CHAPTER SEVEN

Property Calculations and Analysis

7.1 Introduction

The *PC* program performs property calculations (i.e., band dispersion relations, DOS, PDOS, and COOP). It requires an input file *filename.PI* and the *filename.BE*, *filename.BW* and *filename.BV* files generated by the *BC* program. The numerical and graphical results produced by the *PC* program are stored in the files *filename.PO* and *filename.PG*, respectively. The file *filename.PO* can be read by using any text editor, and the *filename.PG* file is used by the *PP* program to display plots of band dispersion relations, DOS, PDOS, and COOP.

7.2 Property calculation program *PC*

7.2.1 Input file *filename.PI*

An input file *filename.PI* for the *PC* program can be generated by running the *NEWPI* program or by modifying an existing *filename.PI* file using any text editor. When the *NEWPI* program is launched, it opens the *New.PI File* dialog box (*Figure 7.1*), which has four fields of parameters to consider.

•Memo

The *Memo* field is used to write a short comment describing the computational task.

•Calculation Options

This field provides four choices, i.e., *DOS*, *Projected DOS*, *Overlap Population* and *Dispersion*. If the option *Projected DOS*, *Overlap Population* or *Dispersion* is checked, the corresponding button of the *Details...* field is activated to enable the specification of more computational details.

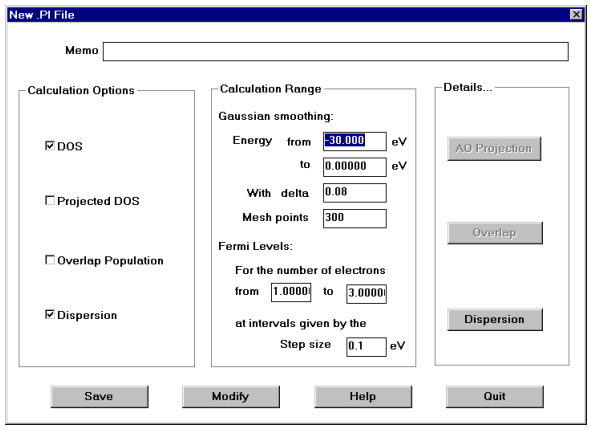

Figure 7.1. Dialog box *New.PI File* creating a new input file *filename.PI*.

•*Calculation Range*

This field allows the user to set computational parameters for the *Gaussian smoothing* (e.g., to obtain DOS, PDOS and COOP curves) and those for *Fermi Levels* calculations.

Gaussian smoothing:

The energy range (e.g., from E_1 to E_2) defines an energy window within which to plot DOS, PDOS, and COOP curves as a function of energy. The number of mesh points, N_{mesh}, is used to divide the energy region between E_1 and E_2 such that one can calculate the values of a DOS, PDOS or COOP curve at each energy E_m defined by

$$E_m = E_1 + (m-1)\frac{E_2 - E_1}{N_{mesh} - 1} \qquad (m = 1, 2, ..., N_{mesh}) \qquad (7.1)$$

A reasonable value for N_{mesh} is between 100 and 400. The delta, δ, is the Gaussian smoothing factor defined in Eq. 4.59. As δ becomes larger, the Gaussian function becomes flatter. The recommended value is around 0.1.

Fermi Levels:

Given the number of electrons ranging from N_1 to N_2, one can define a set of intermediate values given by

$$N_m = N_1 + m \times \Delta N \qquad (7.2)$$

where ΔN is the step size, and m = 0, 1, 2, 3, ···, $(N_2 - N_1)/\Delta N$. Then the *PC* program calculates the Fermi levels corresponding to each of these N_m values ($N_1 \le N_m \le N_2$). As described *in Section 4.5.2*, the step size, ΔN, is used to find the e_{max} and e_{max+1} levels corresponding to each N_m value. The energy difference $e_{max+1} - e_{max}$ found for the case when $N_m = N_{elec}$ is the band gap

for normal semiconductors and insulators. For normal metals, this difference should be very small. The step size can be any positive number (e.g., 0.1, 0.5, 1.0).

•*Details...*

If one wishes to calculate only DOS plots, it is unnecessary to use any command of the *Details...* box. The *AO Projection*, *Overlap* and *Dispersion* buttons are activated only when the corresponding calculations are required.

AO Projection:

The button *AO Projection* of the *Details...* field opens the *AO Projection Information* dialog box (*Figure 7.2*), which is used to define up to five projections. There are two ways of specifying the atoms involved in a projection. If a *filename.CI* file exists, use the *Select* button to copy the names of the unit cell atoms into the box underneath the button. Then select an atom or atoms to be included in a projection. If a *filename.CI* file does not exist, activate the *Type in* button and type the name of each atom to be included in a projection in the box lying underneath the button. The name of an atom can be Sy-xx-yy, Sy-xx or Sy. After completing the *Atoms* field, select the orbitals of the selected atom(s) to project from the *AOs* field. Then click the *Add* button to copy the projection information into the *Projection* box.

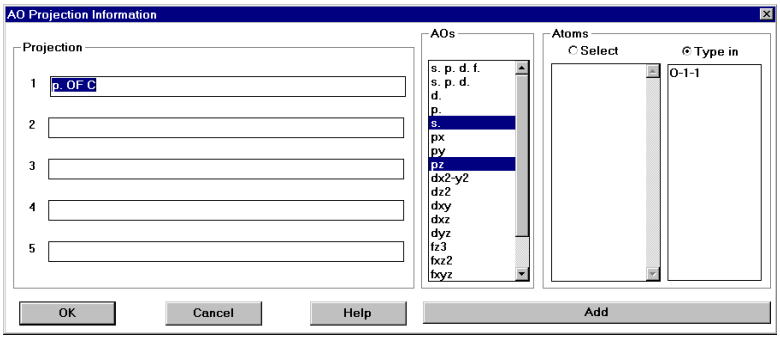

Figure 7.2. Dialog box for entering the information about PDOS plots.

It is possible to select several orbitals for one atom from the list of the *AOs* field. The user can delete, add or edit the projection strings. As an example, *Figure 7.2* shows that all p orbitals of each carbon atom in the system were selected for the first AO projection. The s and p_z orbitals of the atom O-1-1 are being selected.

Overlap:

The *Overlap* button is used to define bonds for overlap population analysis. This button opens the dialog box, *Overlap Population Information* (*Figure 7.3*), which allows the user to define up to five different COOP curves. A crystal structure can have many different kinds of bonds, and each kind may consist of several bonds per unit cell that occur within a unit cell as well as between unit cells. To define a specific kind of bonds, type the names of the two atoms forming the bonds in the *Overlap between* field, specify in the *Distance between Atoms* field the range of distances in Å that will include only those bonds under consideration, and click the *Set* button to transfer the information to the *Overlap Population* box.

As an example, consider that in a unit cell of a crystal structure there are two A1-A2 bonds of 1.34 Å, three A1-A2 bonds of 1.40 Å, and four A1-A2 bonds of 1.52 Å. The different kinds of these A1-A2 bonds are distinguished by specifying the range of their distances properly. Only the three A1-A2 bonds of 1.40 Å are chosen by using *From 1.35 To 1.45* in the *Distance between atoms* field. If one used *From 1.30 To 1.55* instead, all nine A1-A2 bonds will be regarded as forming a set of equivalent bonds. Therefore it is necessary to examine the crystal structure in some detail using the

Builder program before attempting to calculate overlap populations. The user may edit the strings in the *Overlap Population* field. In *Figure 7.3*, all bonds between the atoms C-01 and O-01 that have the bond lengths between 1.5 and 2.5 Å were selected as the first projection. The other projection, which includes all C-P bonds with bond lengths of 1.5 to 3.0 Å, is being defined. This input assumes that there is only one kind of C-O bonds between C-01 and O-01 in the distance range of 1.5 - 2.5 Å, and only one kind of C-P bonds in the distance range of 1.5 - 3.0 Å.

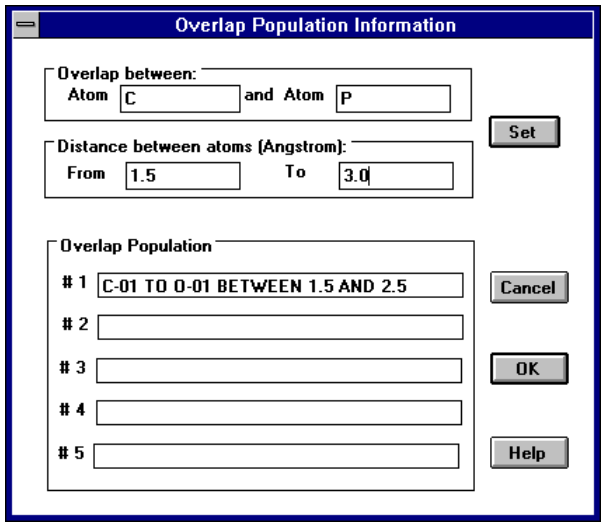

Figure 7.3. Dialog box for entering the information about COOP plots.

