box.

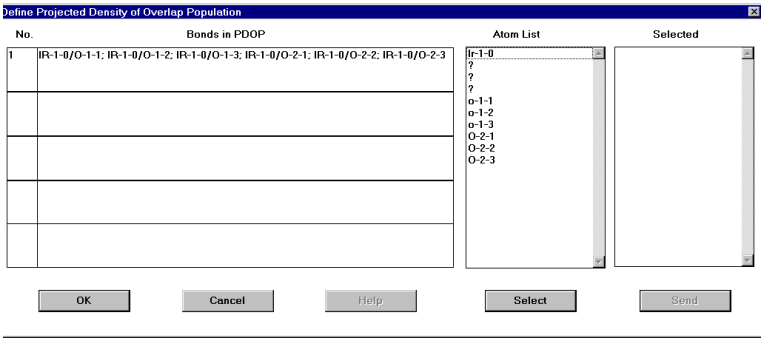


Figure 5.8. Define Projected Density of Overlap Population dialog box.

To perform a PDOP analysis, check the *PDOP analysis* option. This activates the *Define PDOP* button. When clicked, this button opens the *Define Projected Density of Overlap Population* dialog box (*Figure 5.8*). A PDOP may contain a bond or a number of similar bonds. To define a PDOP consisting of many bonds, it is necessary to first highlight the two atoms of each bond belonging to the PDOP from the *Atom List* field and click the *Select* button to send the information to the *Selected* field. When all the bonds of the PDOS are selected, click the *Send* button to send the collected information in

the *Selected* field to the *Bonds in PDOP* field. These procedures may be repeated to define up to five PDOP plots.

•*Output Options*

The *Output Options* button opens the *Output Options* dialog box (*Figure 5.9*). There are three groups of options to consider.

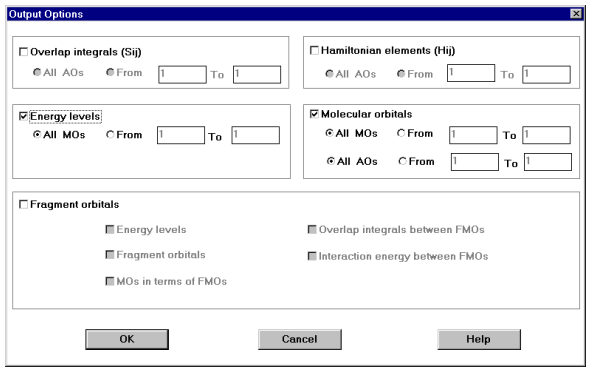


Figure 5.9. Output Options dialog box.

The options *Overlap integrals (Sij)* and *Hamiltonian elements (Hij)* are used to print the matrix elements between atomic orbitals. If the button *All AOs* is checked, the *MC* program prints the whole S_{ij} or H_{ij} matrix. To print only a certain part of the matrix, the range of the atomic orbitals should be selected by giving the sequence numbers of the starting and end atomic orbitals of the chosen range. These numbers are determined first by the atom sequence and then by the orbital sequence within each atom (e.g., s for H; s, x, y, z for non-transition metal elements; x^2-y^2, z^2, xy, xz, yz, s, x, y, z for transition metal atoms) in the file *filename.MI*.

The *Energy levels* and *Molecular orbitals* options control the extent of the output. To print all energy levels of the MO's or a part of them, check the *Energy level* option. To print the MO coefficients, check the *Molecular orbitals* button and specify the range of the MO's and that of the atomic orbitals for each MO chosen. The default is to print all.

Once a fragment orbital analysis is carried out, use the *Fragment orbitals* option to print the fragment orbitals and their energies, the expressions of the MO's in terms of the FMO's, and the values of the overlap and the interaction integrals between FMO's. The default is to print all these outputs.

•*Basis Choice*

The STO basis sets stored in the data base of the *CAESAR* package are automatically copied into the input file *filename.MI* being made. The user can examine them only after completing the *Atom Positions* field. Click the *Basis Choice* button of the *Details...* field to open the *Basis Set Options* dialog box (*Figure 5.10*), which displays the default values of the atomic orbital parameters copied into the input file *filename.MI*. There are three built-in atomic orbital basis sets (i.e., the *CRMM*, *ADF* and *Collected* sets). For most elements, each set has single zeta and double zeta options.

The CRMM set:

For the occupied valence atomic orbitals of the elements from H to U, the CRMM set provides the exponents of the STO's taken from the Hartree-Fock calculations by Clementi and Roetti [1] and by McLean and McLean.[2] The H_{ii} (i.e., VSIP) values of these orbitals were approximated by their orbital energies obtained from the Hartree-Fock calculations. For the unoccupied valence atomic orbitals (e.g., 2p orbitals of Li and Na, 4p orbitals of Ti and V, etc.), for which the Hartree-Fock

calculations do not provide any information, their parameters were taken from the ADF set described below.

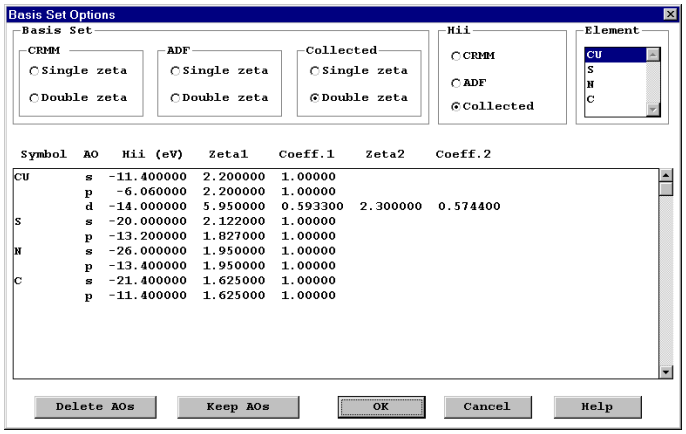


Figure 5.10. Basis Set Options dialog box.

The ADF set:

For the valence atomic orbitals of the elements from H to U, this basis set provides the exponents of the STO's used in the Amsterdam Density Functional (ADF) program package.[3] The H_{ii} values of these orbitals were approximated by their orbital energies calculated from ADF calculations for atoms.

The Collected set:

This provides a collection of the atomic orbital parameters used for EHTB calculations over the years.[4] Parameters are not available for some elements.

A mixture of different basis sets can be used in calculations but not recommended. If the user selects a mixed basis set, a warning massage appears to confirm the user's intention for doing so. The selected basis set is copied into the *filename.MI* file upon clicking the *OK* button.

The default choice for all the elements of a molecule is the *Collected* set. In EHTB calculations for a molecule containing a transition metal or a lanthanide element, it is typical to represent the ns and np orbitals of non-transition metal elements by single zeta STO's, the nd orbitals of the transition metal element by double zeta STO's, the (n+1)s and (n+1)p orbitals of the transition metal elements by single zeta STO's, and the f orbitals of the lanthanide element by double zeta STO's.

To change the basis set for each element of the molecule listed in the *Basis Set Options* dialog box, click the element from the *Element* list, and then select either the single zeta or the double zeta option of the three basis set choices. The VSIP values are automatically adjusted to the selected basis set, and the selected orbital parameters of the element are copied into the *Basis Set Options* dialog box. Repeat this operation for all the elements of the *Element* list. The user can modify the orbital parameters copied into the dialog box by editing. Then the edited parameters will be copied into a *filename.MI* file, when the *OK* button is clicked.

The *Basis Set Options* dialog box provides two other options, *Delete AOs* and *Keep AOs*, which are used to carry out calculations using a subset of the full atomic orbital set. For instance, if the user is interested only in the π-orbital electronic structure of a planar molecule, it is necessary to employ only the p_π atomic orbitals. This can be achieved by keeping only the p_π orbitals using the *Keep AOs* option or by deleting all but the p_π orbitals using the *Delete AOs* option. Click the *Keep AOs* button to open the *Keep AOs in Basis Set* box (*Figure 5.11*), which provides two selection lists, *Atom List* and *Orbitals*. The *Atom List* shows the existing elements in the input file *filename.MI*, and the *Orbitals* list has all possible orbitals. The notations *p.*, *d.* and *f.* refer to all the atomic orbitals within the sub-shells

(e.g., *p*. means x, y and z orbitals; *d*. means x^2-y^2, z^2, xy, xz and yz orbitals). By checking the items in these two lists, atoms and their orbitals can be selected, and the selected ones are shown in the small editing boxes, *Element* and *Orbitals to be kept*. To send the selected items to the drop-down list lying below, click the *Keep* button. The items in the drop-down list can be modified by editing. To copy the selected list into the input file *filename.MI*, click the *OK* button. *Figure 5.11* shows an example in which only the d orbitals of Ni are kept for electronic structure calculations.

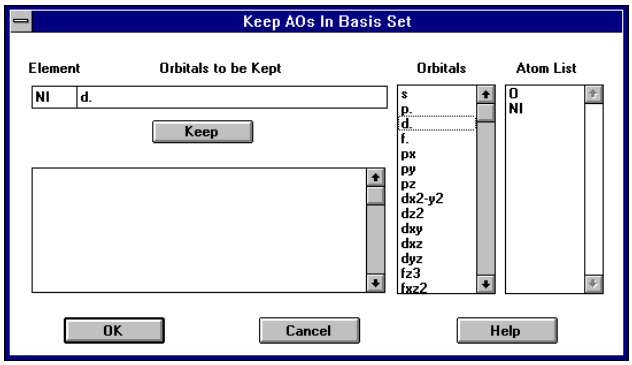


Figure 5.11. Dialog box *Keep AOs in Basis Set*.

If the user checks the *Delete AOs* option, the *Delete AOs From Basis Set* dialog box opens (*Figure 5.12*). The use of this box is similar to that described for the *Keep AOs in Basis Set* box. The difference is that only those not selected are used for electronic structure calculations. *Figure 5.12* shows that the one valence s and the three valence p orbitals of Ni will be deleted from calculations. The selections made in *Figures 5.11* and *5.12* lead to the same result, i.e., only the 4d orbitals of Ni are used in electronic structure calculations. The *Keep AOs* and *Delete AOs* options are exclusive from each other. For example, once the *Keep AOs* option is clicked, is assumed that the *Delete AOs* option will not be used. If the *Delete AOs* button is clicked later, the user will be reminded of the need to avoid it. If the insists on using the *Delete AOs* option, all the atoms and their orbitals selected by using the *Keep AOs* option are deleted from the editing buffer.

