The basics: Changing the theme
The desktop theme can include the set of fonts and colors used on the desktop, the size and style of icons, the size, shape and color of the borders of each window, whether there are 3-D or animation effects, and even whether the buttons have icons. Changing your theme is just as easy and changing background wallpaper.

MATE and Cinnamon:
1. On MATE: Menu > Control Center > Appearance > Theme
   On Cinnamon: Menu > System Tools > System Settings > Themes
2. Select the theme you want to use from the list. Note that you have the choice to get additional themes from online repositories.
3. On Cinnamon you must also click the Apply theme button.
4. Your Theme changes immediately. Click Close

KDE:
(Thanks to Carlos F Lange for this section)
Menu > Configure Desktop > Workspace Appearance > Desktop Theme Select the theme you want and "apply" You can also change the window decorations (windows frames, buttons and distinction between active and non-active windows), cursor theme(type and color of mouse cursor), and the login splash screen.

The basics: Changing the panel
The panel, known as the "taskbar" in Windows, can usually be moved into a different position, and you can also have more than one panel if you wish.

MATE:
1. Right-click a blank space in the panel and choose "Preferences" from the menu.
2. From within the dialog box you can edit "Orientation" to choose whether you want the panel at the top, at the bottom of on one of the sides of your screen.
3. You can increase the size of the panel, and its corresponding icons.
4. Choose the "Expand" checkbox to make the panel go completely across the screen. Uncheck it to make it behave more like a dock.
5. Use the "Show hide buttons" setting with "Expand" unchecked to make buttons appear at either end of the panel to let you adjust its size.

6. The "Autohide" setting causes the panel to vanish when you move the mouse cursor away from it and reappear when your mouse reaches the edge of the screen where you placed the panel.

7. The "Background" tab gives you more options on the appearance of the panel, including the ability to make it completely transparent, a solid color, or add a graphic background image to the panel.

8. To add an additional panel, right-click an existing panel and choose "New Panel".

9. Right-click the new panel and choose "Add to panel" to add launchers, monitors and other panel items.

10. Now start over at step one, above, and edit the preferences for your shiny new panel!

Cinnamon:
1. Right-click a blank space in the panel and choose "Panel Settings" from the menu.

2. The "Panel layout" setting lets you move a single panel between the top and the bottom of the screen, or to have one panel on the top, and one on the bottom. Currently in Cinnamon, there is no option to put panels on the left or right edge of your screen.

3. As with MATE you can auto-hide the panel as your mouse approaches and leaves the edge of the screen where the panel is located. With Cinnamon you also have control over how quickly it vanishes and reappears.

4. You can manually set the panel size or let it be controlled by the theme you have chosen.

5. To add or remove items from a panel on Cinnamon, you must put the panel into "edit mode". The checkbox in Panel Settings lets you do that, or you can use the selection on the menu that appears when you right-click a panel to enter edit mode.

KDE:
(Thanks to Carlos F Lange for this section)

1. Right-click and "unlock widgets", if they are locked.

2. Click on the golden bean, called Panel Tool Box.

3. You can change the panel size by sliding the "Height" arrows.

4. You can change panel location by clicking on "Screen Edge" and dragging the panel in the direction of the screen edge you want.

5. Change panel visibility and hiding controls by clicking on "More Settings".

6. Click on Add Widgets and you can select from a wide variety of widgets (or active icons, if you prefer) to add to the panel. These widgets can also be added to the plasma desktop simply by dragging and dropping them where you want.
The basics: Editing the menu

The main menu can be edited from within many desktop environments. This can be very helpful if you have a bash script that you want to use from the menu, like any other application. You can even give it a custom icon.

Cinnamon

1. Right-click on the menu button on the panel.
2. Select Edit menu from the context menu that appears.
3. In the left panel, select the category under which you want your menu item to appear.
4. Click the New Item button to start creating your new menu item.
5. Select "Application" in the Type: field.
6. Enter the text that you want to appear in the menu in the Name: field.
7. Click the Browse button and navigate to, and open the application or script you want to run. Alternatively, in the Command: field, you can type a command as you would enter it in a terminal to run the application. This could be the name of the application, or a command like the one in the screen shot, below, where I'm running a python script.
8. To change the icon for the menu item, click on the icon that is displayed. It's a button! Navigate to, and select the icon you want to use and click Open.
9. Click OK to create you menu item.
10. Click Close to finalize your edits to the menu.

A little more advanced

In this section, we'll be describing some modifications you can make to your desktop that are a little more advanced. Since most of these involve using configuration tools or utilities that are not part of the desktop environment itself, the instructions for making many of these tweaks will be the same regardless of your desktop.

Source: http://goinglinux.com/articles/CustomizeYourDesktop_en.htm