Dispersion:

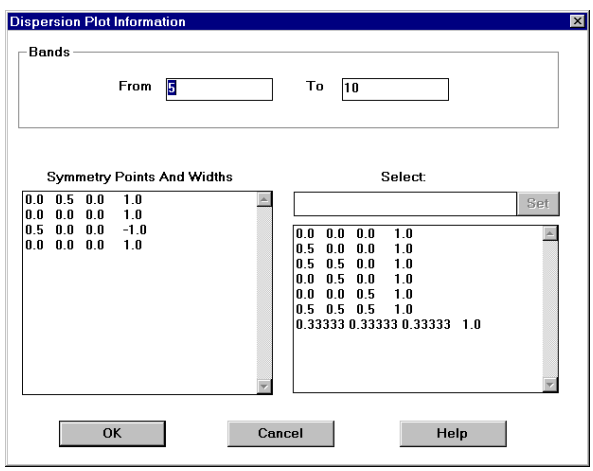

Figure 7.4. Dialog box for entering the information about dispersion plots.

The *Dispersion* button of the *Details...* field opens the dialog box, *Dispersion Plot Information* (*Figure 7.4*). First the user should define the range of the band levels to be plotted by specifying the sequential numbers of the starting and ending band levels in the *Bands* field. Then define the line segments of the FPZ (e.g., Γ-X-M-Y-Γ) by specifying their end points (e.g., Γ, X, M, Y, Γ) and the relative width for each segment (e.g., Γ-X, X-M, M-Y, Y-Γ). For this purpose the box underneath the *Select* field lists typical k-points to use. Here the first three numbers of each k-point

line are the k_a, k_b and k_c components, while the last number refers to the relative width between the current k-point being defined and the preceding k-point already defined. Once a k-point is selected from the list, it shows up in the *Select* field to allow the user to edit the numbers if necessary. This need arises most often to change the value of the width. Then send the k-point and width information to the *Symmetry Points And Widths* box by clicking the *Set* button. Repeat this process until all the needed symmetry points are chosen. There must be at least two symmetry points in this box before clicking the *OK* button.

When the width value is absent, the default value of 1.0 is used. If the width value is negative for a symmetry point, then the band dispersion relations are not plotted for the line segment from that point to the preceding symmetry point. This is used to separate band dispersion plots belonging to different line segments. Suppose the construction of dispersion plots along the segments Y-Γ-X and Γ-Z side by side. Then the correct sequence of the required symmetry points is Y, Γ, X, Γ, and Z. To indicate that the X-Γ segment should have no dispersion plot, the width of the second Γ point should be given a negative number (*Figure 7.4*).

7.2.2 Editing an input file

An experienced user may wish to create a new input file, *filename.PI*, by modifying an existing one. This can be achieved by using any text editor or by using the *Modify* command of the *New .PI* 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 *New .PI File* dialog box. Then the user can edit the file by going through the appropriate fields of the *New .PI File* dialog box where changes have to be made.

7.2.3 Limitations of *PC*

PC employs a dynamic memory management technique. The limitations of the computational capacity comes from the preceding program *BC*. Namely, the maximum number of atoms allowed for a unit cell is 500, which covers almost all practical cases. The maximum numbers of atomic orbitals and chemical bonds allowed in a unit cell are 1,500 and 2,000, respectively. In addition, the maximum number of symmetry points for plotting the dispersion relation diagram is limited to 20. The maximum number of projections in PDOS and overlap populations is limited to five. These restrictions are made to produce a clean and well-organized picture.

7.3 Property analysis program *PP*

7.3.1 Input file *filename.PG*

The *filename.PG* file includes all data needed for plotting the properties on the screen or the printer and serves as the only input file for *PP*. Depending on how many different properties are calculated by *PC*, the *filename.PG* file may consist of several parts. The latter include the information about the Fermi level, the energy mesh points, and the values of DOS, PDOS and overlap populations at the energy mesh points.

7.3.2 Display options of *PP*

When the *PP* program is loaded with a proper *filename.PG* file, the *PP* window appears with the DOS plot on the screen if it was calculated**.** Otherwise, the *PP* window shows the dispersion plot. The *PP* window has a number of menus (*Figure 7.5*), i.e., *DOS*, *Dispersion*, *OVLPOP*, *Total energy*, *Fermi level*, *Redraw*, *Save* and *Help*. The menus for which the required data are absent in the *filename.PG* file is disabled. The functions of these menus are described below.

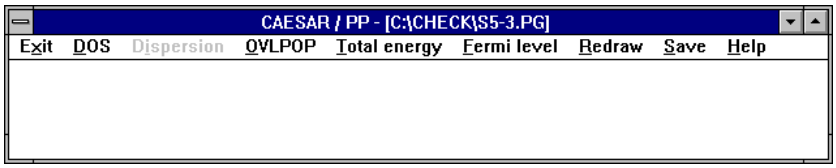

Figure 7.5. Main window of *PP*.

•*DOS*

This menu provides four options (*Figure 7.6*). The *Total* and *IDOS* options show the plots of the total DOS and the integrated DOS as a function of the energy, respectively. The *Projected* option allows the user to select one of the calculated PDOS plots (*Figure 7.7*). As shown in *Figure 7.7*, only the available plots are activated in the list. The *Combined* option provides two ways of displaying several curves simultaneously. The *All* command presents the total DOS and all individual PDOS curves on the screen simultaneously. The *Chosen* command opens the dialog box, *Choose PDOS* (*Figure 7.8*), where the user can select (or unselect) plots to appear together.

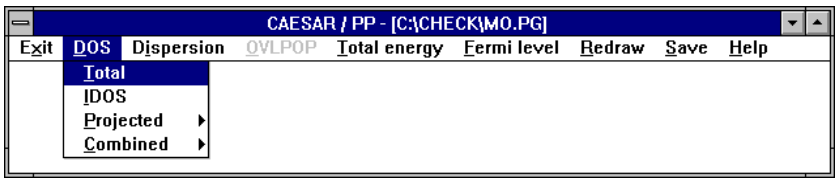

Figure 7.6. Items of the *DOS* menu.

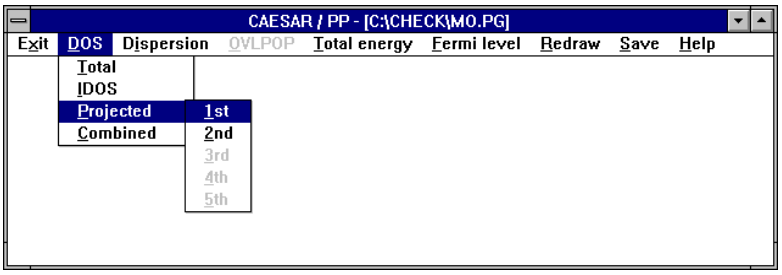

Figure 7.7. Items for displaying an individual PDOS plot.

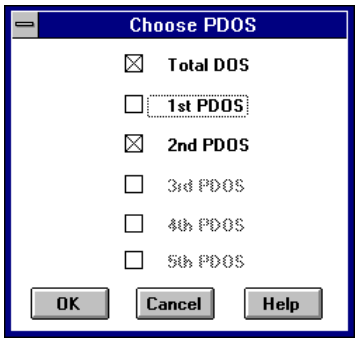

Figure 7.8. Choose PDOS dialog box for selecting DOS/PDOS plots to display.

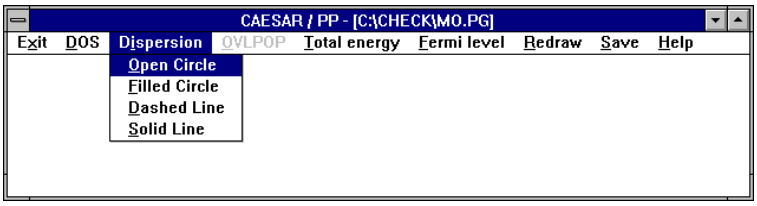

Figure 7.9. Items for displaying plots of dispersion relations.

•*Dispersion*

If the information about dispersion relations is present in the graphic file *filename.PG*, the *Dispersion* menu is activated. It provides four curve formats to use in creating band dispersion plots (*Figure 7.9*). The options *Open Circle* and *Filled Circle* display curves in terms of isolated circles. The number of the circles in a given line segment depends on how many k-points lie on that segment. The options *Dashed Line* and *Solid Line* present dispersion relations in terms of continuous curves. In cases when band crossing happens between two bands, the use of continuous curves may create a misleading impression, because the curve fitting procedure introduces an energy gap in the region of the crossing.

•*OVLPOP*

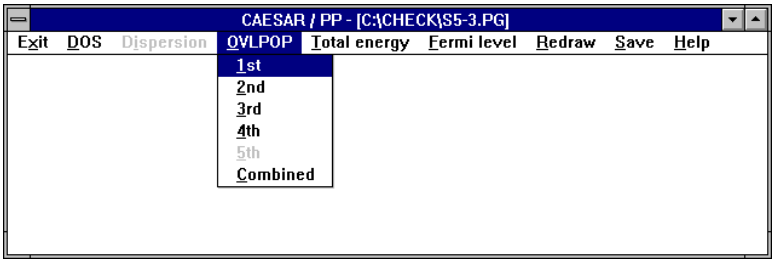

Figure 7.10. Items for displaying COOP plots.