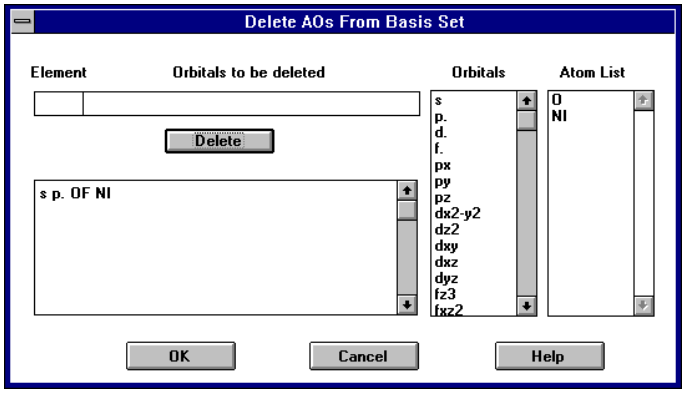


Figure 5.12. Dialog box *Delete AOs From Basis Set*.

•*Method*

The *Method* button opens the *Method* dialog box (*Figure 5.13).* The *Approximation* field allows the user to choose either the *Extended Hückel method* or the *Simple Hückel method*. The default is the

Extended Hückel method. The *Hij Parameters* field allows the user to choose the *Normal Wolfsberg-Helmholz* formula or the *Weighted Wolfsberg-Helmholz* formula for calculating the off-diagonal energy matrix elements $H_{\mu\nu}$.

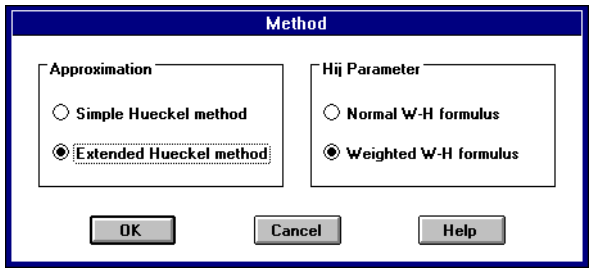


Figure 5.13. Dialog box *Method*.

To save a newly created *filename.MI* file, check the *Save* button of the *New .MI File* box (*Figure 5.1*). This opens the *Save File* dialog box, which allows the user to save it in a proper directory (*Figure 5.14*).

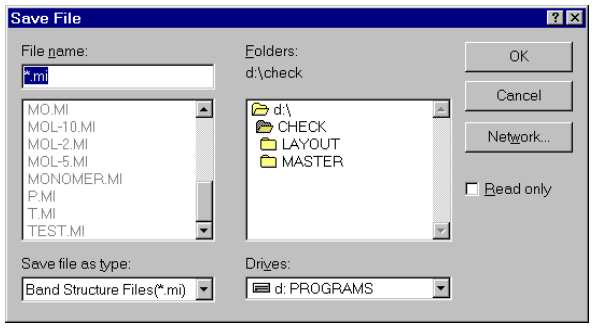


Figure 5.14. Dialog box *Save File*.

5.2.3 Modifying *filename.MI*

It is often convenient to generate a new *filename.MI* file by editing an existing *filename.MI*. This can be achieved by using any text editor or by using the *Modify* command of the *New .MI File* dialog box. When clicked, it opens the *Open* dialog box to allow the user to locate the existing file and copy its contents into the parameter fields of the *New .MI File* dialog box. Then the user can edit the file by going through the appropriate items of the *New .MI File* dialog box where changes have to be made.

5.3 Output file *filename.MO*

MC creates an output file, *filename.MO*, which is a text file. It records the input data, the whole computational process and results, and error messages when run-time errors occur. If there is an error in an input file *filename.MI*, running of *MC* is interrupted, and a brief error message is displayed on screen. Details of this run-time error and the possible remedy are written in *filename.MO*.

5.4 Limitations of *MC*

The dynamic memory management is employed in *MC*. There are a few limitations of *MC*. The maximum number of atoms allowed for a molecule is 500, and that of atomic orbitals is 1,500. The maximum number of fragments of a molecule is 5.

5.5 MO analysis program *MP*

When the *MP* program is loaded, the *MP* window appears with the MO energy level diagram calculated for the molecule (*Figure 5.15*). The *MP* window has several menus that allow the user to analyze and display the results of MO calculations.

It should be noted that the gross and overlap populations can be read interactively only when the screen shows the molecule for which MO calculations were performed using the *MC* program. When the MO levels are displayed on the screen, an MO level can be selected and its energy and atomic orbital coefficients can be read interactively. When the screen displays the FMO levels, one can interactively read the expressions of a selected MO in terms of the FMO's, the energies and the atomic orbital coefficients of the FMO's, and the overlap and interaction energy integrals between FMO's.

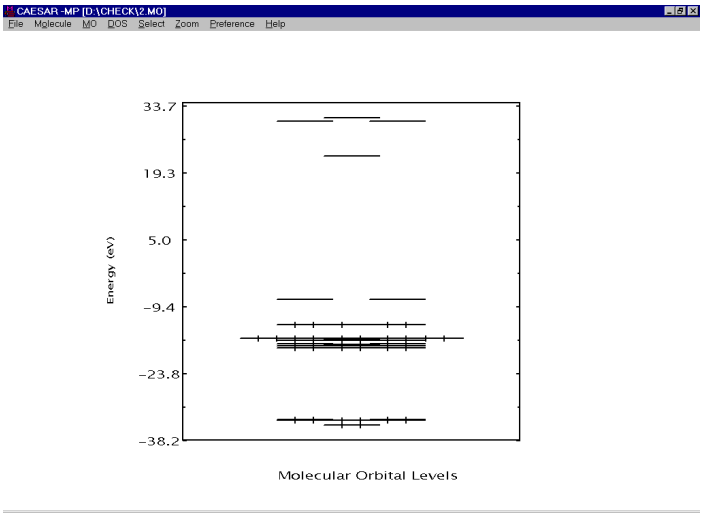


Figure 5.15. Main menu of the *MP* Program.

The menus of the *MP* window have the following functions:

•*File*

This menu is used to load another *filename.MO* file into the *MP* program by using the *Open* option and also to print or save any graphic display on the screen by using the *Print...* option.

•*Molecule*

This menu is used to show and manipulate the structure of a molecule for which a *filename.MO* file is present. The functions of the commands of this menu (*Figure 5.16*) are described below.

Show Molecule:

To display the structure of a molecule on the screen.

Show Fragments:

To highlight the fragments of a molecule.

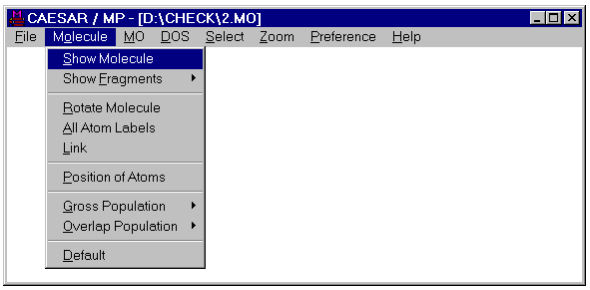


Figure 5.16. Commands of the *Molecule* menu.

Rotate Molecule:
To rotate the structure of a molecule.

All Atom Labels:
To label all the atoms of a molecule.

Link:
To link any two atoms of a molecule with bond, when selected by using the mouse click method.

Position of Atoms:
To display the Cartesian coordinates of the atoms of a molecule on the screen.

Gross Population:
To inspect the gross populations of the atoms.

Overlap Population:
To inspect the overlap populations of the bonds.

Default:
To restore the original structure of a molecule.

•*MO*

This menu facilitates the browsing of the levels and the coefficients of the MO's as well as those of the FMO's. The functions of the commands of this menu (*Figure 5.17*) are described below.

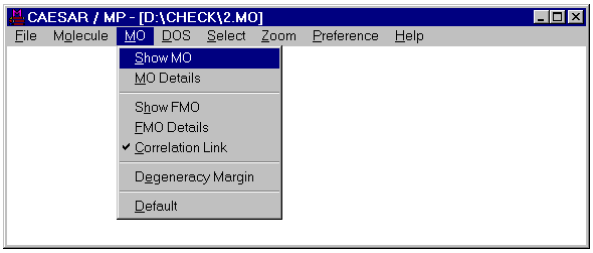


Figure 5.17. Commands of the *MO* menu.

Show MO:
To display the MO energy levels.

MO Details:

To display the atomic orbital coefficients of an MO level selected by using the mouse click method.

Show FMO:
To display the FMO energy levels.

FMO Details:
To display the FMO coefficients of an MO level selected by using the mouse click method.

Correlation Link:
To add or eliminate correlation lines between MO and FMO levels. By default the levels of the FMO's with coefficient not smaller than 0.5 will be linked to the MO level. The threshold value for linking the levels can be modified in the *MO in terms of FMO* dialog box.

Degeneracy Margin:
To change the value of the energy difference between two levels below which the two levels should be considered as degenerate. The default value is 0.0001 eV.

Default:
To restore the original MO levels of a molecule.

•*DOS*

This menu has a number of commands designed to facilitate the presentation of PDOS and PDOP plots. The functions of the commands of this menu (*Figure 5.18*) are described below.

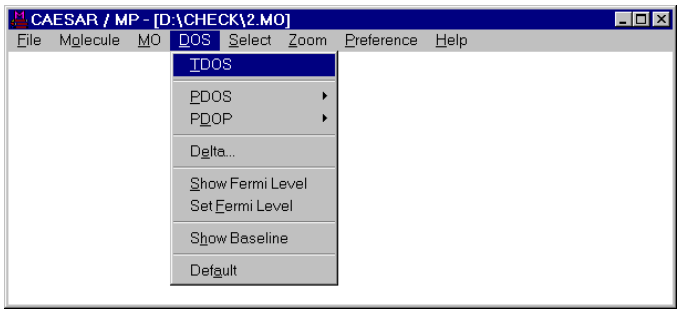


Figure 5.18. Commands of the *DOS* menu.

TDOS:
To display the total DOS plot of a molecule.

PDOS:
To display the PDOS plots of a molecule. This menu opens the drop-down list where the available projections are activated. The user can select an individual plot to display. If several are to be combined, use the *Combined* option to open the *Choose PDOS* dialog box (*Figure 5.19*), from which the user can select more than one plot to display simultaneously.

PDOP:
To display the PDOP plots of a molecule. This menu opens the drop-down list where the available projections are activated. If several are to be combined, use the *Combined* option to open the *Choose PDOP* dialog box (*Figure 5.20*), from which the user can select more than one plot to display simultaneously.

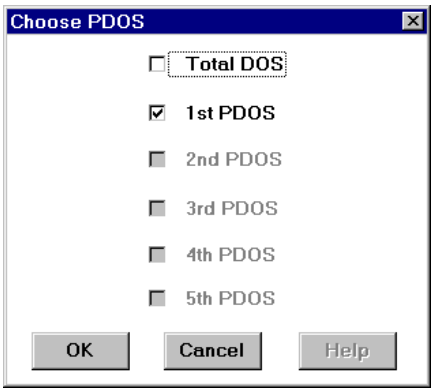


Figure 5.19. Choose PDOS dialog box.

