Why Is Mercury Liquid?

Or, Why Do Relativistic Effects Not Get into Chemistry Textbooks?

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That mercury is liquid at ambient temperatures has been known since ancient times. The Greek name *Hydrargyrum* = "watery silver" (hence the symbol Hg) and the Latin *Argentum Vivum* = "quick silver" show this as do the English and French names of the element alluding to Mercury, the fast-footed messenger of the Latin gods. The Alchemists certainly knew mercury very well, especially its ability to dissolve gold, to amalgamate. As a matter of fact, amalgamation of noble metals with subsequent thermal decomposition was a method of extracting such metals in use in the Mediterranean area already about 500 B.C. Probably all of us have, sometime, dropped a thermometer and tried to chase those evasive small droplets all over the floor. At room temperature there is no doubt that mercury *is* liquid. But *why*? When I ask students, or colleagues for that matter, the answer goes "hm...it is because...hm...it has such a low melting point!" No way!

Purpose

I have consulted a fair number of currently used textbooks and "bibles" of inorganic chemistry including Greenwood and Earnshaw (*1*) and Cotton and Wilkinson (*2*). Nowhere have I found an *explanation* of the well-known fact that Hg is liquid with the exception of Mackay and Mackay (*3*), who very briefly discuss this in a short section "Relativistic effects". Cotton and Wilkinson do mention relativistic effects a few times, but they do not give any consistent account of the great influence of relativity on chemical properties. However, there is an embarrassingly large literature including several excellent articles in *this* very *Journal* on this and related problems. See Pyykkö (*4*, *5*) and Suggested Readings. "Embarrassing" to us teachers of chemistry, that is. *How come this knowledge has not yet got into the mainstream textbooks*?

The purpose of this article is to present a fresh constellation of experimental facts, theoretical calculations, and a discussion of the chemical bonding in mercury that hopefully throws some new light on a number of classical issues in inorganic chemistry.

Mercury and Gold

It is most interesting to compare mercury with gold since the two elements are "next-door neighbors" in the periodic table but have dramatically different properties. The melting points, for example, Au 1064 °C and Hg −39 °C, differ more than for any other pair of neighboring metals in the periodic table (except for Li–Be where the difference also is about 1100 °C but for a different reason). The densities, Au 19.32 and Hg 13.53 g cm^{-3}, also differ more than anywhere else. The enthalpies of fusion are quite different, Au 12.8 and Hg 2.30 kJ mol^{-1}. However, the entropies of fusion are very similar, Au 9.29 and Hg 9.81 J K^{-1} mol^{-1}, which demonstrates that here is actually "nothing wrong" with the thermodynamic data of Hg. They consistently speak the same language: the *bonding forces* are much weaker in Hg than in Au. These data just restate what we already know but do not *explain* why mercury is liquid at ambient temperatures.

The electrical properties of gold and mercury are quite different. Au is an excellent conductor with a conductivity of 426 kS m^{-1}. Hg, on the other hand, is a much poorer conductor with a conductivity of only 10.4 kS m^{-1}. (All data given in this article are taken from Greenwood and Earnshaw (*1*) *unless otherwise stated.*)

From a structural point of view we note that Cu, Ag, and Au have cubic and Zn and Cd (slightly distorted) hexagonal close-packed crystal structures. However, Hg is rhombohedrally distorted and the Hg–Hg distance in the less-than-close-packed planes is about 16% "too large". Again, the metal–metal bonds in Hg are obviously weaker than they "should" be.

Although Au and Hg necessarily have very similar electron structures,

$$_{79}\mathrm{Au(g)}{:}\,_{54}\mathrm{Xe}|4f^{14}, 5d^{10}, 6s^{1}$$
$$_{80}\mathrm{Hg(g)}{:}\,_{54}\mathrm{Xe}|4f^{14}, 5d^{10}, 6s^{2}$$

we might expect that the slight difference, somehow, lies behind their strikingly different properties. *How*?