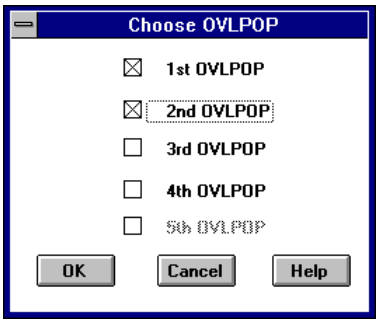

Figure 7.11. Choose OVLPOP dialog box for displaying a combined COOP plot.

The *OVLPOP* menu is activated only if the *filename.PG* file has overlap populations. This menu opens the drop-down list where the available overlap population projections are activated

(*Figure 7.10*). The user can select an individual plot to display. If several are to be combined, use the *Combined* option to open the dialog box, *Choose OVLPOP* (*Figure 7.11*), from which the user can select more than one plot to display simultaneously.

•*Total energy*

The item *Total energy* shows the plot of the total electronic energy as a function of the Fermi level (i.e., as a function band filling with electrons). In this calculation, all band levels below the Fermi level are doubly occupied. As discussed in *Section 4.6.1*, this picture is valid only when the electron localization or the spin polarization is absent.

•*Fermi level*

When the Fermi level information is present in *filename.PG*, it is indicated in dispersion relations, DOS, PDOS and COOP plots by a dashed line vertical to the energy scale. The *Fermi level* menu has three options (*Figure 7.12*). The option, *Show Fermi level*, shows the Fermi level while the option, *Hide Fermi level*, hides it.

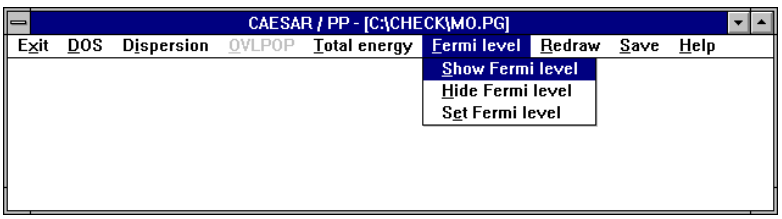

Figure 7.12. Items for handling the Fermi level.

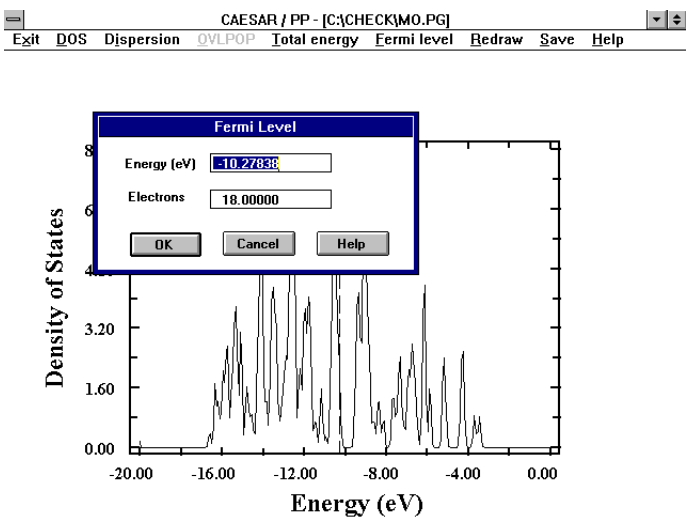

Figure 7.13. *Fermi Level* dialog box for shifting the Fermi level.

The *Set Fermi level* option opens the *Fermi Level* dialog box (*Figure 7.13*), which shows the Fermi level corresponding to the number of electrons per unit cell for a given system. It should be recalled that the *PC* program calculates the Fermi level as a function of the number of electrons per unit cell for the values from N_1 to N_2 specified by the user. The user can choose any number between N_1 and N_2 as the value for the *Electrons* field. Then the Fermi level corresponding to this value will be

shown on the plot. The user can click the *Set Fermi level* option again to examine the Fermi level corresponding to the newly specified number of electrons. Alternatively, the user can specify in the *Energy (eV)* field to move the Fermi level. In this case, the number of the *Electrons* field do not correspond to the newly chosen Fermi level if the entered Fermi level is outside the energy range covering the N_1 to N_2 electrons.

•*Redraw*

The menu *Redraw* provides four groups of commands useful for obtaining well-organized plots. These commands allow the user to re-draw, re-size, re-scale, and change labels and the curve attributes (*Figure 7.14*).

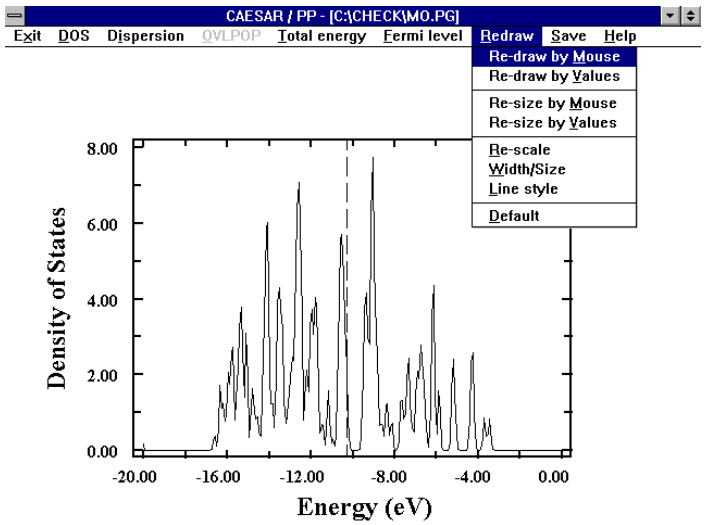

Figure 7.14. Items of the *Redraw* menu.

Re-draw:

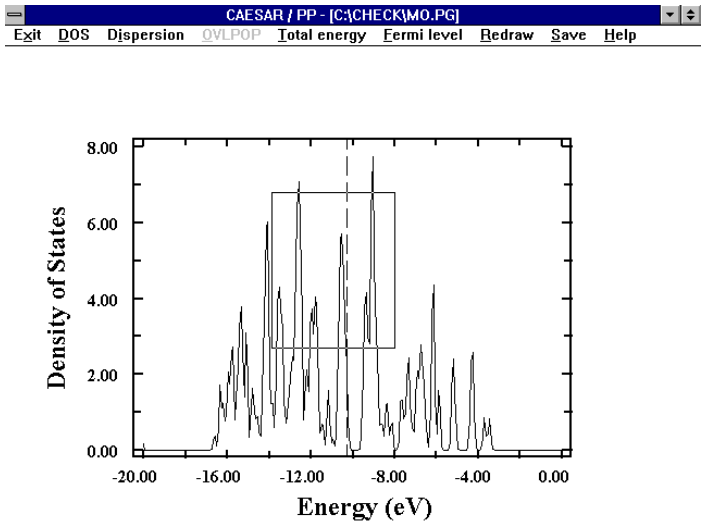

Figure 7.15. Rectangle area for re-drawing selected by the mouse.

One can extend the borders or select a part of a current picture on the screen using the command *Re-draw by Mouse* or *Re-draw by Values*. With the command *Re-draw by Mouse*, use the left mouse button to select an area by the mouse drag method, which appears as a rectangle (*Figure 7.15*). If the selected area is not satisfactory, repeat the same selection procedure. When the selection is satisfactory, click the right mouse button to draw the selected part as a new picture on the whole screen (*Figure 7.16*). The option *Re-draw by Mouse* is mainly used to draw a part of the current picture. This procedure can be repeatedly used to zoom-in a picture.

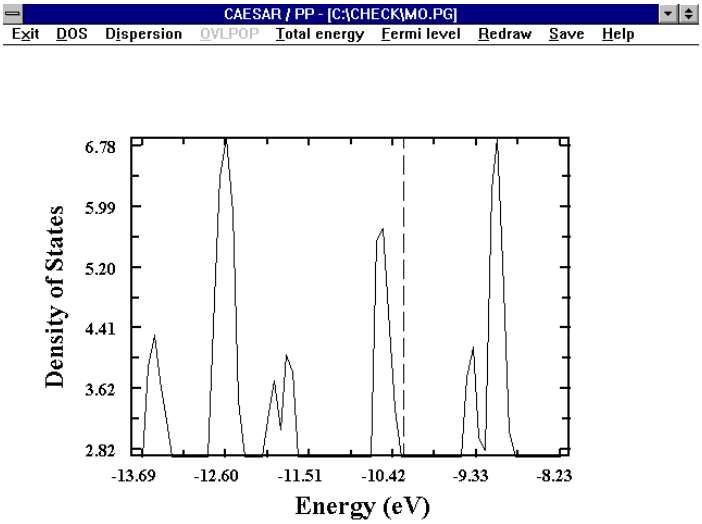

Figure 7.16. Selected part of *Figure 7.15* after zooming-in.