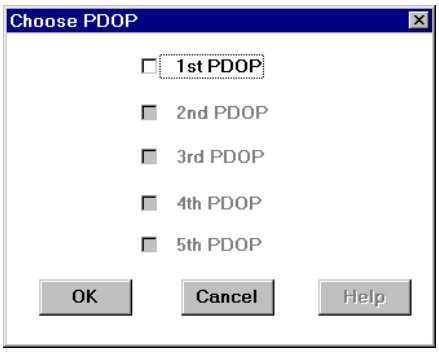


Figure 5.20. Choose PDOP dialog box.

Delta:

To change the value of the gaussian smoothing factor δ. This command opens the *Delta Value* dialog box (*Figure 5.21*), from which the user may choose an appropriate δ value.

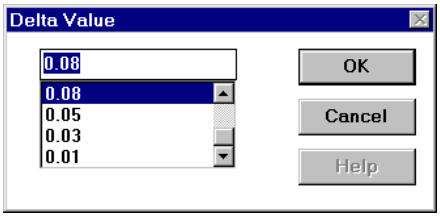


Figure 5.21. Delta Value dialog box.

Show Fermi Level:

To display the HOMO level of a molecule corresponding to its total number of valence electrons.

Set Fermi Level:

To change the HOMO level. This command opens the *Fermi Level* dialog box (*Figure 5.22*), which allows the user to change the HOMO level either in terms of the energy or in terms of the total number of valence electrons.

Show Baseline:

To include a base line in TDOS, PDOS and PDOP plots.

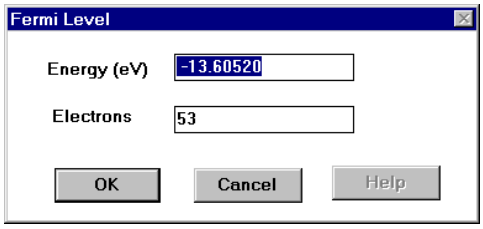


Figure 5.22. Fermi Level dialog box.

Default:

To display a plot on the screen with the default setting.

•*Select*

This menu provides commands by which to select a part of the plot on the screen (e.g., the molecular structure, the MO level diagrams, and the TDOS, PDOS and PDOP plots). The functions of the commands of this menu (*Figure 5.23*) are described below. The command *Customize...* is not applicable for the selection of the molecule.

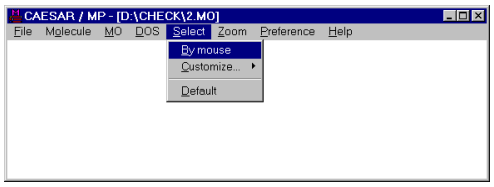


Figure 5.23. Commands of the *Select* menu.

By Mouse:

To select a part of the plot on the screen by using the mouse.

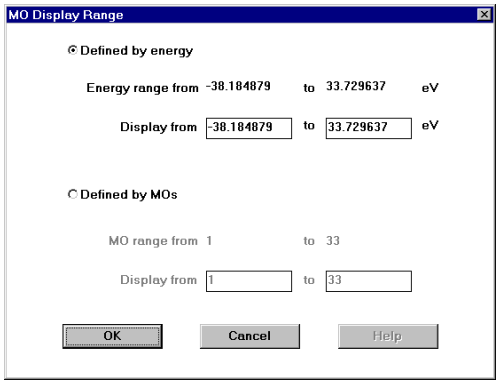


Figure 5.24. MO Display Range dialog box.

Customize:

To select a part of the plot on the screen by specifying the values for the plot ranges. This command has the drop-down list consisting of two items, *MO*... and *PDOS/PDOP*.... The former opens the *MO Display Range* dialog box (*Figure 5.24*), and the latter the *PDOS/PDOP Display Range* dialog box (*Figure 5.25*).

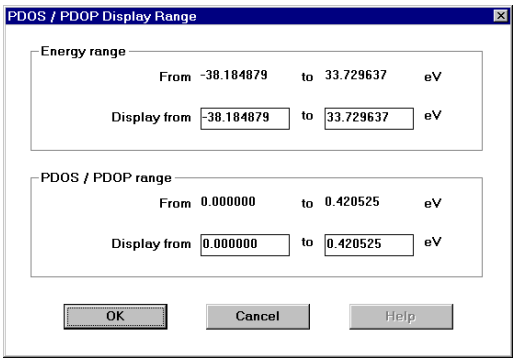


Figure 5.25. PDOS/PDOP Display Range dialog box.

Default:

To display a plot on the screen with the default setting.

•*Zoom*

This menu has several commands by which to zoom-in or zoom-out a graphic display on the screen. The functions of the commands of this menu (*Figure 5.26*) are described below.

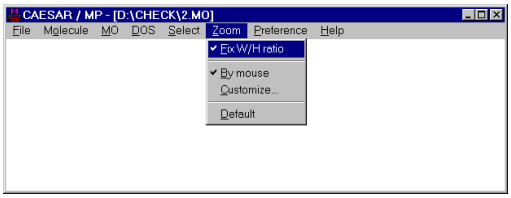


Figure 5.26. Commands of the *Zoom* menu.

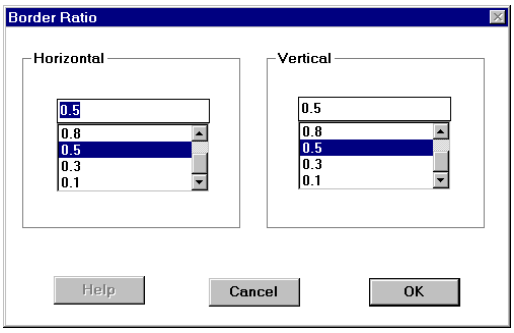


Figure 5.27. Border Ratio dialog box.

Fix W/H ratio:

When checked by clicking, this command fixes the width-to-height ratio of the zooming operation.

By Mouse:

To zoom by using the mouse.

Customize:

To zoom by specifying the relative values for the zooming. This command opens the *Border Ratio* dialog box (*Figure 5.27*) if the *Fix W/H ratio* command is not checked, and the *Zoom Ratio* dialog box (*Figure 5.28*) if the *Fix W/H ratio* command is checked.

Default:

To display a plot on the screen with the default setting.

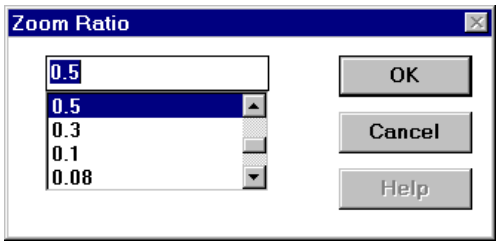


Figure 5.28. Zoom Ratio dialog box.

•*Preference*

This menu provides commands for changing a graphic display of a diagram on the screen. The functions of the commands of this menu (*Figure 5.29*) are described below.

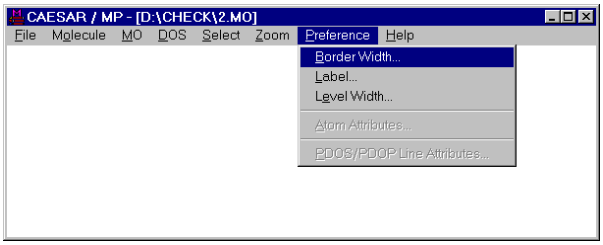


Figure 5.29. Commands of the *Preference* menu.

Border Width:

To change the width of the border lines of a diagram on the screen. This command opens the *Border Width* dialog *box (Figure 5.30*).

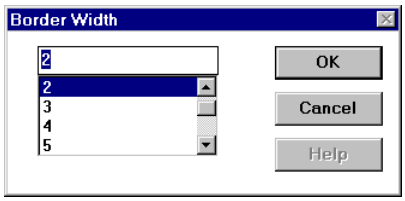


Figure 5.30. Border Width dialog box.

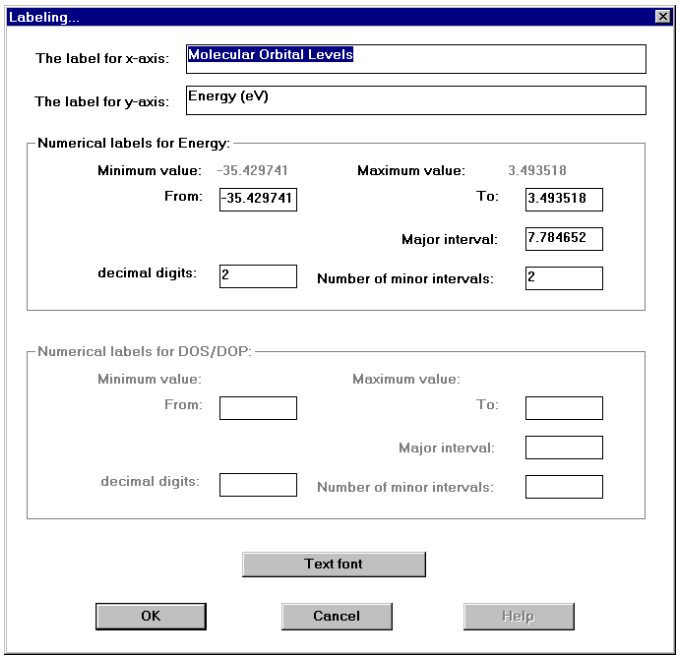


Figure 5.31. Labeling... dialog box.

Label:

To change the labels of a diagram on the screen. This command opens the *Labeling...* dialog box (*Figure 5.31*).

Level Width:

To change the width of the levels of a MO diagram on the screen. This command opens the *Level Width...* dialog box (*Figure 5.32*)..

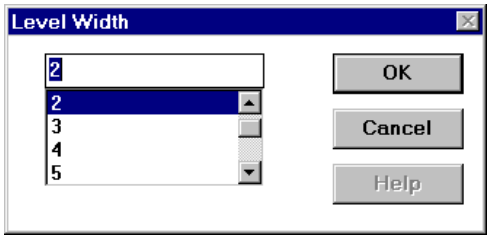


Figure 5.32. Atom Attributes dialog box.

Atom attributes:

To change the attributes of the atoms of a molecule. This command opens the *Atom Attributes* dialog box (*Figure 5.33*), which allows the user to change how each atom appears on the screen. An atom of each element is represented as a circle with a specific color and a predefined radius. The colors of elements are defined by three integers of the RGB format. The line width of the circle boundary can be defined by an integer in a relative scale. The atom radius, which determines the circle size shown on the screen, is specified in Ångstroms. The product of the atom radius multiplied by the connection factor works as a formal radius of the element. Two atoms are shown as linked when the distance between them is shorter than the sum of the formal radii of the two atoms.

