

Original by Dave Heisterberg, 1994.

Relativity in Chemistry: The Color of Gold

A reader asks:

Why is gold yellow?

Metals exhibit their characteristic shininess as the delocalised electron sea in the metallic bonds are able to absorb and re-emit photons over a wide range of frequencies. Thus the reflectance spectra of most metals appears fairly flat and they appear silver in colour.

A few metals, such as copper and gold, have a reflectance spectrum where the red end (400–700nm) dominates. Why is this so?

I first thought that it may be something to do with the single unpaired electron in the outermost valence shell, but Silver also displays this but has a flatter reflectance curve.

Can anybody shed some light (*groan*) on this?

Chemists often consider the first sub-shell of a given angular momentum to be anomalous. The 3d, filled in copper, is less shielded by the s and p subshells than you might otherwise expect. Silver, with a filled 4d behaves more like you think it should. Now when you get to gold (5d) relativistic effects become important. Compared to non-relativistic results the s and p subshells are more contracted (the so-called relativistic stabilization) while d and f are destabilized and more diffuse. So gold also behaves somewhat differently. If you were to do a solid state calculation on gold without including relativistic effects you would predict it to be silvery. Including relativistic effects you get reasonably good agreement with reality.

Pekka Pyykko's *Relativistic theory of atoms and molecules* gives a nice overview of this and many other phenomena, as well as a huge bibliography of papers dealing with relativistic effects in chemistry. Oh, that mercury is a liquid is another one.
