Limitations of Aufbau Principle

1. The Aufbau Principle failed to explain the electronic configurations of atoms after ionisation.
i.e Aufbau rule is unable to explain the fact which electron should be removed when an ion is made from atom.

Let us Consider the example of Fe^{2+} ion.
To discuss the electronic configuration of Fe^{2+} ion 1st we have to Consider the electronic configuration of Fe. Is $1s^2 2s^2 2p^6 3s^2 p^6 3d^6 4s^2$
or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
In the above Configuration the 4s electrons energy level $(n+l) = 4+0 = 4$
where 'n' is Principal quantum number and 'l' is Azimuthal Quantum Number

Now by the above electronic Configuration, Energy level of 3d electron is $(n+l) = 3+2 = 5$
So it is clear that electron will first enter in 4s then in 3d, i.e Energy level of 4s is less than 3d. $(4s < 3d)$

But when we Consider the electronic Configuration of Fe^{2+} ion.
According to Aufbau's Principle the electronic Configuration of Fe^{2+} will be $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
(Because the electron in lower energy state 4s is more stable than higher 3d)

But Other Spectral and Magnetic Studies have Confirmed that the electronic Configuration of Fe^{2+} is as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0$
Here '4s' electron is removed to form Fe^{2+} ion
It is Contradictory to the Aufbau's Principle.

2. The $(n-1)d$ sub-shell and ns sub shell's are close to each other still the former has higher energy.
The Predicted Aufbau's outer Configuration of
Cr $(Z=24)$ is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$ (Which is incorrect)
because Experimentally Confirmed Configuration is
Cr $(Z=24)$ $1s^2 2s^2 2p^6 3s^2 p^6 3d^5 4s^1$

Similarly electronic Configurations of Cu $(Z=29)$, Ag $(Z=47)$ & Au $(Z=79)$

Aufbau's Configurations	≠	Experimentally Confirmed Configurations
(i) $_{29}Cu \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$	≠	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
(ii) $_{47}Ag \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^9 5s^2$	/	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$
(iii) $_{79}Au \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^9 6s^2$	/	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$