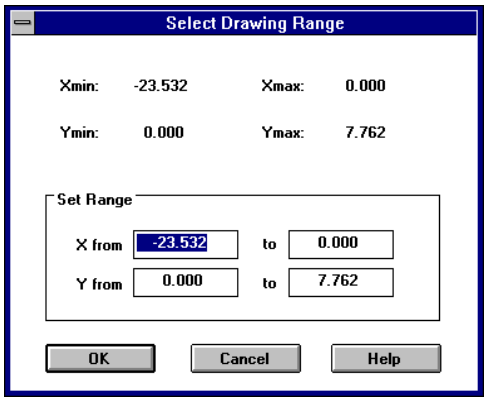

Figure 7.17. Select Drawing Range dialog box for selecting a drawing range.

The option *Re-draw by Values* is used to change the range of the plot data. This option opens the new dialog box *Select Drawing Range* (*Figure 7.17*). The minimum and maximum values of the x-axis (horizontal) and the y-axis (vertical) used for the current picture are listed above the *Set Range* field. Using these values as a guide, new values can be chosen in the *Set Range* field to select a part of an area within the current picture. After entering the desired values of the x- and y-axes and clicking the *OK* button, the current picture is replaced with the selected part of the picture. The purpose of extending the border is to produce neat labels for the scales of the axes (see *Re-scale*).

Re-size:

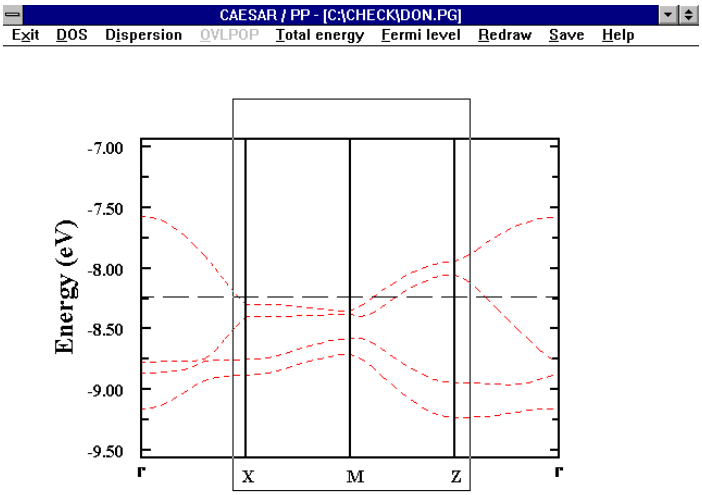

Figure 7.18. Rectangle for re-sizing selected by the mouse.

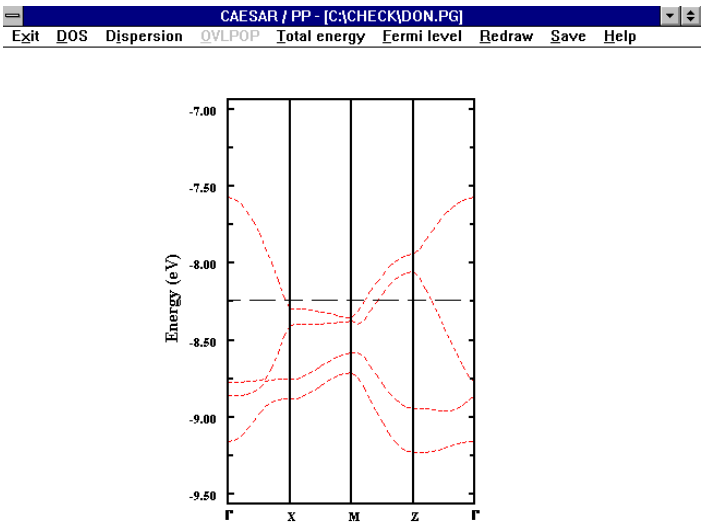

Figure 7.19. Re-sized diagram of *Figure 7.18*.

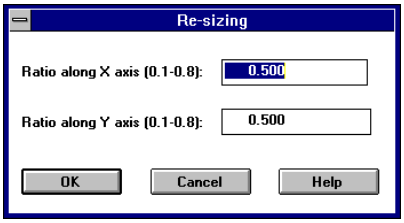

Figure 7.20. *Re-sizing* dialog box for re-sizing.

The size and the picture orientation can be changed using the command *Re-size by Mouse* or *Re-size by Values*. With the option *Re-size by Mouse*, one can use the mouse drag method with the left mouse button to define a new area (*Figure 7.18*). Then click the right mouse button to enlarge or

shrink the whole current picture to fit into the newly-defined area (*Figure 7.19*). The option *Re-size by Values* opens the *Re-sizing* dialog box (*Figure 7.20*) so that the parameters for the new size can be defined. Clicking the *OK* button replaces the current picture with the same picture fitted into a newly-defined size.

Re-scale, Width/Size,* and *Line style:

The option *Re-scale* allows the adjustment of the labels, the major and minor intervals along the axes, and the tick marks. This option opens the *Labeling...* dialog box (*Figure 7.21*). One can modify the text strings for the labels along the x- and y-axes in the first two editing boxes. The fields, *Numerical labels for x-axis* and *Numerical labels for y-axis*, contain currently used values. These values can be modified. The meanings of the parameters are straightforward. It should be noted that the parameters for the *From* and *To* boxes must be within the region defined by *Xmin* and *Xmax* and also by *Ymin* and *Ymax*. (One can use the *Re-draw* command to extend the border first, if necessary. See *Re-draw by Values*.) The *Re-label* button changes the scaling and the labels immediately.

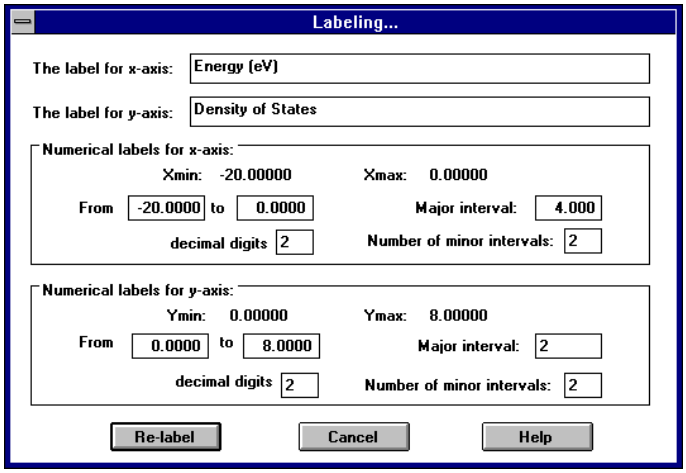

Figure 7.21. Labeling... dialog box for labeling and re-scaling.

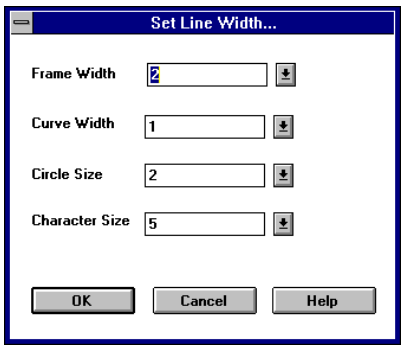

Figure 7.22. Set Line Width... dialog box for setting the widths of frames and curves as well as the sizes of circles and characters.

When one attempts to re-scale a plot of dispersion relations, the *label for x-axis* box displays a string of the symbols, and the *Numerical labels for x-axis* field is disabled. The symbols represent the symmetry points that appear along the x-axis of the diagram from left to right. For example, a string 'GXMYG' shown in the *label for x-axis* field means that there are five symmetry points along

the x-axis of the dispersion plot. From the left to the right, they are Γ, X, M, Y and Γ. One can modify them, if necessary. The parameters for the y-axis (the energy axis in this case) can be modified.

The options *Width/Size* and *Line style* are used to reset the attributes of the plot curves. The *Width/Size* option opens the dialog box *Set Line Width* (*Figure 7.22*), which includes four pull down lists for modifying the frame width, the curve width, the circle radius and the character size. One can click proper numbers in the pull down lists to define new attributes for the picture. *Figure 7.23* displays the *Line Style* dialog box, which appears when the option *Line style* is clicked. The box includes six pull down lists. Each item in the list has the information about the color and style of the line chosen for each plot. For example, in a case when DOS and PDOS plots are made, *Figure 7.23* shows that the total DOS is represented by a black solid line, the PDOS plot #1 by a red dotted line, the PDOS plot #2 by a green dashed line, etc. One can change the default setting for the color and style using the pull-down menu located at the end of each box.

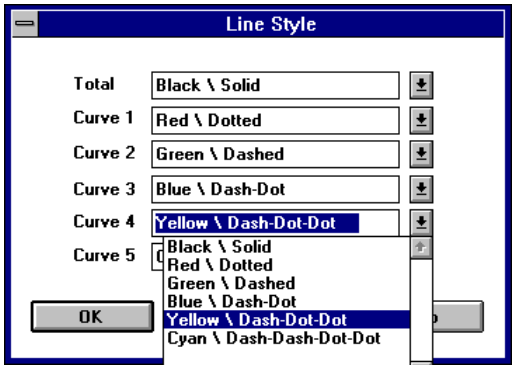

Figure 7.23. Line Style dialog box for setting the colors and styles of lines.