Anomalies

There are a number of unexpected periodic properties, at least unexpected from a systematic point of view, when we look at the elements past the rare earths. A familiar example is the striking similarity between Hf and Zr. The *lanthanoid contraction* is the usual explanation for this, which is caused by the filling of the 4f orbital group (generally called a "subshell"). 4f electrons do not shield the nuclear charge nearly as well as do s and p electrons or even d electrons. One also speaks of the lesser *penetration* of the 4f orbitals, which means that the 14 protons that are added as we go along the rare earths are not fully shielded off by the 14 4f electrons. This leads to gradually larger effective nuclear charges and a corresponding contraction of the electron cloud. This is certainly a true effect that is largely responsible for $_{71}Lu^{3+}$ being about 0.03 Å smaller than $_{39}Y^{3+}$, although there are 32 more electrons within the volume of the lutetium ion. The lanthanoid contraction is usually also held responsible for the metallic radii of Ag and Au both being 1.44 Å and those of Cd and Hg both being 1.51 Å.

Why is Au gold-colored? Why is it not silver-colored? Why does Au have the highest electron affinity, −223 kJ mol^{-1}, outside the really electronegative elements? Higher than sulfur and almost as high as iodine. Why is Tl stable in the oxidation state +I, Pb in +II, and Bi in +III, while their congeners are more stable as +III, +IV and +V, respectively?

The lanthanoid contraction alone does not explain all of these anomalies, even if it is a very useful concept. The "inert $6s^2$ pair" introduced by Sidgwick in 1933 is another idea invoked; see, for example, an inorganic chemistry classic like Phillips and Williams (*6*). However, this latter concept does not really *explain* why mercury is liquid or why Pb(II) is more stable than Pb(IV). To find the real cause of all those anomalies we will have to look into an entirely different realm of science, namely *relativity* and its influence on chemical properties.

Relativity

Einstein taught us with his special relativity theory of 1905 that the mass of any moving object increases with its speed,

$$m_{rel} = m_{rest}/\sqrt{(1 - (v/c)^2)}$$

Bohr calculated the speed of a 1s electron in the hydrogen atom in its ground state as 1/137 of the speed of light when it is orbiting at the Bohr radius 0.53 Å. This speed is so low that the relativistic mass is only 1.00003 times the rest mass. Although small, Sommerfeld took relativistic effects into account when, in 1916, he refined Bohr's model introducing elliptic trajectories. However, when we turn to the heavy elements $_{79}$Au, $_{80}$Hg, and onward, the situation is quite different. The expected average radial velocity for a 1s electron in an atom heavier than hydrogen is

$$\langle v_r \rangle \approx (Z/137)\cdot c$$

which for Hg means $(80/137)\cdot c = 0.58c$, or 58% of the speed of light. m_{rel} then becomes 1.23 m_{rest}. This in turn means that the Bohr radius shrinks by 23%, since the mass of the electron enters in the denominator. Thus the 1s orbitals in Au and Hg contract *very much*. Because all orbitals must be orthogonal to one another, an almost equally large mass–velocity contraction occurs for 2s, 3s, 4s, 5s, 6s, and 7s orbitals as well. Now, in order to appreciate what really is going on we need to look into Paul Dirac's *relativistic quantum mechanics*.

Dirac Quantum Mechanics

Schrödinger quantum mechanics with its probability contours, node patterns, and energy levels familiar to all undergraduate students of chemistry is not adequate when treating the heavy elements. Within the framework of spin–orbit coupling we learn that the angular and spin quantum numbers l and s are "no good" for the heavy elements but that their vector sum $j = l + s$ still is, so that we get j–j coupling instead of L–S (Russell–Saunders) coupling.

