Subject – Chemistry
Year/Semester – 3
CEMA –CC-3-6-TH

Relativistic Effect

Group ▶ / Period ▼	10	11	12	13	14	15	16	17	18
2				5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
3				13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
4	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
5	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
6	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
7	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

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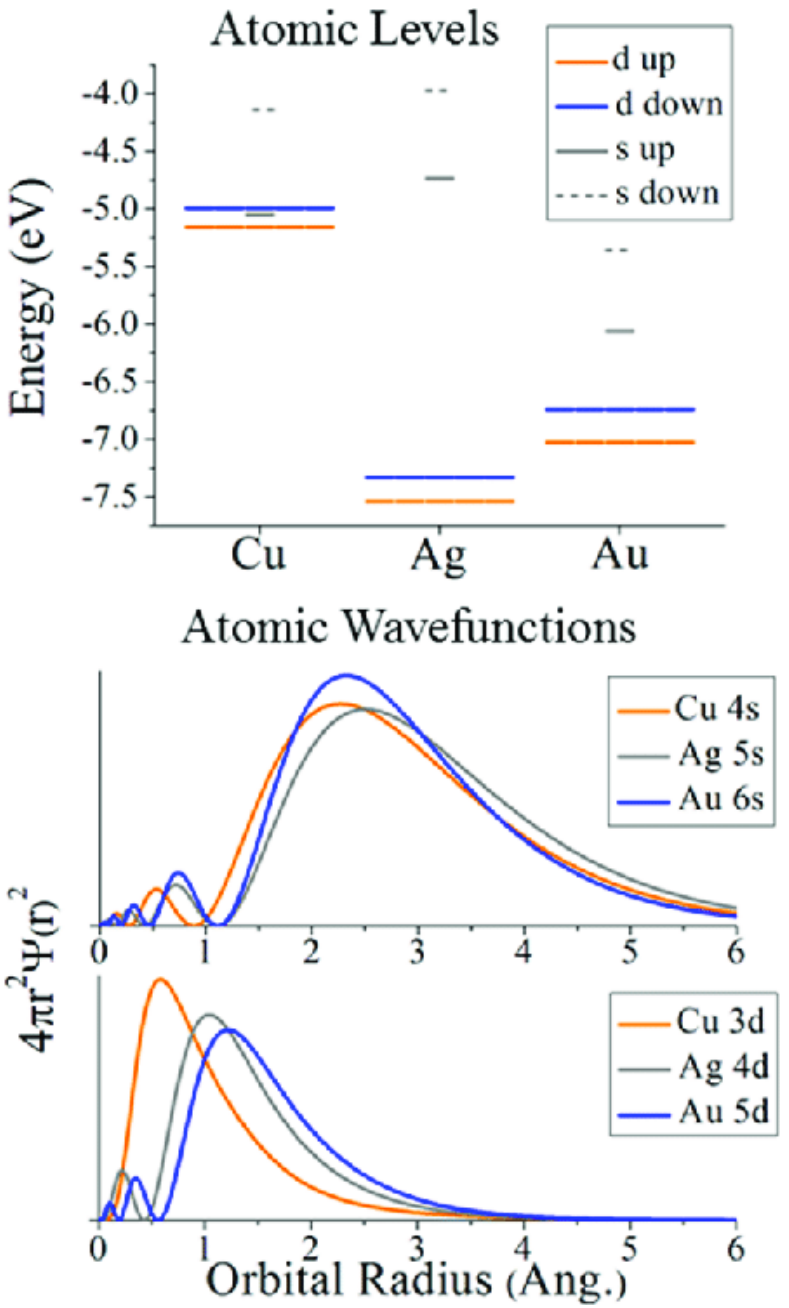
Why Hg is liquid at room temperature?

Mercury is the only metallic element that is liquid (It has a freezing point of −38.83 °C and a boiling point of 356.73 °C,) at standard conditions for temperature and pressure; the only other element that is liquid under these conditions is the halogen bromine, though metals such as cesium, gallium, and rubidium melt just above room temperature.

Hg electronic configuration – $[Xe]4f^{14}5d^{10}6s^2$

Colour of Cu, Ag and Au in metallic state..