The last option of the *Redraw* menu is *Default*. If this item is selected, the plot returns to its original form generated by the default setting.

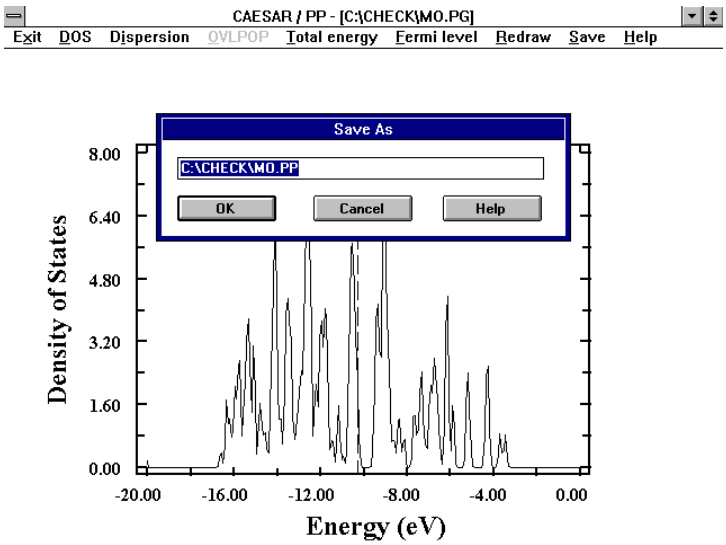

Figure 7.24. Saving a picture on the screen as a PostScript file *filename.PP*.

•***Save***

CAESAR provides a function that saves all graphics using the PostScript format. Once the picture displayed on the screen is satisfactory, one can choose the *Save* menu to capture the content of the current window and save it in a PostScript file *filename.PP*. This opens the *Save As* dialog box (*Figure 7.24*), which allows the user to save the file in a proper directory.

Several different pictures can be saved in one *filename.PP* file. Each picture is saved as one full page. Once a *filename.PP* file has been created, many pages can be appended to it. Before appending a new picture, the program asks one to confirm appending action or to open a new *filename.PP* (*Figure 7.25*).

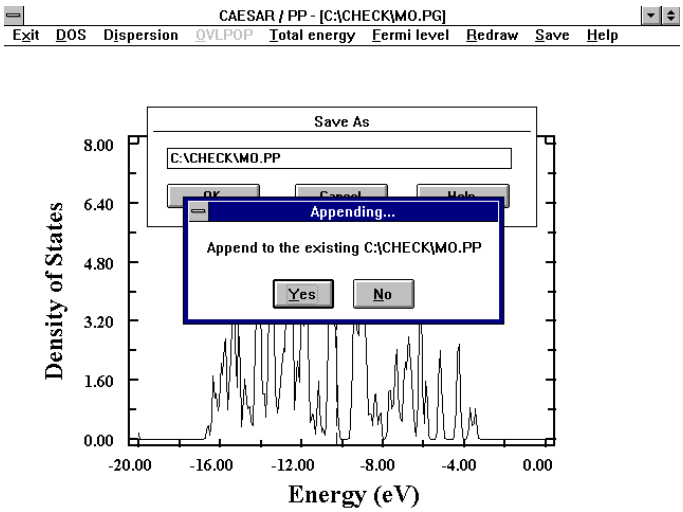

Figure 7.25. Confirmation request for appending a picture.

7.3.3 Limitations of *PP*

The mesh points for the fitting procedure defined in the input file *filename.PI* for *PC* is limited to 2,000. The total number of steps for Fermi level calculations is limited to 1,000. The maximum number of bands displayed on a plot for dispersion relations is limited to 100. The total k-points along the directions between symmetry points should be less than 1,500.

7.4 Examples

As described above and in Chapter 6, the *BC* program calculates the electronic band structure of a solid as a function of k-point for a set of k-points selected by the user. The results of this calculation can be displayed and analyzed only after running the *PC* program based on the outputs of *BC*. In this section, we discuss a number of examples to illustrate how the *BC*, *PC* and *PP* programs are used.

7.4.1 Polyacetylene [1]

As for the carbon skeleton of trans-polyacetylene, one may consider the ideal structure with no C-C bond alternation (*Figure 7.26a*) or the distorted structure with C-C bond alternation (*Figure 7.26b*). The repeat unit for each of these structures has the formula C_2H_2 and 10 valence electrons.

In the CAESAR\Examples\Chapter7\Polyacet directory, the input data for *BC* for the ideal structure is *E.BI*, and that for the distorted structure *A.BI*. The C and H atoms are placed in the

coordinate xz-plane, so that the π orbitals of polyacetylene are given by the p_y orbitals of the carbons. The inputs *E.BI* and *A.BI* are designed to study the total DOS, the PDOS of the π orbitals, and the dispersion relations.

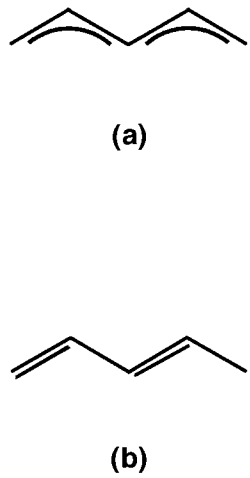

Figure 7.26. Carbon skeletons of the (a) ideal and (b) distorted structures of trans-polyacetylene.

In the CAESAR\Examples\Chapter7\Polyacet directory, the input data for *PC* for the ideal and distorted structures are *E.PI* and *A.PI*, respectively. The dispersion plots for the ideal and distorted structures are shown in *Figures 7.27a* and *7.27b*, respectively, where the dashed lines refer to the highest occupied energy levels. For simplicity, the lowest two occupied bands are not shown. The total DOS and the PDOS of the π orbitals are plotted in *Figures 7.28a* for the ideal structure, and in *7.28b* for the distorted structure.

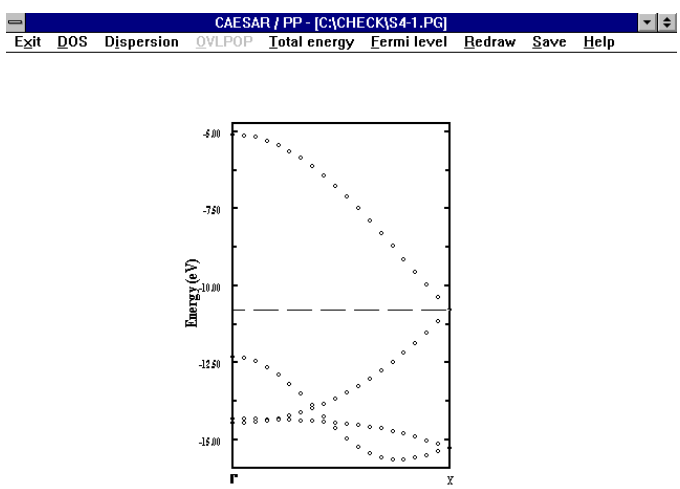

Figure 7.27. (a) Dispersion relations of the bands calculated for the ideal structures of trans-polyacetylene.

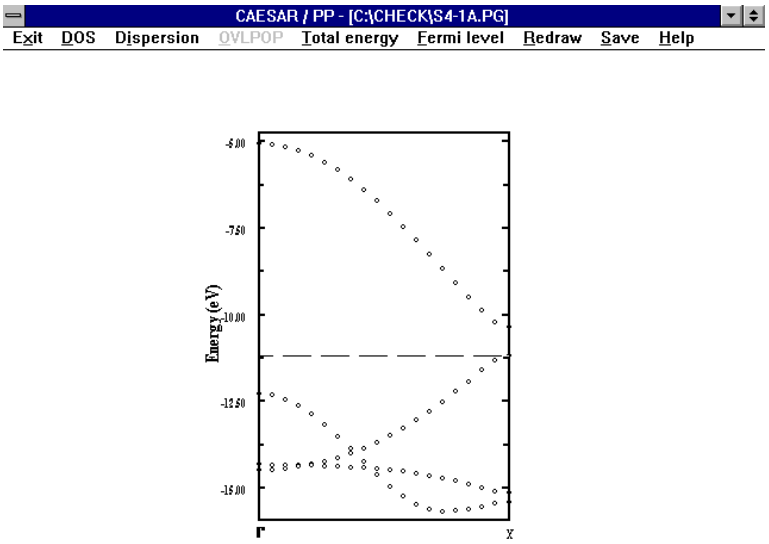

Figure 7.27. (b) Dispersion relations of the bands calculated for the distorted structures of trans-polyacetylene.

It is clear from *Figures 7.27* and *7.28* that the highest occupied and lowest unoccupied bands are π bands. They merge at the X point for the ideal structure but are separated by a band gap for the distorted structure. Therefore, the ideal structure has a partially filled band, while the distorted structure does not. The electronic structures for the ideal and distorted structures represent metallic and semiconducting states, respectively. The structural distortion from the ideal to the distorted structure opens a band gap at the Fermi level of the ideal structure and is an example of Peierls distortion.