The electron spin was "invented" by the Dutch physicists Uhlenbeck and Goudsmit in 1925 to explain the fine structure of the hydrogen spectrum. The Stern and Gerlach experiment of 1922, where a beam of vaporized silver atoms was split in two by an applied external inhomogeneous magnetic field, seemed to prove this idea. The idea of electron spin, that we usually meet as part of the *Pauli exclusion principle*, is a *postulate* added to the Schrödinger solution of the wave equation. It is interesting to note that Pauli, who was so instrumental in the development of the quantum mechanical model of the atom and was the one that introduced the fourth quantum number in the early 1925, did not himself believe in Uhlenbeck and Goudsmit's interpretation of it as an intrinsic motion of the electron. Finally, in 1928, Dirac made the *synthesis between quantum mechanics and relativity*. He showed spin–orbit coupling to be a purely relativistic effect and that electrons really do not spin at all, contrary to what I am sure most chemists think. According to Dirac *all* electrons, including s electrons, have *angular momentum*, and there is no distinction between "orbital" and "spin" angular momentum. There is only one quantity labeled by the angular momentum quantum number j. An s orbital then gets the label $s_{1/2}$. It is this angular momentum that operates in "electron spin" spectroscopic measurements. Furthermore, the Dirac treatment demonstrates that the p_x, p_y, and p_z orbitals are quite different from our common belief. They form two groups of orbitals (or "spinors" in the Dirac parlance) designated $p_{1/2}$ and $p_{3/2}$ and labeled by the angular quantum numbers j. Since $s_{1/2}$ and $p_{1/2}$ atomic orbitals have the same angular dependence, a $p_{1/2}$ orbital is in fact *spherically symmetrical*. It is also lower in energy than the $p_{3/2}$ orbital, which is doughnut-shaped in the way we usually see d_{z2} orbitals pictured. This relativistic splitting of orbital energies is according to Dirac the real explanation of the traditional spin–orbit coupling energy, which for a heavy element like Pb amounts to as much as 2 eV or nearly 200 kJ mol^{-1}.

Relativistic Effects

In summary, following Dirac we may speak of three relativistic effects

(1) $s_{1/2}$ and $p_{1/2}$ orbitals contract quite a lot but $p_{3/2}$ to a much lesser extent.
(2) This in turn *induces* an extension outward of d and f orbitals relative to s and p orbitals.
(3) "Spin–orbit coupling" is actually the relativistic splitting of p, d, and f orbital energies. This effect becomes large for the heavier elements.

The sum of these effects becomes very important for Au and Hg, making the energy difference between the $5d_{5/2}$ and $6s_{1/2}$ orbitals much smaller, see below. There is actually at least one more relativistic effect to consider called the *Darwin term*, which accounts for the oscillatory motion of the electron (*"Zitterbewegung"*) that becomes important near the atom nucleus. This term gives s electrons higher energy and expands s orbitals, which partially counteracts the velocity–mass contraction. It is implicitly included in "effect 2" above. The Darwin term is usually explicitly invoked in the "Pauli relativistic" treatment of the Schrödinger equation, which is less cumbersome to use than a pure Dirac model.

Relativistic Calculations

Relativistic energy band structures for gold, see Takeda (*7*), and other heavy metals and alloys have been calculated by a variety of methods, see Pyykkö (*4*, *5*) and Christensen (*8*). Illustrations of such band-structure calculations are not easy to employ for the purpose of this article. They actually need Brillouin zone theory and a whole host of concomitant concepts to be fully appreciated. Figure 1 has been chosen instead as a simpler illustration of the main points to be made. It portrays the relativistic calculations on the molecular species AgH(g) and AuH(g) by Pyykkö (*9*) and Pyykkö and Desclaux (*10*). The energy differences between the 4d and 5s orbitals of Ag and 5d and 6s of Au are obviously quite different, although their nonrelativistic counterparts are very similar. There are differences, of course, between a free gaseous gold atom, or a AuH(g) molecule, and the crystalline solid, but the main features of the relativistic effects are still the same. For extensive discussions of this point see Christensen (*8*) and Koelling and MacDonald (*11*). Excellent articles on relativistic effects on gold chemistry have been given by Schwerdtfeger et al. (*12*, *13*). First-principle calculations by Takeuchi et al. (*14*) demonstrate that the higher cohesion energy of gold compared to silver is a relativistic effect.

X-ray photoelectron spectroscopy (ESCA) experiments on Au and other heavy metals and alloys thereof have shown that relativistic calculations are much closer to observations than are nonrelativistic ones. On the basis of both experiments and calculations one can conclude that the metal–metal bonds in Au(s) are brought about by the single 6s electrons with a 5d admixture but (almost) no 6p.