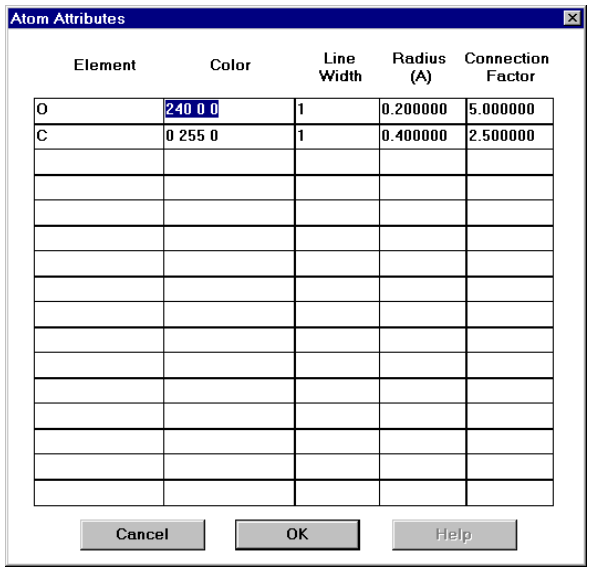


Figure 5.33. Atom Attributes dialog box.

PDOS/PDOP Line Attributes:

To change the line shapes of the curves representing the PDOS and PDOP plots. This command opens the *Curve Attributes* dialog box (*Figure 5.34*).

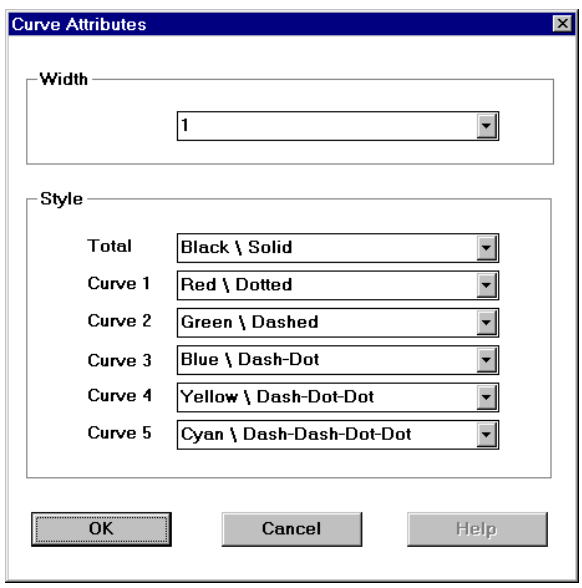


Figure 5.34. Curve Attributes dialog box.

5.6 Examples

5.6.1 Interaction between donor molecules in the $(BEDT\text{-}TSF)_2KHg(SCN)_4$ salt

Figure 5.35 shows a perspective view of the unit cell of the organic conducting salt $(BEDT\text{-}TSF)_2KHg(SCN)_4$ [5] using the *khg.CI* file from the CAESAR\Examples\Chapter5\BETS directory.

Here BEDT-TSF is derived from BEDT-TTF by replacing the S atoms of the TTF moiety with Se atoms (see *Figure 8.20*). With the oxidation states of K^+, Hg^{2+}, and SCN^-, the average oxidation state of each donor molecule +0.5. Namely, every two BEDT-TSF molecules lose an electron to the monovalent anion unit $KHg(SCN)_4^-$, so that the salt can be written as $[(BEDT\text{-}TSF)_2]^+[KHg(SCN)_4]^-$. The crystal structure has a layer of donor molecules BEDT-TSF alternate with a layer of the anion units $KHg(SCN)_4$ along the b-axis direction. Because of the oxidation state $BEDT\text{-}TSF^{0.5+}$, the highest occupied band of each donor molecule layer, which is largely made up of the HOMO's of the donor molecules, becomes partially empty. This is responsible for the metallic character of this salt.

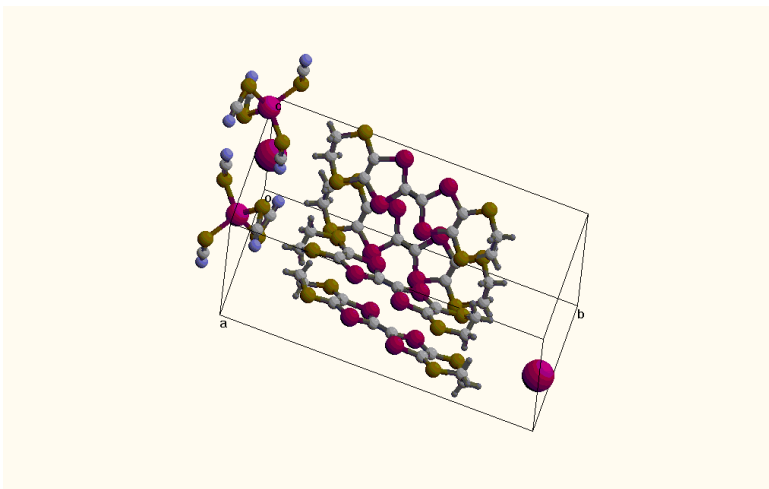


Figure 5.35. Perspective view of the unit cell of $(BEDT\text{-}TSF)_2$ $KHg(SCN)_4$.

In understanding the nature of the partially filled HOMO band of such a salt (see Chapter 6), it is often informative to examine how strongly the nearest neighbor donor molecules A and B interact within the donor molecule layer. The strength of this interaction can be measured by calculating the HOMO-HOMO overlap integral $\tilde{S}_{AB}$ and the HOMO-HOMO interaction energy $\tilde{H}_{AB}$

$$\tilde{S}_{AB} = \langle \psi^A | \psi^B \rangle \tag{5.1}$$

$$\tilde{H}_{AB} = \langle \psi^A | H^{eff} | \psi^B \rangle \tag{5.2}$$

where ψ^A and ψ^B refer to the HOMO's of the molecule A and B, respectively. The $\tilde{S}_{AB}$ and $\tilde{H}_{AB}$ values can be obtained by performing MO calculations for the dimer A-B and then FMO calculations using the molecules A and B as fragments.

To find all unique nearest-neighbors A and B in the donor layer, delete the anion units $KHg(SCN)_4$ from the structure, rotate the remaining donor layer structure such that the donor molecules are projected approximately along their central C=C bonds, and extend the structure (*Figure 5.36*). Save this structure file as *khg-e.CI*. From such an extended view, the user may select any nearest-neighbor dimer and save it as *khg-2.CI*.

We now illustrate how to carry out MO and FMO calculations for the dimer unit stored in *khg-2.CI*.

(1) To make the input *khg-2.MI*, first launch the *NEWMI* program to open the *New .MI* dialog box, click the *Atom Positions* button to copy the atom positions of the *khg-2.CI* file into the atom position field of the *khg-2.MI* file being made.

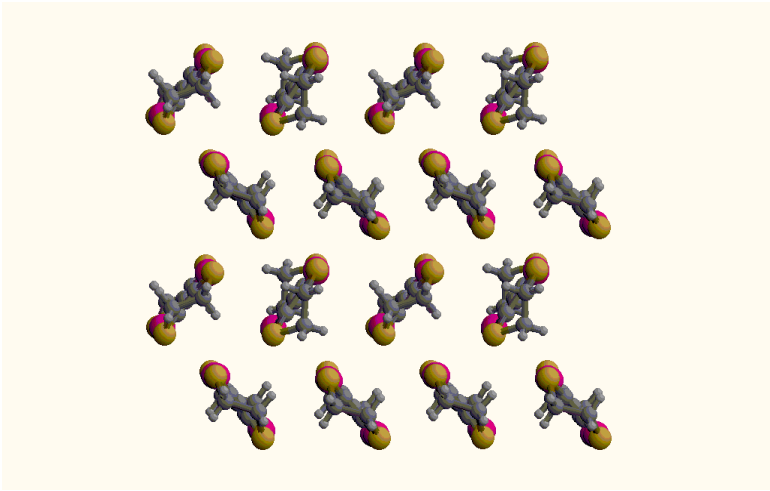


Figure 5.36. Projection view of a donor molecule layer of (BEDT-TSF)$_2$KHg(SCN)$_4$ approximately along the central C=C bond of the donor molecule.

(2) Then click the *Properties* button of the *Details...* field to open the *Property Calculation Options* box, and check the *Fragment orbital analysis* option and click the *Define Fragments* button to open the *Define Fragments* box. Define each fragment by choosing all the atoms belonging to the fragment and then clicking the select button and return to the *New .MI* dialog box.

(3) The *Output Options* button of the *Details...* field will let the user open the *Output Options* box, which is used to limit the extent of outputs. Make sure that the *Fragment orbitals* option and its associated options are properly checked (*Figure 5.37*) and return to the *New .MI* dialog box.

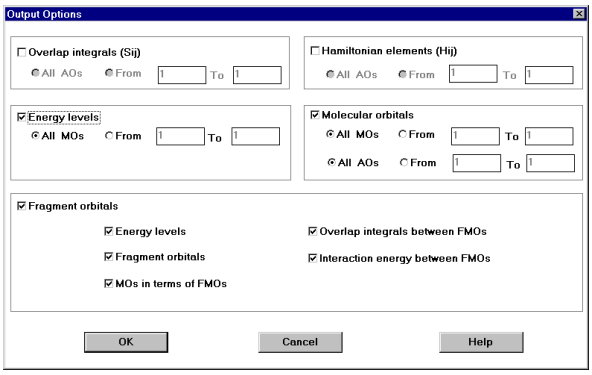


Figure 5.37. Output Options dialog box.

(4) Then click the *Basis Choice* button to open the *Basis Set Options* box (*Figure 5.38*), and then choose a proper basis set for each element. For all the elements (H, C, S and Se) of BEDT-TSF, the default is the single zeta STO from the *Collected set*. The overlap between molecules is largely determined by the diffuse atomic orbitals. To emphasize such overlap, the user might choose the

double-zeta STO's for the C, S and Se atoms of BEDT-TSF. In *Figure 5.38*, the *CRMM* double-zeta STO's are selected for the C, S and Se atoms. Return to the *New .MI* dialog box.

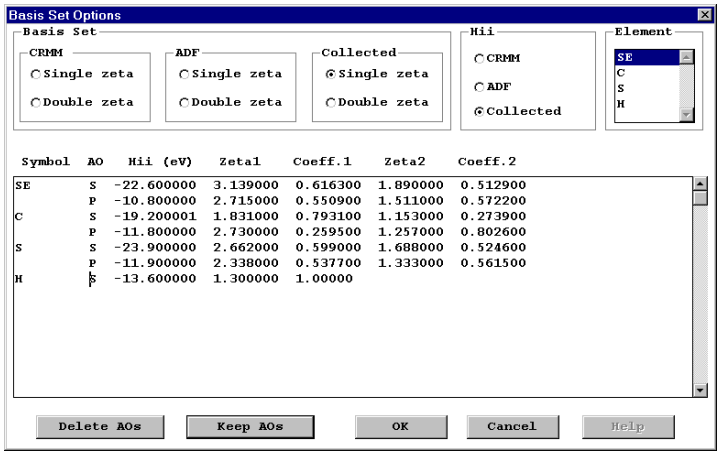


Figure 5.38. Basis Set Options dialog box.

(5) Save the resulting file as *khg-2.MI*. Then run the *MC* program with the *khg-2.MI* file as input. This generates the output file, *khg-2.MO*.

