Relativistic Effects in Chemistry

Moving across the d-block metals, from left to right, an electron and a proton is successively added to each element. The proton increases the nuclear charge by one unit and the electron is added to one of the d-orbitals, n = 3, L = 1,2,3 and m_l = 0, +/- 1, +/- 2. and m_s = +/- 1/2. The d-orbitals have two radial nodes and they shield the nuclear charge poorly, resulting in Z_{eff} increasing across the series and the d-orbitals are accordingly stablilized. Moving down a column, the d-electrons are not fully shielded by the core-electrons and they move to lower energy.

In the heavier elements, the core electrons are subjected to substantial electrostatic fields, due to the increasing nuclear charge, Z_{eff}. This results in a contraction of the metal radius since the electrons are confined to a smaller volume of space. Due to the uncertainty principle, restricting the elecrtron to a smaller space results in a much higher radial velocity (approaching c) since the position and speed cannot be known with equal precision. As the electron velocity approaches the speed of light, the mass increases relative to the rest mass. Therefore, the relativistic effects on the core electrons are to give them larger masses that gives more kinetic energy to the particle and this shrinks the Bohr radius.

In, for example, platinum, the inner s- and p-orbitals experience a direct relativistic contraction and they shrink in size. However, the effect on the d-orbitals is different, since their probability of approaching the nucleus is small. In fact, due to screening by the s- and p-electrons, the d-orbitals are effectively shielded and they experience a relativistic expansion. Thus, they expand radially, increase their energy and they are destabilized. Hence, proceeding from Ni(II) to Pd(II) to Pt(II), two opposing effects determine the energy of the $3d^8$, $4d^8$, and $5d^8$ -electrons:

(1), the increasing nuclear charge stabilizes them and

(2), the relativistic effect destabilizes them.

The net result is that the 5d-orbitals lie in between the 3d- and 4d-electrons in energy. In Au(III), the 3^+ charge stabilizes the 5d-orbitals and the relativistic effect destabilizes them, with the net result that the 5d-orbital in Au(III) is much lower in energy than the 5d-orbital in Pt(II).