In the analysis of anomalous periodic properties a problem still remains, for relativistic effects do not vary smoothly with Z. They rather seem to culminate for $_{79}$Au. The relativistic velocity–mass contraction of the radius of the 6s orbital of the free Au(g) atom has been calculated to about 16% (*8*). Furthermore, the relativistic effects are overlaid with the lanthanoid contraction, which in itself is relativistic to about 15%, as well as with an analogous 5d orbital contraction. For the 6s electron in solid gold the total stabilization of 2.8 ev (270 kJ mol^{-1}) arises 2/3 from relativistic effects and 1/3

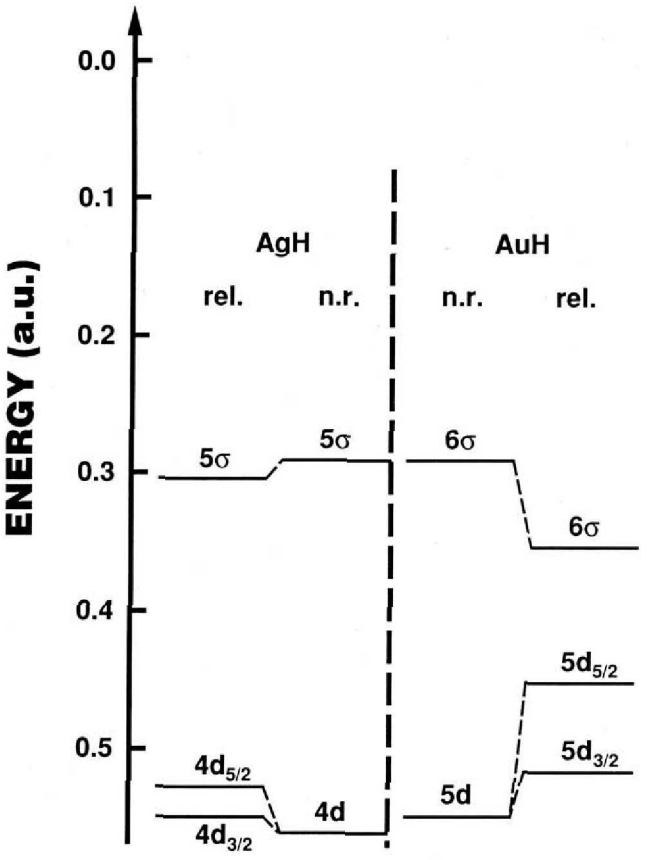

Figure 1. Orbital energies of the diatomic molecules AgH(g) and AuH(g) from relativistic and nonrelativistic calculations. Energies in atomic units, 1 a.u. = *27.212 eV = 2625.5 kJ mol*$^{-1}$. *Thus* $\Delta E \approx$ *260 kJ per step of the ordinate axis.* Adapted from Pyykkö (*9*).