Before inspecting the results of the above MO calculations, it is important to do electron and orbital counting. The BEDT-TSF molecule has 96 valence electrons and 80 valence atomic orbitals. Thus the $(BEDT\text{-}TSF)_2$ dimer has 96 doubly occupied MO's out of 160 MO's. In a molecular crystal, the interactions between adjacent molecules are generally weak. Therefore, the main contributor to the highest two occupied MO's of the dimer (i.e., the MO #95 and #96) is expected to be the HOMO (i.e., the MO #48) of each fragment, i.e., BEDT-TTF.

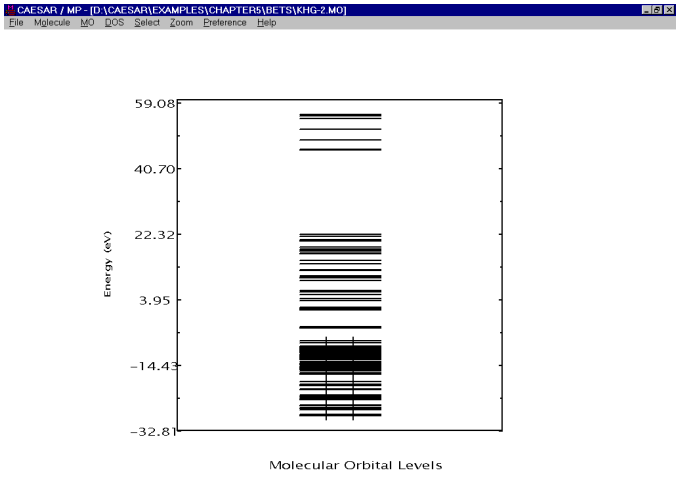


Figure 5.39. MP window with all MO levels.

To analyze the results of the MO calculations, run the *MP* program with the *khg-2.MO* file as input. This opens the *MP* window with the MO level diagram in which all calculated levels are shown (*Figure 5.39*). This diagram is too crowded to extract any useful information. The user may select the

region of this diagram around the highest occupied levels by activating the *By mouse* command of the *Select* menu and then using the mouse drag method. This method can be repeated until a suitable diagram is obtained, as in *Figure 5.40*. This shows that the highest two occupied MO's of the dimer are reasonably well separated from other occupied MO's lying below.

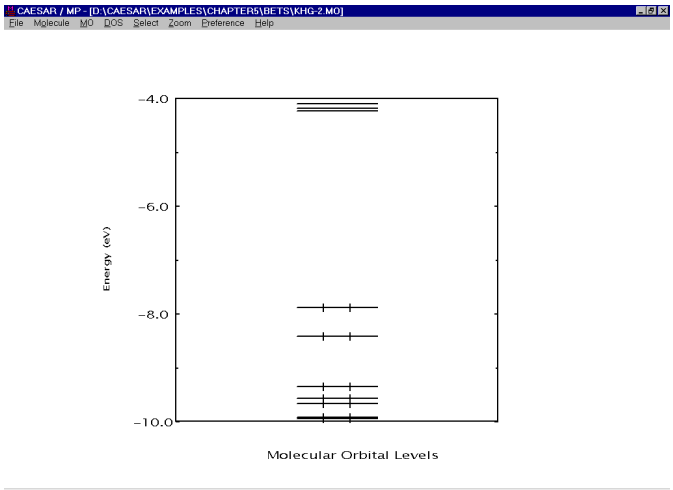


Figure 5.40. MP window with selected MO levels.

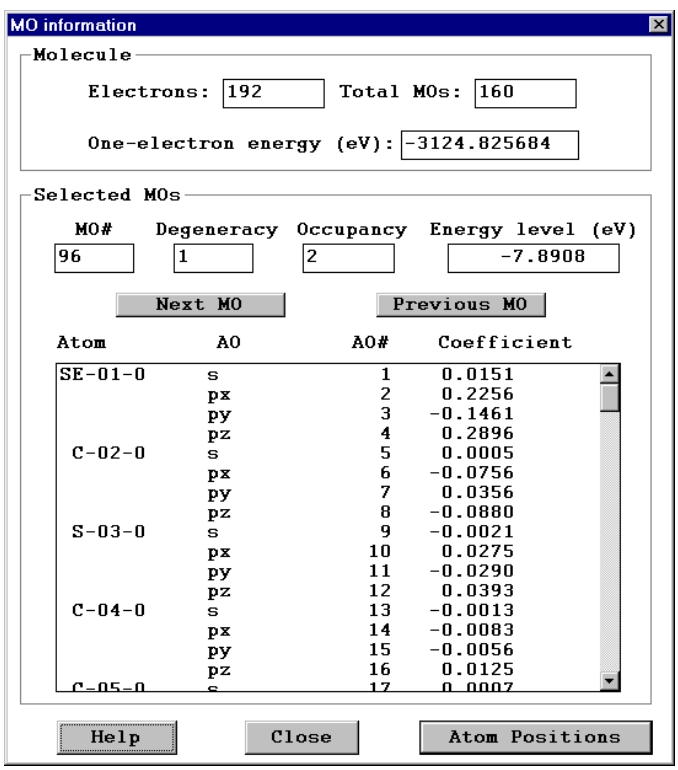


Figure 5.41. MO Information dialog box.

To see the details of an MO (e.g., the HOMO of the dimer), click the *MO Details* command, which changes the mouse cursor into a cross, and click that MO level on the diagram. This opens the

MO information box (*Figure 5.41*), where the *Molecule* field provides information about the total number of electrons, that of MO's, and the total energy of the molecule for its lowest possible spin state. The *Selected MOs* field provides information about the sequence number, the degeneracy, the occupancy and the atomic orbital coefficients of a chosen MO. The *Next MO* and *Previous MO* buttons of this field allows the user to browse through the details about other MO's. From *Figure 5.41*, the HOMO of the dimer (i.e., the MO #96) is -7.89 eV. One can easily find by using the *Previous MO* button that the energy of the MO #95 is -8.42 eV. Thus, the energy split ΔE between the two highest occupied MO's of the dimer is ΔE = 0.53 eV.

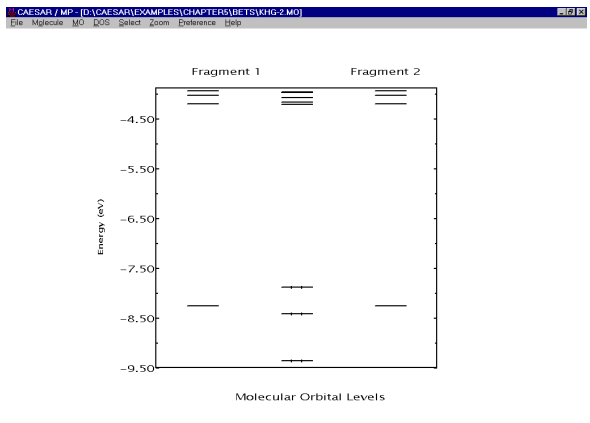


Figure 5.42. MP window with selected MO/FMO levels.

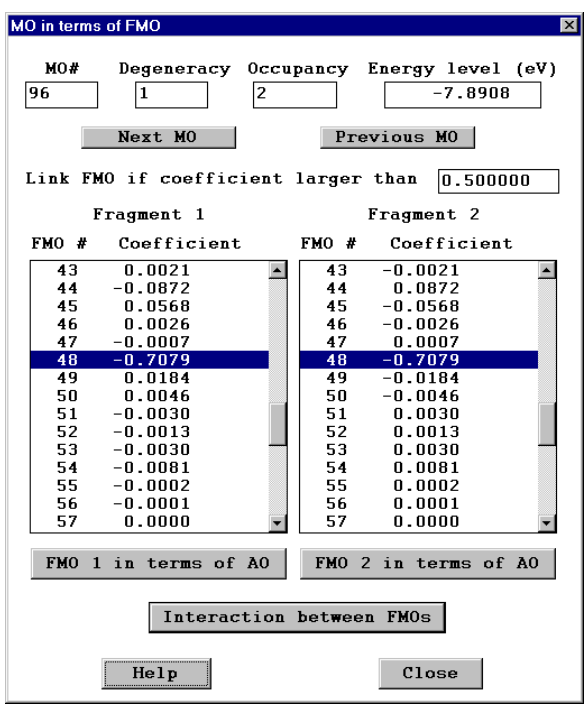


Figure 5.43. MO in terms of FMO dialog box.

To examine the HOMO of the dimer in terms of the MO's of its fragments (i.e., the FMO's), select the *Show FMO* command to display the FMO levels on either side of the MO energy levels

(*Figure 5.42*). To see the details of the FMO analysis for the HOMO of the dimer, click the *FMO Details* command and click that level on the screen to open the *MO in terms of FMO* box (*Figure 5.43*). This box shows the coefficients of the FMO's making up the selected MO. The *Next MO* and *Previous MO* buttons can be used to inspect the coefficients of the FMO's making up other MO's. By using the scroll bar, it is found that the FMO #48 of each fragment (namely, the HOMO of BEDT-TSF) is the primary contributor to the HOMO of the dimer (*Figure 5.43*). To find the $\tilde{S}_{AB}$ and $\tilde{H}_{AB}$ values, highlight the FMO #48 of each fragment as in *Figure 5.43* and then click the *Interaction between FMOs* button. This opens the *Interaction between FMOs* box (*Figure 5.44*), which shows that $\tilde{S}_{AB}$ = -0.025 and $\tilde{H}_{AB}$ = 0.45 eV.

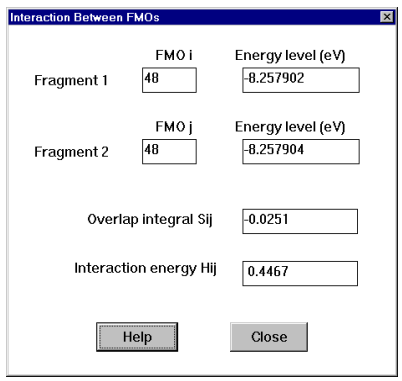


Figure 5.44. Interaction between FMOs dialog box.

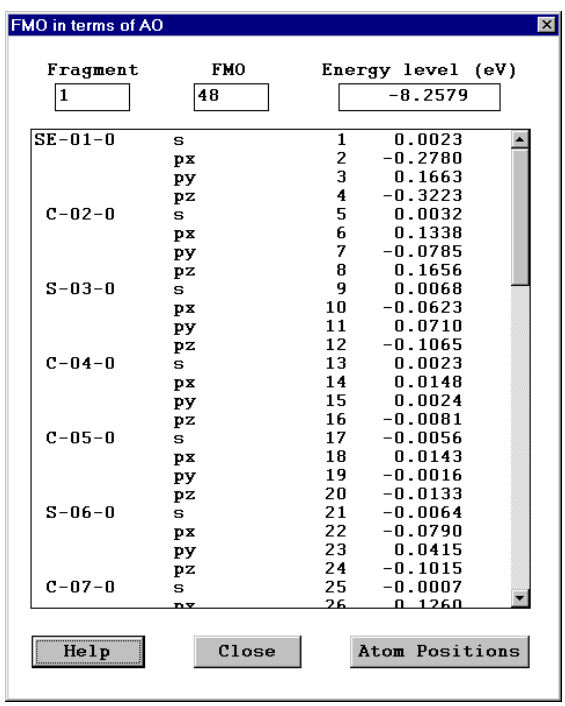


Figure 5.45. FMO in terms of AO dialog box.