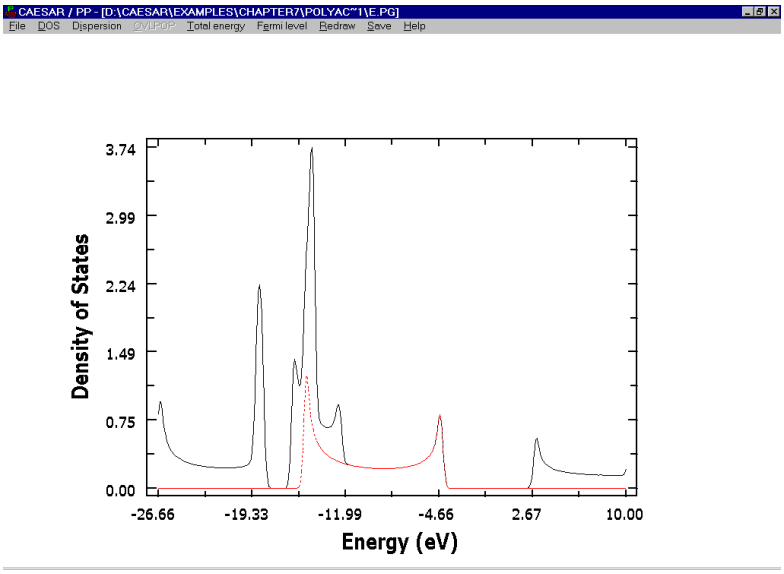

Figure 7.28. (a) Total DOS and PDOS plots of the π orbitals calculated for the ideal structures of trans-polyacetylen. The solid and dashed lines refer to DOS and PDOS, respectively.

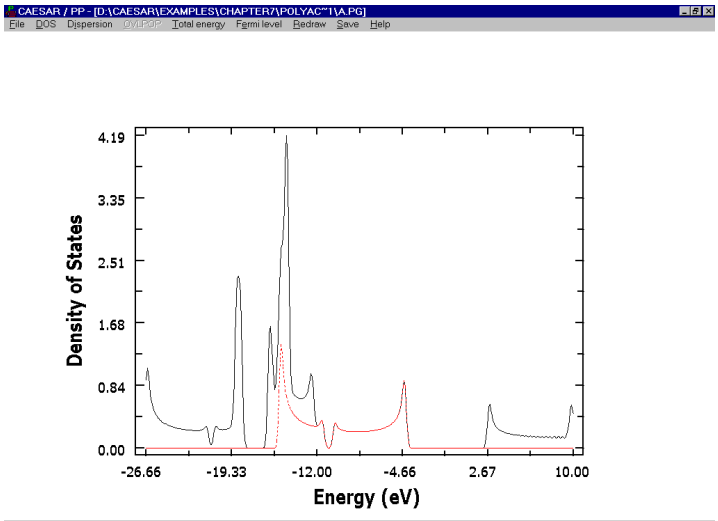

Figure 7.28. (b) Total DOS and PDOS plots of the π orbitals calculated for the distorted structures of trans-polyacetylen. The solid and dashed lines refer to DOS and PDOS, respectively.

7.4.2 Graphite [1]

In the CAESAR\Examples\Chapter7\Graphite\2D directory, the structural information of an isolated graphite layer is stored in the *1Gr.CI* file. The input files for the *BC* and *PC* programs for a single graphite layer are designed to carry out calculations using only the π orbitals. The inputs *2D-Dsp.BI* and *2D-Dsp.PI* are used to obtain a dispersion plot, while the *2D-Dos.BI* and *2D-Dos.PI* are used to obtain a DOS plot. The dispersion and DOS plots obtained from the above inputs are presented in *Figures 7.29* and *7.30*, respectively. There are two π electrons in a single graphite layer. Thus the occupied and unoccupied π bands touch at K, and hence the two bands as a whole become a partially filled band. This renders metallic properties to graphite. The DOS plot shows a deep minimum in the region where the Fermi level occurs.

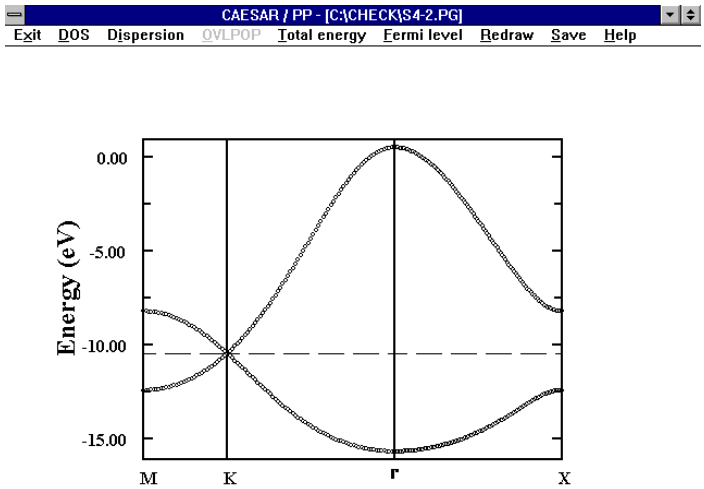

Figure 7.29. Dispersion relations of the bands calculated for a graphite layer.

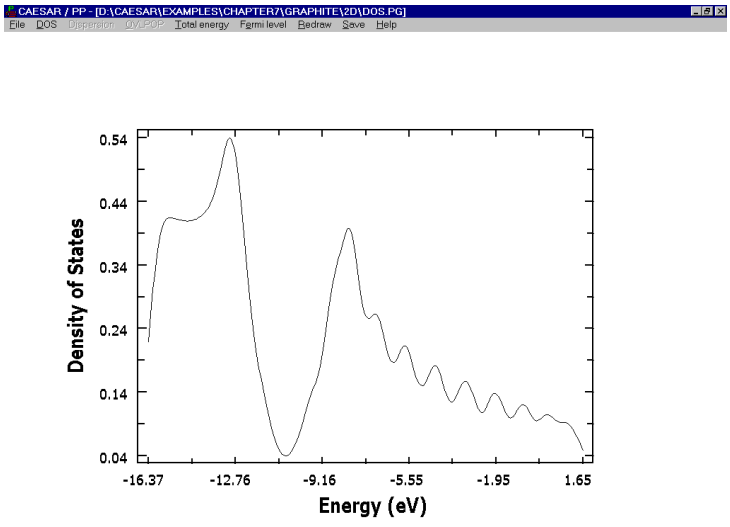

Figure 7.30. DOS plot calculated for a single graphite layer.

In the CAESAR\Examples\Chapter7\Graphite\3D directory, the structural information of 3D graphite is stored in the *3D-Gr.CI* and *3D-GR-e.CI* files. The input files for the *BC* and *PC* programs for 3D graphite layer are designed to carry out calculations using only the π orbitals. The inputs *3D-Dsp.BI* and *3D-Dsp.PI* are used to obtain a dispersion plot, while the *3D-Dos.BI* and *3D-Dos.PI* are used to obtain a DOS plot. The dispersion plot obtained from the above inputs is shown in *Figure 7.31*. Clearly, the band dispersion is very weak along the Γ-Z direction, i.e., the interlayer direction. The DOS plot for 3D graphite is quite similar to that for a single graphite layer and therefore is not shown.

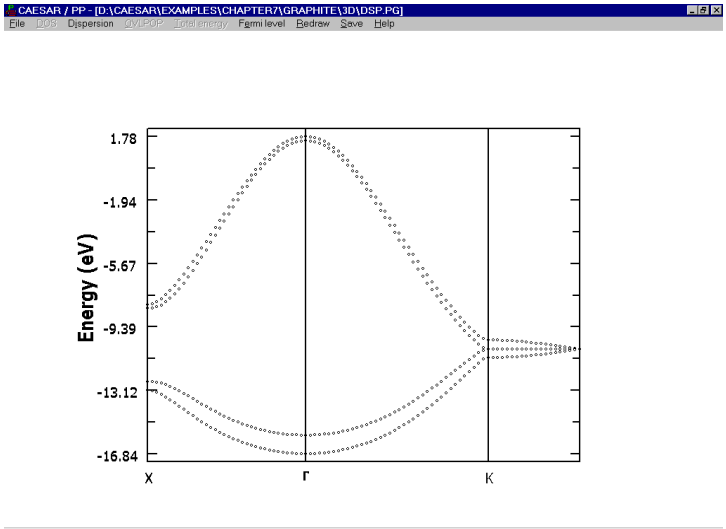

Figure 7.31. Dispersion relations of the bands calculated for a 3D graphite layer.

The Fermi level of 3D graphite occurs at the (1/3, 1/3, 1/2) point. The input file *One.BI* is designed to run the *BC* program only for this k-point to find the Fermi level.