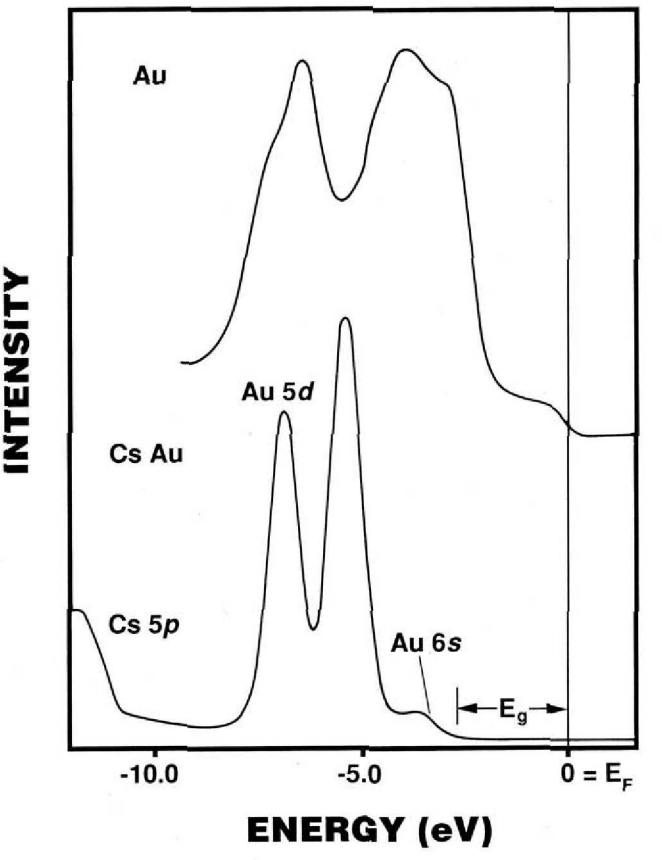

Figure 2. ESCA (XPS) spectra showing the band structures of metallic gold and semiconductor CsAu. Energies in eV are relative to the Fermi level, E_F. In Au the 6s and 5d bands merge (hybridize) and extend to the Fermi level. In CsAu electron density has been transferred from Cs to Au. The 6s band is now localized, does not mix with the 5d band, and is separated from the E_F by a band gap E_g of ~2.6 eV. The relativistic splitting of about 1.5 eV of the Au 5d energies is distinct in CsAu. Adapted from Wertheim (*19*).

from the lanthanoid contraction. See Bagus et al. (*15*) and Christiansen et al. (*16*). The net result of all these effects is generally difficult to predict.

Silver and Gold

We are now able to explain several of the differences between Ag and Au. The color of Au arises when blue light is absorbed and 5d electrons are exited to the 6s level, or strictly speaking to the Fermi level, which lies just at the top of the conduction band. Silver, however, having a larger band gap absorbs in UV and appears colorless. The first ionization energy of Au is slightly larger than that of Ag, while the second and third are larger for Ag. Therefore, we more often encounter Ag(I) than Au(I) but Au(III) more frequently than Ag(III). Furthermore, Au shows more pronounced covalent bonding in its complexes thanks to d–s hybrid orbitals that are energetically more favored than in Ag. Figure 1 is in qualitative agreement with all of this. See also Desclaux and Pyykkö (*17*).

Electron Affinity

The high electron affinity of Au may be qualified in the following way. The 6s orbital has such a low energy that "it feels good", cit. Pyykkö and Desclaux (*10*), for an extra electron to jump in and fill it. Cole and Perdew (*18*) have calculated that relativistic effects boost the electron affinity of gold by as much as 65%. Relativistic effects also explain why Au_2(g) is such a surprisingly stable molecule having a dissociation energy of 221 kJ mol^{-1}, which is more than I_2(g) (151 kJ mol^{-1}) and just a bit less than the single-bond energy of Cl_2(g) (243 kJ mol^{-1}).

Intermetallic Compounds

The intermetallic compound CsAu is not a metallically conducting alloy but a red transparent semiconductor crystallizing with the CsCl structure. This is another example of the yearning for one more electron in the 6s orbital of Au. We see a tendency toward an ionic compound Cs^+Au^-. Experimental data are reproduced in Figure 2, from Wertheim (*19*). Calculations of the electronic structure of CsAu by Christensen and Kollar (*20*) confirm that the semiconductivity in this case is an altogether relativistic effect. Gold is here not unlike iodine and has been called a "pseudo-halogen".

Why Is Mercury Liquid?

Now, how about the central question of this article? *Why is mercury liquid*? We may find the answer taking a detour to the gas phase and to Hg(I). Hg does not form any strong covalent single bonds comparable to Au_2. However, Hg_2^{2+}, which is isoelectronic with Au_2, is a very stable species indeed well known from both aqueous solution and solid compounds. In fact, calculations by Ziegler et al. (*21*) show that relativistic effects shorten the bonds as much as 16% in both Au_2 and Hg_2^{2+}, making the bonding distances shorter than in the analogous silver and cadmium species. To draw an analogy, one could say that the difference between gold forming a strongly bonded stable dimer molecule in the gas phase, Au_2(g), and mercury, which is unique among metals by being almost entirely *monomeric* in the gas phase Hg(g), is of the same nature as the difference between H_2(g) and He(g), which is strictly monomeric. The common explana-

tion is that $He_2(g)$ does not exist because the third and the fourth valence electron would populate the *antibonding* $1\sigma^*$ orbital thus completely destabilizing a diatomic molecule. In Hg the relativistically contracted 6s orbital is filled, and therefore the two 6s electrons do not contribute much to the metal–metal bonds. This is obviously the opposite of gold. One must conclude that the bonding is brought about largely by van der Waals forces, see Pyper et al. (*22*), and probably also through weak 6p orbital interaction. *This is why the Hg–Hg bond is so weak.*

Incidentally, this also explains why the electrical conductivity is so much lower for mercury than for gold: the two 6s electrons are rather *localized* and contribute only little to the conduction band. Mercury could in the vein of this analogy be called a pseudo noble gas.