The atomic orbital coefficients of a selected FMO can be inspected from the *FMO in terms of AO* box (*Figure 5.45*), which opens by clicking the appropriate button (either *FMO 1 in terms of AO* or

FMO 2 in terms of AO) in the *MO in terms of FMO* box. On returning to the *MP* window, the FMO levels making up the MO are linked when their coefficients are larger than 0.5 in magnitude. However, this number can be changed by the user in the *MO in terms of FMO* box.

5.6.2 Oxidation state of Au in $(Et_4N)_4Au_2Te_{12}$

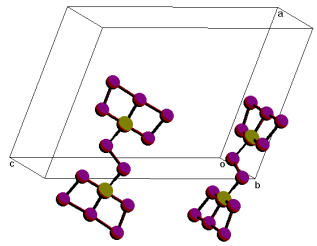


Figure 5.46. Perspective view of two $[Au_2Te_{12}]^{4-}$ anions.

This compound has two $[Au_2Te_{12}]^{4-}$ anions per unit cell [6] as shown in *Figure 5.46*, which was obtained using the *AuTe.CI* file in the CAESAR\Examples\Chapter5\Au2Te12 directory. (For convenience, the Et_4N^+ cations are not shown.) This $[Au_2Te_{12}]^{4-}$ anion consists of two Au atoms, one Te_2, and two Te_5 units, with each Au atom in a square-planar coordinate. Thus the oxidation state of Au is often regarded as Au^{3+} (d^8), which leads to the electron counting $[Au^{3+}]_2[(Te_2)^{2-}][(Te_5)^{4-}]_2$ for the anion $[Au_2Te_{12}]^{4-}$. The ionic electron counting scheme based on the oxidation state was formulated under the implicit assumption that in a compound of a transition metal element, the d-orbitals of the transition metal lie much higher than the p-orbitals of its ligands. The validity of this assumption is questionable for compounds of late transition metal atoms (e.g., Cu, Ag and Au) with weakly electronegative ligands (e.g., S, Se, Te, Br and I). Indeed, in $AuTe_2$ which has both two-coordinate and four-coordinate Au atoms at the extremes of its structural modulation, all Au atoms are monovalent (i.e., Au^+).[7,8] In $Cs_2Au_2I_6$ which consists of two-coordinate and four-coordinate Au atoms, all Au atoms are monovalent.[9,10] Therefore, it is probable that the Au atoms of $(Et_4N)_4KAuAs_4Te_8$,[11] $(Et_4N)_3AuTe_7$,[12] and $(Et_4N)_4Au_2Te_{12}$ [6] should also be regarded as monovalent.

Let us now consider the most likely oxidation state of Au in the $[Au_2Te_{12}]^{4-}$ anion by carrying out MO calculations. For this purpose, we select one anion from the structure of *Figure 5.46* and save it as *AuTe-h.CI*. In addition, we delete the two "Au^{3+}" cations of the $[Au_2Te_{12}]^{4-}$ anion to make the hypothetical $[Te_{12}]^{10-}$ anion and save the resulting structure as *AuTe-Te.CI*. By comparing the charge distributions of the $[Au_2Te_{12}]^{4-}$ anion with those of the $[Te_{12}]^{10-}$ anion, it would be possible to gain insight into the nature of charge redistribution that might occur when the "Au^{3+}" cations interact with the "$[Te_{12}]^{10-}$" anion. For this purpose, we compare gross and overlap populations in the $[Au_2Te_{12}]^{4-}$ and $[Te_{12}]^{10-}$ anions.

The input files *AuTe-h.MI* and *AuTe-Te.MI* needed for the MO calculations for the $[Au_2Te_{12}]^{4-}$ and $[Te_{12}]^{10-}$ anions, respectively, can be easily generated by using the *AuTe-h.CI* and *AuTe-Te.CI*

files. Running the *MC* program with these inputs produce the output files *AuTe-h.MO* and *AuTe-Te.MO*. We now examine these results by running the *MP* program.

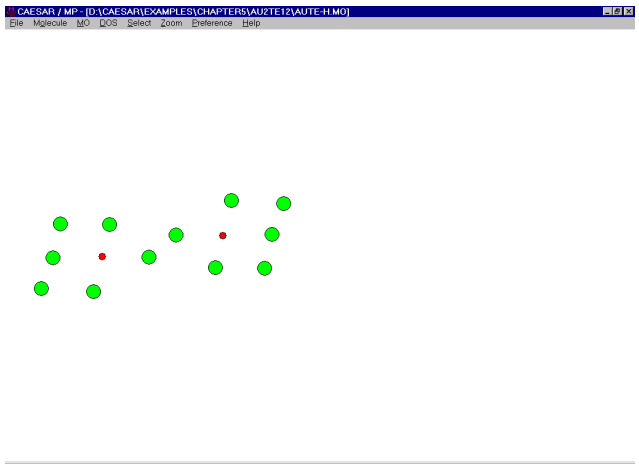


Figure 5.47. MP window with the $[Au_2Te_{12}]^{4-}$ anion structure.

When the *MP* program is loaded with the *AuTe-h.MO* file, the *MP* widow appears with the MO level diagrams. Then click the *Show Molecule* command of the *Molecule* menu. Then the structure of the $[Au_2Te_{12}]^{4-}$ anion appears on the left half of the screen (*Figure 5.47*). After activating the *Rotate Molecule* command, the user can rotate the molecule by dragging the mouse cursor on the screen. By labeling all atoms, the user can find that there are six non-equivalent Te atoms, i.e., Te(1), Te(2), Te(3), Te(4), Te(5) and Te(6), and that the two Au atoms are equivalent, i.e., Au(1). The atom connectivity of the Te_2 unit is given by Te(1)-Te(1), and that of the Te_5 units by Te(2)-Te(3)-Te(4)-Te(5)-Te(6). The Au(1) atom is surrounded by the Te(1), Te(2), Te(4) and Te(6) atoms forming a nearly square-planar $AuTe_4$ unit.

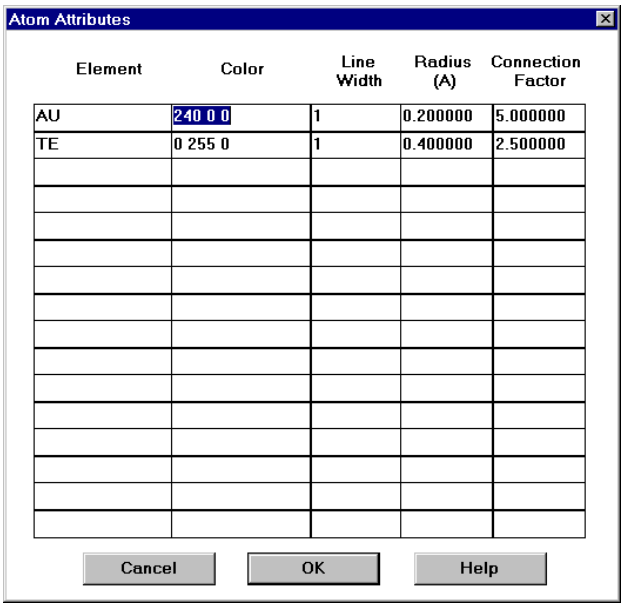


Figure 5.48. Atom Attributes dialog box.

The Te atoms do not appear bonded in the structure of *Figure 5.47*. To make bond connections, the user may activate the *Link* command of the *Molecule* menu and then click every two atoms to be connected. Alternatively, the user may click the *Atom Attributes* command of the *Preference* menu to open the *Atom Attributes* box (*Figure 5.48*). By changing the values for *Radius* and *Connection Factor*, a desired bond connectivity can be achieved. Note that the color for the circle representing an atom is determined by three integers.

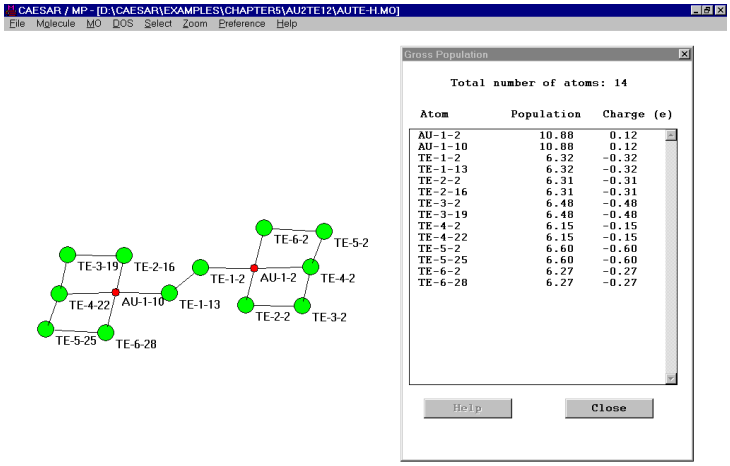


Figure 5.49. Gross Population dialog box.

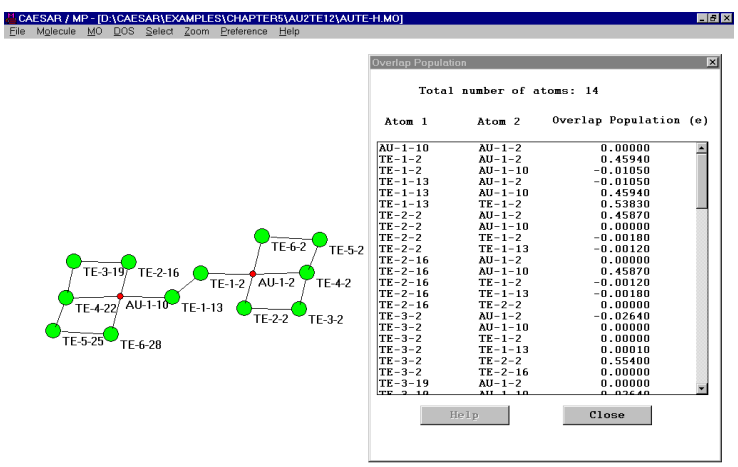


Figure 5.50. Overlap Population dialog box.

