Erm, you should NEVER EVER leave the PSU plugged into the wall when working on a computer, unless you want to be electrocuted. Besides, the electrical 'ground' in your house wiring may actually be carrying a small level of voltage, since part of it's purpose is to dissipate stray voltage from faulty wiring.

Grounding yourself to the same level as the metal in the computer case is perfectly acceptable as a grounding method since that's the same metal case the components in your PC are grounded to anyway.