Here's a simple list from my favourite website:

- The Zend Engine II with a new object model and dozens of new features.
- XML support has been completely redone in PHP 5, all extensions are now focused around the excellent libxml2 library (http://www.xmlsoft.org/).
- A new SimpleXML extension for easily accessing and manipulating XML as PHP objects. It can also interface with the DOM extension and vice-versa.
- A brand new built-in SOAP extension for interoperability with Web Services.
- A new MySQL extension named MySQLi for developers using MySQL 4.1 and later. This new extension includes an object-oriented interface in addition to a traditional interface; as well as support for many of MySQL's new features, such as prepared statements.
- SQLite has been bundled with PHP. For more information on SQLite, please visit their website.
- Streams have been greatly improved, including the ability to access low-level socket operations on streams.
- And lots more...
    - Sublists
    - work
    - too!