To inspect the gross populations of the atoms of the $[Au_2Te_{12}]^{4-}$ anion on the screen, use the *All Atoms...* option of the *Gross Population* command to open the *Gross Population* box (*Figure 5.49*), where the gross populations and the net charges of all the atoms are listed. If the user employs the *Select...* option, the *Gross Population* box opens without any content. As the user selects an atom on the screen by clicking, its gross population and net charge appear on the *Gross Population* box. In a

similar manner, the overlap populations of the bonds in the $[Au_2Te_{12}]^{4-}$ anion can be inspected by using the *All Bonds...* option of the *Overlap Population* command, which opens the *Overlap Population* box (*Figure 5.50*). Alternatively, the user may use the *Select...* option to open the *Overlap Population* box without any content. As the user selects two atoms on the screen by clicking, their overlap population appears on the *Overlap Population* box.

The net charges of the atoms and overlap populations of the bonds in the $[Au_2Te_{12}]^{4-}$ anion are summarized in Table 5.1. By applying the same procedures for the $[Te_{12}]^{10-}$ anion, one can find the net charges and overlap populations of this anion as summarized in Table 5.1. Important points to note from this Table are as follows:

(a) The overlap populations of the Te(1)-Te(1), Te(2)-Te(3), Te(3)-Te(4), Te(4)-Te(5) and Te(5)-Te(6) bonds of the $[Au_2Te_{12}]^{4-}$ anion are very similar to those of the $[Te_{12}]^{10-}$ anion, respectively.

(b) The net charges of the Te(3) and Te(5) atoms, not coordinated to the Au(1) atoms, of the $[Au_2Te_{12}]^{4-}$ anion are very similar to those of the $[Te_{12}]^{10-}$ anions, respectively.

(c) The net charges of the Te(1), Te(2) and Te(4) atoms, coordinated to the Au(1) atoms, of the $[Au_2Te_{12}]^{4-}$ anion are significantly reduced (by about 0.7 electron per Te) from those of the $[Te_{12}]^{10-}$ anions, respectively.

Table 5.1. Net charges and overlap populations calculated for the $[Au_2Te_{12}]^{4-}$ and $[Te_{12}]^{10-}$ ions

(a) Net charge

Atom	$[Au_2Te_{12}]^{4-}$	$[Te_{12}]^{10-}$
Au(1)	+0.12	-
Te(1)	-0.32	-0.98
Te(2)	-0.31	-0.99
Te(3)	-0.48	-0.50
Te(4)	-0.15	-0.90
Te(5)	-0.60	-0.64
Te(6)	-0.27	-0.98

(b) Overlap population

Bond	Length (Å)	$[Au_2Te_{12}]^{4-}$	$[Te_{12}]^{10-}$
Au(1)-Te(1)	2.630	0.46	-
Au(1)-Te(2)	2.649	0.46	-
Au(1)-Te(3)	2.624	0.50	-
Au(1)-Te(4)	2.661	0.41	-
Te(1)-Te(1)	2.747	0.54	0.49
Te(2)-Te(3)	2.746	0.55	0.51
Te(3)-Te(4)	2.983	0.23	0.21
Te(4)-Te(5)	3.044	0.14	0.11
Te(5)-Te(6)	2.740	0.56	0.51

Therefore, from the viewpoint of the interaction between the Au^{3+} and $[Te_{12}]^{10-}$ ions, each "Au^{3+}" ion of the $[Au_2Te_{12}]^{4-}$ anion receives about 2.8 electrons from the Te atoms directly coordinated with it. Therefore, the most reasonable oxidation state of Au in the $[Au_2Te_{12}]^{4-}$ anion is Au^+ (d^{10}), i.e., all the d-block levels of Au are completely filled in this anion.

To explore the above finding further, it is necessary to examine where the d-block levels of Au lie in the energy spectrum of the $[Au_2Te_{12}]^{4-}$ anion. For this purpose, it is convenient to examine the

TDOS plot for the $[Au_2Te_{12}]^{4-}$ anion and the PDOS plot for the d-orbitals of the Au atoms. *Figure 5.51* presents such a plot calculated for the $[Au_2Te_{12}]^{4-}$ anion, where the TDOS is represented by a solid line, and the PDOS of the Au d-orbitals by a dashed line. It is clear that the d-block levels of the Au atoms lie well below the Fermi level, i.e., the highest occupied level of the $[Au_2Te_{12}]^{4-}$ anion.

Obviously, the observation reflects the fact that the 5d-level of Au lies considerably lower than the 5p-level of Te. (Namely, -17.6 vs. -9.73 eV in the *CRMM Basis set*, -14.27 vs. -9.79 eV in the *ADF Basis set*, and -15.08 vs. -13.2 eV in the *Collected Basis set*.) The present calculation is based on the *Collected Basis set*, which provides the smallest energy difference between the Au 5d and the Te 5p levels. The user may repeat calculations after decreasing this energy difference further (by either raising the Te 5p level or lowering the Au 5d level). For any reasonable variation of the VSIP values of the Au 5d and the Te 5p levels, the user will find that the above observation remains unchanged. Thus, with some confidence, we may conclude that not only in the $[Au_2Te_{12}]^{4-}$ anion but also in other binary compounds of Au and Te, the Au atoms should be monovalent.

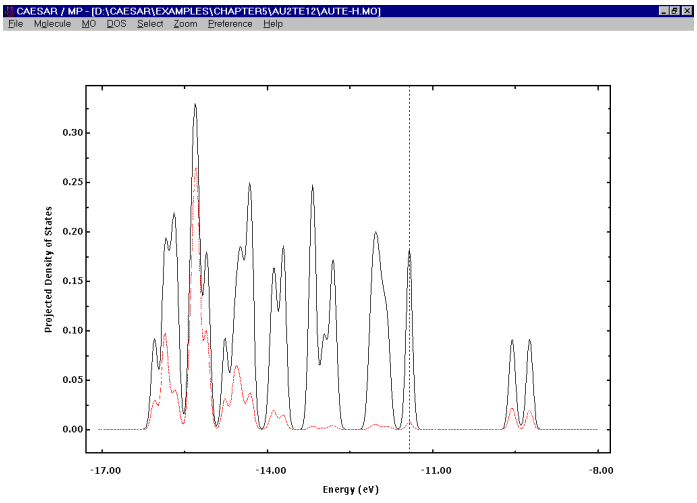


Figure 5.51. DOS and PDOS plots for $[Au_2Te_{12}]^{4-}$ anion.

5.6.3 Magnetic interactions between the V^{4+} ions in $[H_2N(CH_2)_4NH_2]V_4O_9$

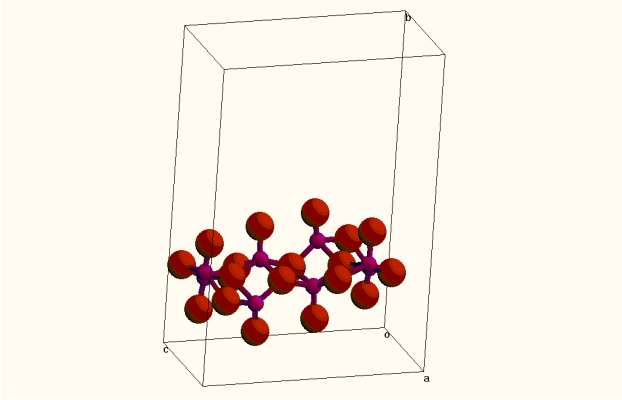


Figure 5.52. Unit cell view of one layer of $[H_2N(CH_2)_4NH_2]V_4O_9$.

The $[H_2N(CH_2)_4NH_2]V_4O_9$ salt has two equivalent $[V_4O_9]^{2-}$ layers per unit cell.[13] *Figure 5.52* shows a perspective view of one $[V_4O_9]^{2-}$ layer, which was obtained by using the *v4-o.CI* file in the CAESAR\Examples\Chapter5\AV4O9 directory. This layer has four different vanadium atoms V(1), V(2), V(3) and V(4), each V atom is in a square-pyramidal coordinate, and the bond valence sum analysis [14] for each VO_5 unit shows that the oxidation state of each V atom is V^{4+} (d^1).

The magnetic susceptibility-versus-temperature (χ-vs.-T) curve for the $[H_2N(CH_2)_4NH_2]$ V_4O_9 salt (*Figure 5.53*) shows that the spins of the V^{4+} ions interact antiferromagnetically. The χ-vs.-T plot has a maximum at 30 K (i.e., χ_{max} = 0.011 emu/mol at T_{max} = 30 K), but the decrease of χ in the temperature region above T_{max} is not sharp.[13] To understand this general feature of the χ-vs.-T plot, it is necessary to examine how the nearest-neighbor spins interact in the $[V_4O_9]^{2-}$ layer.

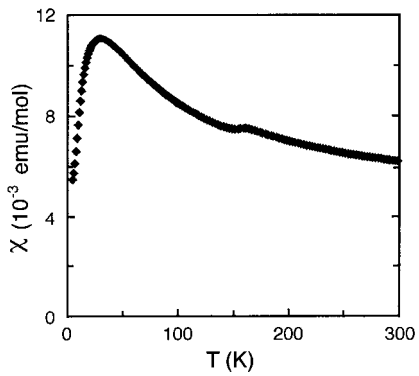


Figure 5.53. Magnetic susceptibility vs. Temperature plot determined for $[H_2N(CH_2)_4NH_2]$ V_4O_9.

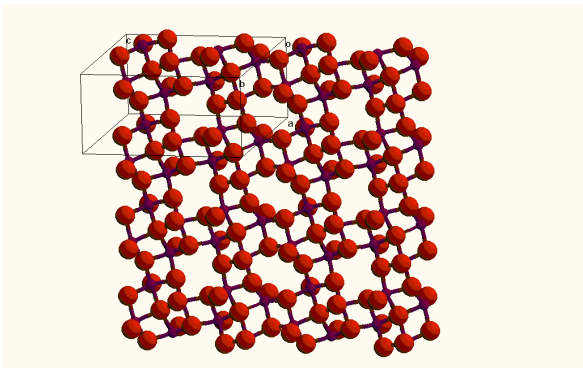


Figure 5.54. Extended view of the $[V_4O_9]^{2-}$ layer.

For this purpose, we make an extended view of the layer, as presented in *Figure 5.54* (obtained by using the file *v4-e.CI*), to see the pattern of how the V(1), V(2), V(3) and V(4) atoms repeat. To simplify the pattern of this extended layer, the user may delete all the apical oxygen atoms [i.e., O(1) from V(1), O(5) from V(2), O(6) from V(3), and O(9) from V(4)]. Then a layer structure shown in *Figure 5.55* is obtained (with file *V4-na.CI*). By identifying the vanadium atoms, the user can show

that the V(1), V(2), V(3) and V(4) atoms of this layer show the repeat pattern of *Figure 5.56*, where each square represents the base of a VO_5 square pyramid, and the numbers 1, 2, 3 and 4 refer to the V(1), V(2), V(3) and V(4), respectively. The squares with solid and dashed diagonal lines indicate that the apical oxygen atom lies above and below the base, respectively.