What is Relativistic Effect

- **Consider electron motion of H atom (from Bohr's theory) –**

$$m = m_0 / \sqrt{1 - v^2/c^2} \qquad \text{(i)}$$

M_0 = rest mass of electron, m = actual mass, v = velocity of electron, c= velocity 0f light

According to Bohr model, the radial velocity 'v' of an electron in an atom is given by,

$$v = Ze^2/2\varepsilon_0 nh \qquad \text{(ii)}$$

For the 1s orbital of H atom, Z = 1 and n = 1, hence $v = 2.19 \times 10^6\ ms^{-1}$

From eqn. (i) we get, v/c = 0.0073, hence the value of 'v^2/c^2' is negligible with respect to 1. this gives

$$m = m_0$$

For heavier elements -

For Hg (Z = 80), equation (ii) indicates 80 times increase of velocity of electron and gives v/c = 0.58 and

$$m = 1.2m_0$$

It indicates 20% increase in the mass of an electron in 1s orbital of Hg.
On the other hand, mass and radius of orbit is inversely proportional to each other –

$$r = Ze^2/4\pi\varepsilon_0 mv^2 \qquad \text{(iii)}$$

Hence, increase of mass results significant contraction in the radius of the orbit..

RELATIVISTIC CONTRACTION

Since, v is inversely proportional to n (eqn. (ii)), the effect will be most pronounced with the orbital density closure to the nucleus.

Summery -

- For heavy atoms, electrons in the inner core causes a small but significant increase in mass and velocity.
- It results some contraction of the orbitals closure to the nucleus.
- this effect is more pronounced for s orbitals than p orbitals as they have low electron density near nucleus.
- d and f orbital electrons have adverse effect. As the screening power of d and f electrons are very poor, they are screened more by s and p electron from attractive force of nucleus. Hence these orbitals experience slight **expansion of orbit ⟹ RELATIVISTIC EXPANSION**

At the orbital level, the relativistic effect is apparent in the radial contraction of penetrating s and p shells, expansion of nonpenetrating d and f shells, and the spin-orbit splitting of p-, d-, and f-shells. The appearance of a relativistic effect is indicated in the variation in the electronic configurations of the atoms in the Periodic Table, the appearance of new types of closed electron shells ($6s_{1/2}^{\ 2}$, $6p_{1/2}^{\ 2}$, $7s_{1/2}^{\ 2}$, $5d_{3/2}^{\ 4}$), the stabilization of unstable oxidation states of heavy elements, the characteristic variation in the ionization enthalpies of heavy atoms, their electron affinity, hydration energies, redox potentials, and optical electronegativities. In the spectra of coordination compounds, a relativistic effect is observed when comparing the position of the charge transfer bands in analogous compounds, the parameters characterizing the ligand field strength (10Dq), the interatomic distances and angles in compounds of heavy elements. A relativistic effect is also apparent in the ability of heavy metals to form clusters and superclusters. Relativistic corrections also affect other properties of heavy metal compounds (force constants, dipole moments, biological activity, etc.).

Why Hg is liquid at room temp.?

Hg – $[Xe]4f^{14}5d^{10}6s^2$

Due to relativistic contraction of 6s orbital, $6s^2$ electrons remain inert. Bonding forces are weaker for Hg–Hg bonds than for its immediate neighbors such as cadmium (m.p. 321°C) and gold (m.p. 1064°C). Mercury (Hg) is a liquid down to −39°C . In the gas phase mercury is alone in metals in that it is quite typically found in a monomeric form as Hg(g). $Hg_2^{2+}(g)$ also forms and it is a stable species due to the relativistic shortening of the bond.

$Hg_2(g)$ does not form because the $6s^2$ orbital is contracted by relativistic effects and may therefore only weakly contribute to any bonding; in fact Hg–Hg bonding must be mostly the result of van der Waals forces, which explains why the bonding for Hg–Hg is weak enough to allow for Hg to be a liquid at room temperature.

$Au_2(g)$ and Hg(g) are analogous, at the least in having the same nature of difference, to $H_2(g)$ and He(g). It is for the relativistic contraction of the $6s^2$ orbital that gaseous mercury can be called a pseudo noble gas.

N.B - In Tl(I) (thallium), Pb(II) (lead), and Bi(III) (bismuth) complexes a $6s^2$ electron pair exists. The inert pair effect is the tendency of this pair of electrons to resist oxidation due to a relativistic contraction of the 6s orbital.

Colour of Gold -

The human eye sees electromagnetic radiation with a wavelength near 600 nm as yellow. Gold appears yellow because it absorbs blue light more than it absorbs other visible wavelengths of light; the reflected light reaching the eye is therefore lacking in blue compared to the incident light. Since yellow is complementary to blue, this makes a piece of gold under white light appear yellow to human eyes.

The electronic transition from the 5d orbital to the 6s orbital is responsible for this absorption. An analogous transition occurs in silver, but the relativistic effects are smaller than in gold. While silver's 4d orbital experiences some relativistic expansion and the 5s orbital some contraction, the 4d-5s distance in silver is much greater than the 5d-6s distance in gold. The relativistic effects increase the 5d orbital's distance from the atom's nucleus and decrease the 6s orbital's distance.