How can I modify the PYTHONPATH in CASA?

In your home directory you have a directory called ~/.casa/

This directory contains a file called init.py that executes each time you start CASA, just before the prompt is displayed. You should use this file to edit variables and import modules you want to have available as soon as CASA starts. For example, adding a path to the PYTHONPATH variable can be done like so:

print "Appending my script directory to the PYTHONPATH."
sys.path.append("/users/test/casapy")