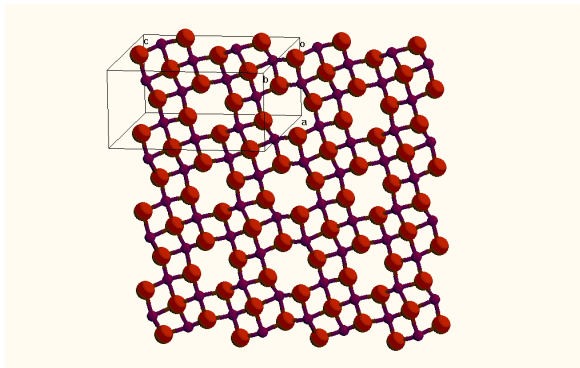


Figure 5.55. Extended view of the $[V_4O_9]^{2-}$ layer without the apical oxygen.

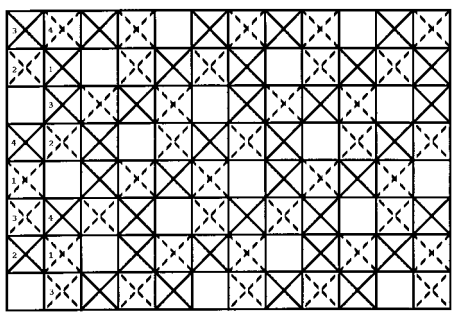


Figure 5.56. Repeat patterns of the V(1), V(2), V(3) and V(4) atoms in the $[V_4O_9]^{2-}$ layer.

The adjacent VO_5 pyramids of the $[V_4O_9]^{2-}$ layer share either O-O edge or a corner O atom, and the adjacent V-O apical bonds lie either on the same side ("cis"-interaction) or on the opposite sides ("trans"-interaction). Consequently, the nearest-neighbor V^{4+} ions of the $[V_4O_9]^{2-}$ layer interact in a number of different ways as classified below.

(a) Edge-sharing/Cis-interaction:
V(1)-V(3)

(b) Edge-sharing/Trans-interaction:
V(2)-V(4), V(1)-V(2), V(2)-V(3), V(3)-V(4), V(4)-V(1)

(c) Corner-sharing/Cis-interaction:
V(1)-V(3), V(2)-V(4), V(1)-V(2), V(3)-V(4)

(d) Corner-sharing/Trans-interaction:
V(1)-V(4), V(2)-V(3)

The exchange coupling constant, J, between two adjacent spins can be written as $J = J_F + J_{AF}$ where J_F and J_{AF} refer to the ferromagnetic and antiferromagnetic interactions, respectively. For

antiferromagnetic systems, J_F is negligible so that $J \approx J_{AF}$.[15] (For simplicity, J_{AF} will be simply represented by J in the remainder of our discussion.) To study the interaction between adjacent V^{4+} (d^1) spins through a shared edge, we carry out MO calculations for the edge-sharing dimer fragment $[V_2O_8]^{8-}$, i.e., $(V^{4+})_2(O^{2-})_8$, containing the two ions. Likewise, to study the interaction through a shared corner, we perform MO calculations for the corner-sharing dimer fragment $[V_2O_9]^{10-}$, i.e., $(V^{4+})_2(O^{2-})_9$. To a first approximation, the strength of the spin-spin interaction (i.e., the magnitude of J) is proportional to the square of the energy difference ΔE between the highest two singly filled levels (E_1 and E_2) of the dimer (*Figure 5.57*), i.e., $J \propto (\Delta E)^2$.[15,16] The structure files for the edge- and corner-sharing dimers can be easily generated by editing the extended structure of the $[V_4O_9]^{2-}$ layer (*Figure 5.54*). The structure files for two edge-sharing dimers (*V13e-c.CI* and *V24e-t.CI*) and two corner-sharing dimers (*V13c-c.CI* and *V24c-c.CI*) are stored in the CAESAR\Examples\Chapter5\AV4O9 directory.

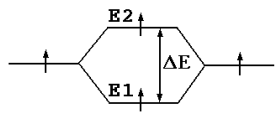


Figure 5.57. Energy split diagram for a spin dimer.

Table 5.2. HOMO levels of the $[VO_5]^{6-}$ fragments and ΔE values of the edge-sharing dimers $[V_2O_8]^{8-}$ and the corner-sharing dimers $[V_2O_9]^{10-}$

(a) HOMO levels of the $[VO_5]^{6-}$ fragments

Vanadium	HOMO (eV)
V(1)	-10.070
V(2)	-10.126
V(3)	-10.066
V(4)	-10.129

(b) Energy levels for the edge-sharing dimers $[V_2O_8]^{8-}$

Metal atom	Interact.	E_1 (eV)	E_2 (eV)	ΔE (eV)
V(1), V(3)	Cis	-10.575	-9.620	0.955
V(2), V(4)	Trans	-10.285	-10.005	0.280

(c) Energy levels for the corner-sharing dimers $[V_2O_9]^{10-}$

Metal atom	Interact.	E_1 (eV)	E_2 (eV)	ΔE (eV)
V(1), V(3)	Cis	-10.126	-10.013	0.113
V(2), V(4)	Cis	-10.201	-10.060	0.141

The interaction depicted in *Figure 5.54* is a degenerate interaction, i.e., the interaction between two equivalent spins. Before we proceed with MO calculations for the dimer fragments, it is important to verify if the four different spin centers of the $[V_4O_9]^{2-}$ layer are equivalent. For this purpose, MO

calculations for the monomer fragments $[VO_5]^{6-}$, i.e., $(V^{4+})(O^{2-})_5$, containing the V(1), V(2), V(3) and V(4) atoms are necessary. The structure files for the $[VO_5]^{6-}$ can be easily generated by editing the dimer structure files. The structure files *V(1).CI*, *V(2).CI*, *V(3).CI*, and *V(4).CI* have the $[VO_5]^{6-}$ fragments for the V(1), V(2), V(3) and V(4) atoms, respectively.

Given the structure files for the monomer and dimer fragments, it is straightforward to generate the corresponding input files for running the *MC* program. Table 5.2(a) summarizes the HOMO levels calculated for the $[VO_5]^{6-}$ fragments. It is clear that the V(1) and V(3) atoms are almost equivalent, and so are the V(2) and V(4) atoms. The V(1) and V(3) atoms are slightly different from the V(2) and V(4) atoms. In general, interactions between degenerate levels are stronger than those between non-degenerate levels. Therefore, the dimer units relevant for the study of the spin-spin interactions are only those containing either the V(1) and V(3) atoms or the V(2) and V(4) atoms.

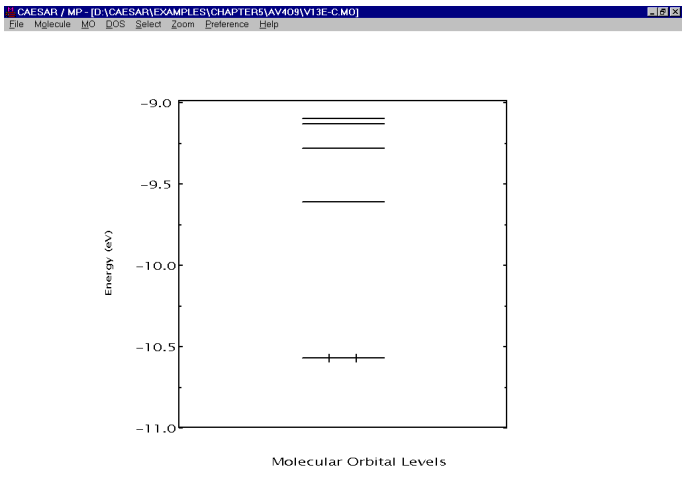


Figure 5.58. MP window with selected MO levels of the dimer.

As an illustrative example for MO calculations for such dimers, consider the edge-sharing dimer $[V(1)V(3)O_8]^{8-}$, whose structure file is *V13e-c.CI*. Run the *MC* program using the *V13e-c.MI* file to obtain the output file *V13e-c.MO*. When this file is loaded into the *MP* program, the *MP* window appears with the calculated MO levels. Once the energy region of the highest occupied level is selected by using the *By mouse* option, the MO level diagram such as shown in *Figure 5.58* can be obtained. There are two d-electrons in the $[V(1)V(3)O_8]^{8-}$ dimer. These electrons are shown as paired in the highest occupied level of the diagram. However, one must recognize that this low-spin representation is incorrect for the $[H_2N(CH_2)_4NH_2]V_4O_9$ salt because it is a magnetic system. The correct representation for the dimer is the triplet state in which the HOMO and LUMO of the MO diagram of *Figure 5.58* are both singly occupied. Tables 5.2(b) and 5.2(c) summarize the values of E_1, E_2 and ΔE calculated for the edge- and corner-sharing dimers containing either V(1) and V(3) atoms or the V(2) and V(4) systems. The ΔE values show that adjacent V^{4+} ions interact more strongly through the shared O-O edges than through the shared O corners, and that the cis-interaction is much stronger than the trans-interaction in the edge-sharing dimers. Consequently, the $[V_4O_9]^{2-}$ layer contains two kinds of spin dimers, i.e., the edge-sharing dimer of V(1) and V(3) with cis-interaction (hereafter, cis-dimer) and the edge-sharing dimer of V(2) and V(4) with trans-interaction (hereafter, trans-dimer).

If spin-dimers are completely isolated, the T_{max} is related to J through [15]

$$|J|/k_BT_{max} = 1.599 \quad (1)$$

and the magnetic susceptibility χ is described by [15]

$$\chi = 2Ng^2b^2/k_BT[3 + \exp(-J/k_BT)] \quad (2)$$

As described above, there are two kinds of spin dimers in the $V_4O_9^{2-}$ layer of $[H_2N(CH_2)_4NH_2]V_4O_9$. The unpaired spins in each cis-dimer are strongly coupled (ΔE = 0.955 eV), while those in each trans-dimer are weakly coupled (ΔE = 0.280 eV). To a first approximation, one may attempt to describe the magnetic susceptibility of $[H_2N(CH_2)_4NH_2]V_4O_9$ in terms of cis-dimers and trans-dimers. Suppose that $[H_2N(CH_2)_4NH_2]V_4O_9$ consists of isolated spin-dimers. Then from the fact that T_{max} = 30 K, Eqs. 1 and 2 lead to χ_{max} = 0.012 emu/mol, which is very close to the observed value 0.011 emu/mol, and to $\chi = 2.4 \times 10^{-3}$ emu/mol at 300 K, which is considerably smaller than the experimental value 6.3×10^{-3} emu/mol. Consequently, the magnetic susceptibility at low temperatures around T_{max} is well described in terms of isolated spin-dimers. These spin-dimers are identified as the trans-dimers, which have the lower ΔE than do the cis-dimers. In other words, the susceptibility at low temperatures around T_{max} is well described in terms of almost non-interacting trans-dimers. The susceptibility at high temperatures above T_{max} should be described in terms of both trans- and cis-dimers and their interactions. The latter explains the slow decrease in χ above T_{max}.

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