For a single graphite layer, the A- and B-site carbon atoms contribute equally in the energy region around the Fermi level. This cannot be the case for 3D graphite, because the p_π orbitals of the A-site carbon atoms participate in the interlayer interaction while those of the B-site carbon atoms do not. We now examine how the interlayer interaction in 3D graphite affects the relative contributions of the A- and B-site carbon atoms around the Fermi level. For this purpose, we carry out PDOS calculations for the π orbitals of the A- and B-site carbon atoms using a set of k-points covering only the immediate vicinity of the Fermi level. For example, the input file *K.BI* employs the 50 k-points covering $0.31 \le k_a \le 0.35$, $0.31 \le k_b \le 0.35$, and $0.0 \le k_c \le 0.5$. The PDOS plot resulting from the input file *K.PI* is shown in *Figure 7.32*. In the immediate vicinity of the Fermi level, the B-site carbon contributes more than does the A-site carbon atom. This reflects the fact that the carbon p_π orbitals of the adjacent A-site carbons make interlayer σ bonding and antibonding interactions while those of the B-site carbons do not. It has an important consequence on the STM image of graphite (see Chapter 9),[2] i.e., the B-site carbons appear bright in the image.

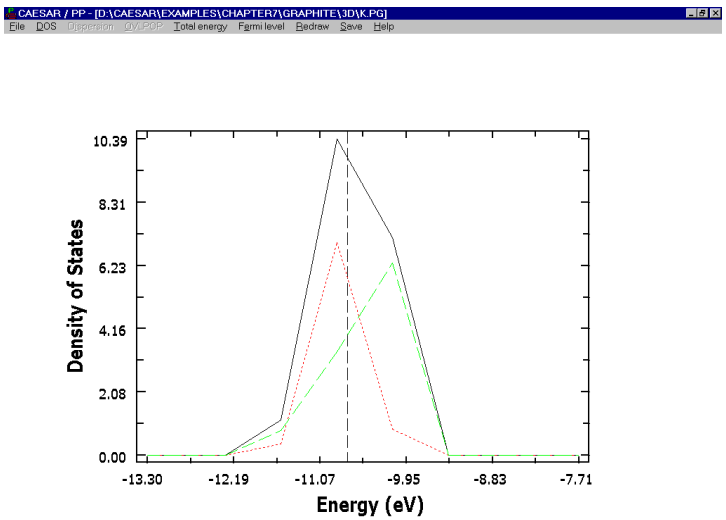

Figure 7.32. DOS plot calculated for a 3D graphite layer.

7.4.3 h-ZrRuP and o-ZrRuP [3]

Two structural types are known for ZrRuP, i.e., the Fe_2P-type hexagonal structure (h-ZrRuP) and the Co_2P-type orthorhombic structure (o-ZrRuP). Superconductivity is found for both phases, but the superconducting transition temperature T_c is higher for h-ZrRuP than for o-ZrRuP (i.e., 13.0 versus 3.5 K).[4] Specific heat measurements for ZrRuP show that the Debye temperature Θ_D, which is a measure of the lattice stiffness, is lower for h-ZrRuP than for o-ZrRuP (345 versus 454 K).[5] Specific heat measurements [6] also reveal that the number of electronic states at the Fermi level, i.e., $n(e_f)$, is low for h-ZrRuP, i.e., 1.52 electrons/(eV·atom).

In the CSASAR\Examples\Chapter7\ZrRuP\Hex and CSASAR\Examples\Chapter7\ZrRuP\Ortho directories, the structural information for h-ZrRuP is stored in *H.CI*, and that for o-ZrRuP in *O.CI*. By analyzing the crystal structures of h-ZrRuP and o-ZrRuP based on these files, one can show that the structural building block common to both h-ZrRuP and o-ZrRuP phases is a -(Zr-Ru)- zigzag chain (*Figure 7.33a*) running along the crystallographic c-axis, whose projection view on the ab-plane can be represented as in *Figure 7.33b*. In h-ZrRuP every three -(Zr-Ru)- chains form a $-(Zr\text{-}Ru)_3-$ triple chain (*Figure 7.33c*), in which the Ru atoms make a stack of Ru_3 triangles along the c-axis such that the plane of each -(Zr-Ru)- zigzag chain bisects the Ru_3 triangles. These triple chains are closely

packed to form a 3D lattice (*Figure 7.33d*), so that each Zr caps one rectangular face of an adjacent Ru_6 trigonal prism, and each Ru caps one rectangular face of an adjacent Zr_6 trigonal prism. This 3D lattice has two different sites for P atoms, i.e., P(1) at the center of each Zr_6 trigonal prism and P(2) at the center of each Ru_6 trigonal prism. Thus a repeat unit of h-ZrRuP is given by $Zr_3Ru_3P(1)_2P(2)$. In the o-ZrRuP phase,[7] every two -(Zr-Ru)- chains form a -$(Zr\text{-}Ru)_2$- double chain (*Figure 7.33e*), in which the Ru atoms make a -Ru-Ru- zigzag chain along the c-axis. These -$(Zr\text{-}Ru)_2$- double chains are closely packed to form a 3D lattice as shown in *Figure 7.33f*, in which each X is located in the middle of a Zr_4Ru_2 trigonal prism, and all P sites are equivalent. Thus a unit cell of o-ZrRuP is given by $Zr_4Ru_4P_4$.

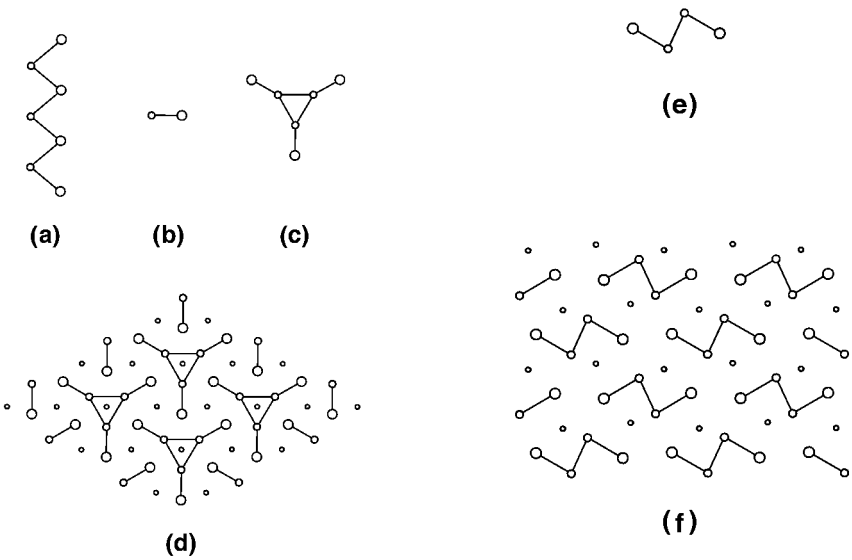

Figure 7.33. Schematic representations of structural building blocks in h-ZrRuP and o-ZrRuP. (a) A perspective view of a -Zr-Ru- chain along the c-direction. (b) A projection view of a -Zr-Ru- chain on the ab-plane. (c) A projection view of a -$(Zr\text{-}Ru)_3$- triple chain. (d) A projection view of the 3D lattice of h-ZrRuP. (e) A projection view of a -$(Zr\text{-}Ru)_2$- double chain. (f) A projection view of the 3D lattice of o-ZrRuP. Large, medium and small circles represent Zr, Ru and P, respectively.

The *BC* input files for h-ZrRuP and o-ZrRuP are saved in *H.BI* and *O.BI*, respectively, and the *PC* input files for h-ZrRuP and o-ZrRuP in *H.PI* and *O.PI*, respectively. These input files are designed to determine the total DOS and the PDOS plots of the Zr, Ru and P atoms.

Figure 7.34 shows the PDOS plots of the Zr, Ru and P atoms calculated for h-ZrRuP. The Fermi level occurs in the energy region where the DOS is low, so the $n(e_f)$ value is calculated to be small, i.e., 0.42 electrons/(eV·atom). This is in reasonable agreement with experiment.[6] *Figure 7.34* shows that major contributions of Ru and P occur below e_f, and those of Zr above e_f. In the occupied region small contributions of Zr occur almost evenly, and in the region between the major peaks of Ru and Zr the contributions of Zr, Ru and P are small. To a first approximation, therefore, the bonding of ZrRuP can be described from the viewpoint of the oxidation state $Zr^{4+}(RuP)^{4-}$, i.e., the energy levels of h-ZrRuP can be approximated as a consequence of interactions between the empty d-orbitals of Zr^{4+} and the occupied orbitals of $(RuP)^{4-}$.

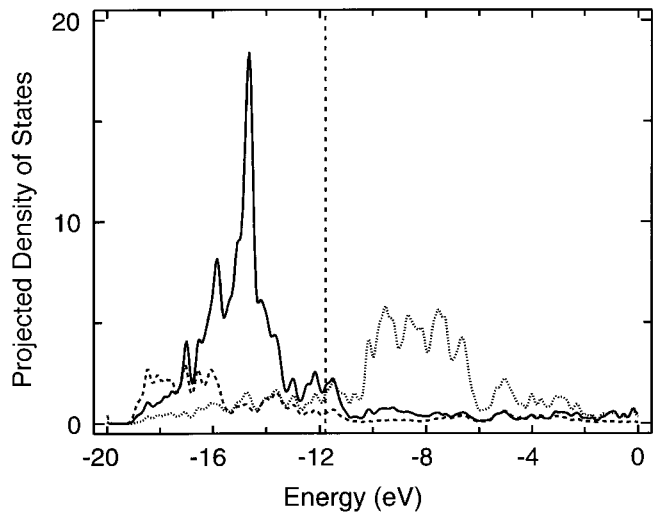

Figure 7.34. PDOS plots calculated for the Zr, Ru and P atoms of h-ZrRuP. The solid, dotted and dashed lines refer to the Zr, Ru and P atoms, respectively.