Amalgamation

Why does liquid mercury dissolve gold and form amalgam? What is the chemical bonding like in an amalgam? Why does Hg amalgamate well with Cu, Ag, Au, and the alkali metals? The reaction with sodium is well known from the chlor–alkali process, where an amalgam (with about 0.5% Na by mass) is formed at the liquid mercury cathode. Why does it react with the ammonium radical NH_4·? Why poorly or not at all with most transition metals? Let us try this for an answer. As mentioned in the introduction, it is easy to retrieve gold from amalgam by simply heating it, so the *bonding forces between Hg and Au are not very strong.* Consider a hypothetical gaseous molecular species HgAu(g). In analogy with He_2^+, which has been spectroscopically characterized, it would have a three-electron bond, Hg···Au, with two electrons in a bonding 6σ orbital and one electron in an antibonding $6\sigma^*$ orbital. This would be weaker than the strong single bond in $Au_2(g)$ but stronger than the bonds between Hg atoms. Silver and gold provide one electron per atom to the amalgam bonds. The same holds for the alkali metals. Most transition metals react poorly with mercury because they contribute *two* s electrons per atom, and we are back to the case of mercury itself; only very weak bonds would be possible. The ammonium radical also provides one electron to the bond with Hg. It seems that if the alloying metal contributes one electron per atom, a good amalgam is formed but not if it contributes two.

It should be clearly stated that no unambiguous calculations have yet proven the ideas discussed above. Detailed relativistic band calculations on solid mercury and amalgam are needed to substantiate these bonding ideas. To carry out such calculations, it is generally necessary to assume that the crystal structure of the metal is either cubic close-packed or body-centered cubic. The rhombohedral distortion in crystalline mercury is quite far from ccp, which therefore would be a rather poor approximation. In the binary system Au–Hg no intermetallic phase richer in mercury than Au_2Hg has been confirmed. This stoichiometric compound has a hexagonal crystal structure and melts incongruently at 122 °C. The solid solubility of Au in Hg is negligible. See Rolfe and Hume–Rothery (*23*). Mercury-rich amalgams are therefore more or less well-crystallized two-phase mixtures of Au_2Hg and Hg. Relativistic calculations on liquid mercury, where the structure of the liquid (a cluster of eight nearest neighbors at 3.0 Å) is taken into account, would likewise be most useful.

The Inert $6s^2$ Pair

Finally, as a last example of relativistic effects on heavy metal chemistry let us compare $_{81}Tl$ and $_{49}In$. Although the radius of the Tl^+ ion is *larger* (1.50 Å) than that of In^+ (1.40 Å), the energy needed to go from oxidation state +I to +III is *higher* for Tl^+ than for In^+. The sum of the second and third ionizations energies is 4848 kJ mol^{-1} for Tl and 4524 kJ mol^{-1} for In, i.e., a difference of about 7%. Tl^+ is isoelectronic with Hg, and the extra energy needed to remove two more electrons to get to Tl^{3+} obviously stems from the relativistic *contraction of the 6s orbital. The "inert* $6s^2$ *pair", so often* encountered but never explained in textbooks, is a relativistic effect.

Bottom Line

The influence of relativity on the properties of heavy elements has been well understood for at least 15 years. This knowledge is naturally finding its way into research work on heavy metal chemistry. See for example the works by Schrobilgen et al (*24–26*). *It is high time that this is also reflected in the teaching of chemistry at the undergraduate level.* Take a look at the literature suggested at the end of this article and enjoy the thought-provoking and elegant answers to the seemingly innocent question "Why is mercury liquid?" and other puzzles of the periodic table!

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