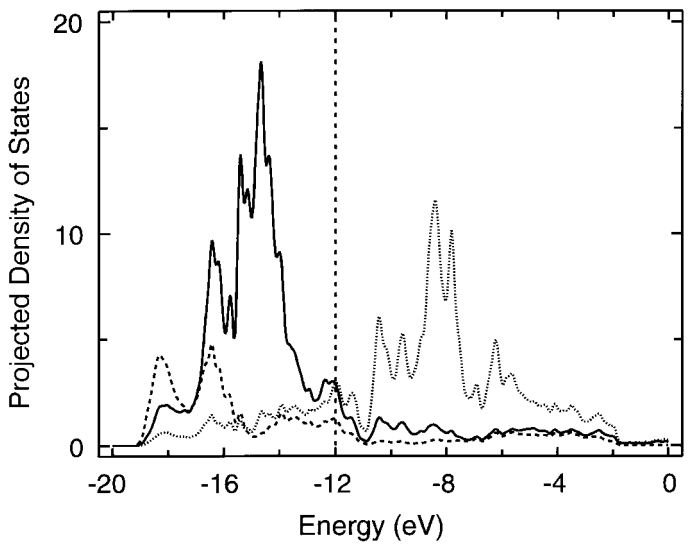

Figure 7.35. PDOS plots calculated for the Zr, Ru and P atoms of o-ZrRuP. The solid, dotted and dashed lines refer to the Zr, Ru and P atoms, respectively.

Figure 7.35 shows the PDOS plots of the Zr, Ru and P atoms calculated for o-ZrRuP. In general, the PDOS plots of o-ZrRuP are similar to those of h-ZrRuP. However, the major contributions of Zr and Ru are spread over a wider region of energy in o-ZrRuP, which means stronger interactions between Zr and Ru in o-ZrRuP than in h-ZrRuP. This reflects the fact that the Zr-Ru distances are shorter in o-ZrRuP (2.903, 2 x 2.926, 2.967, 2 x 2.982 Å) than in h-ZrRuP (2 x 2.95, 4 x 3.00 Å). The Fermi level e_f of o-ZrRuP occurs where the DOS is low. The $n(e_f)$ value of o-ZrRuP, 0.25 states/(eV·atom), is small but is slightly larger than that of h-ZrRuP.

The Debye temperature Θ_D is larger, and the calculated $n(e_f)$ value is larger, for o-ZrRuP than for h-ZrRuP. According to the BCS mechanism of superconductivity (Eqs. 4.81 and 4.82), these two factors predict the T_c to be higher for o-ZrRuP, in disagreement with experiment. This discrepancy can be resolved by considering the dependence of λ on the $M\langle\omega^2\rangle$ term in Eq. 4.82. That is, when the lattice is soft toward the low-frequency phonons crucial for superconductivity, the electron-phonon coupling constant λ is large thereby raising the T_c.[8,9]

7.4.4 K_xWO_3 [10]

As discussed in Chapter 3, the hexagonal potassium tungsten bronze K_xWO_3 has a 3D WO_3 lattice made up of corner-sharing WO_6 octahedra, and the potassium cations K^+ are located in the hexagonal tunnels of the lattice. When all the K^+ sites are occupied, x = 1/3. As the temperature is lowered, K_xWO_3 undergoes a metal-to-semiconductor-to-metal phase transition in its electrical resistivity along the crystallographic c-direction, but not along the directions perpendicular to the c-direction.[11,12] To understand the electrical and superconducting properties of this compound, electronic band structure calculations were carried out.[10]

In the CAESAR\Examples\Chapter7\KxWO3 directory, the input files *Dsp.BI* and *Dsp.PI* are designed to obtain smooth plots of dispersion relations, while the input files *Dos.BI* and *Dos.PI* are designed to obtain the DOS and PDOS plots.

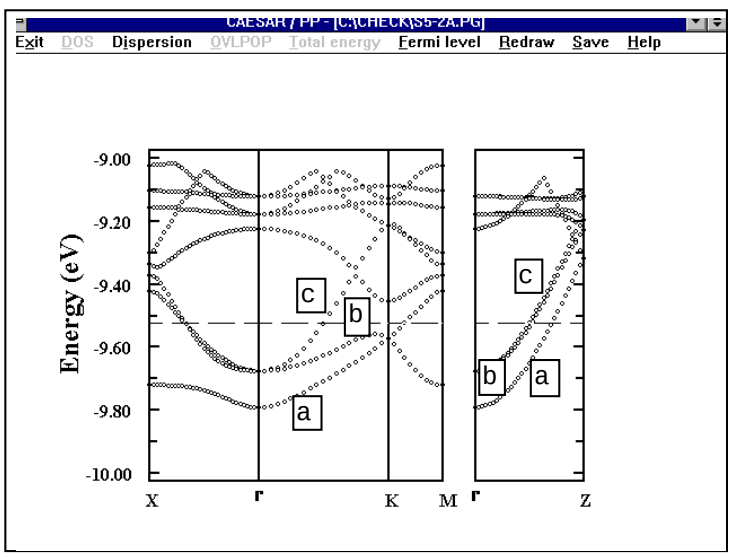

Figure 7.36. Dispersion relations for the bottom portion of the t_{2g}-block bands of the 3D WO_3 lattice of K_xWO_3. The dashed line refers to the Fermi level corresponding to x = 1/3.

Since K_xWO_3 has the formula $(K_xWO_3)_6$ per unit cell, the t_{2g}-block bands of K_xWO_3 consist of 18 bands. Given a complete charge transfer from the potassium atom K to the 3D WO_3 lattice, there are at most two electrons (i.e., 6x) per unit to fill the t_{2g}-block bands. Therefore, only a few bands lying at the bottom of the t_{2g}-block bands become partially filled. (*Figure 7.36*) shows the dispersion relations of the bottom portion of these bands. For the case of x = 1/3, the band dispersion relations along Γ-Z reveal that the bottom three bands are partially filled. The band dispersion relations along

Γ-X and Γ-M (i.e., in the a^*b^*-plane) show that the lowest-lying band does not cross the Fermi level, but the other two bands do. Consequently, the lowest-lying band is 1D, and the other two partially filled bands are 3D in nature. As the x value decreases from 1/3 to 0.18, the Fermi level is lowered and eventually cuts the lowest-lying band around point K = (1/3, 1/3, 0). For x > 0.18, therefore, this band keeps its 1D character, while the other two partially filled bands keep their 3D character.

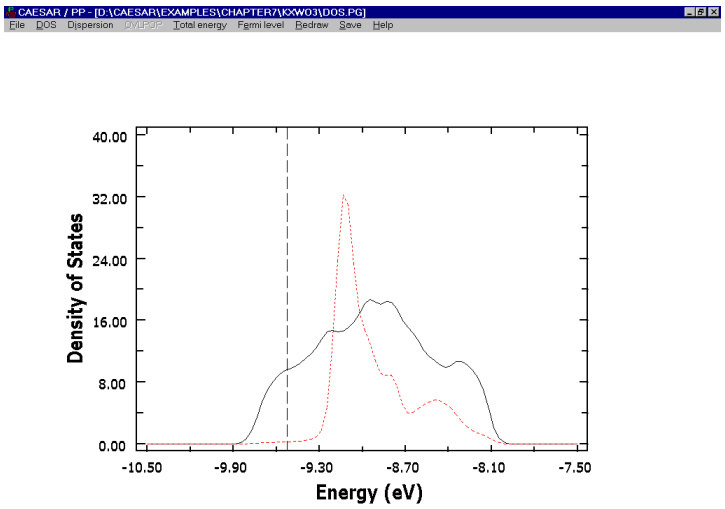

Figure 7.37. PDOS plots calculated for the t_{2g}-block bands of K_xWO_3. The solid curve refers to the contributions of the xz and yz orbitals, and the dotted line to that of the x^2-y^2 orbital. The dashed line refers to the Fermi level corresponding to x = 1/3.

The orbital nature of the three partially filled bands can be examined by calculating contributions of the three d-orbitals making up the t_{2g}-block bands (i.e., xz, yz and x^2-y^2 orbitals). *Figure 7.37* shows the PDOS plots calculated for the xz/yz (i.e., d_π) orbitals and for the x^2-y^2 (i.e., d_δ) orbital, where the dashed line refers to the Fermi levels appropriate for x = 1/3. All three partially filled bands associated with $0.18 \leq x \leq 1/3$ are based on the xz and yz orbitals, and the x^2-y^2 orbital contributes to bands lying above the Fermi level. Thus, in hexagonal tungsten bronze K_xWO_3, it is the π-bands resulting from the xz and yz orbitals that become partially filled and are responsible for their electrical properties.

The metal-to-semiconductor-to-metal transitions and superlattice reflections observed for K_xWO_3 are explained in terms of a CDW associated with the 1D Fermi surface.[10] This will be discussed in the next chapter.

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