Relativistic Effects in Chemistry

Literature Seminar
by
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Background

Classical mechanics is based on a series of assumptions that make its application to problems in the macroscopic world useful and valid. For example, in Newton's Second Law, the equation for force is presented and takes the form

$$F = d(mv)/dt;$$

inherently assumed in the relationship is that the mass, m, is a constant. However, in 1905, Albert Einstein proposed the theory of Special Relativity to account for errors discovered in these classical laws due to the finite speed of light. In classical mechanics, a constant force acting on an object for an extended period of time will continue to pick up speed until it exceeds the speed of light. However, in Einstein's relativistic view of the universe, this is impossible since nothing can exceed the speed of light.[1] In essence, the theory of special relativity applies to inertial frames of reference, or frames that move relative to one another at *constant* speeds. The most important axiom of special relativity is that which states that the speed of light is constant regardless of the speed of the observer. Despite the apparent contradiction to common sense, it is from this axiom that all consequences of special relativity are derived.[2]

Leading up to Einstein's theory, an important experiment was performed in 1887 by Michelson and Morley in an attempt to detect the existence of "ether," or the medium through which electromagnetic waves were thought to propagate. They presumed that if the ether existed, they should be able to detect the motion of the earth through the ether. When their experiment failed, H.A. Lorentz proposed the idea currently known as the Lorentz contraction, or the contraction of a moving body in the direction of its motion. The contraction factor was defined as

$$[1 - (v^2/c^2)]^{1/2},$$

where v is the velocity of the moving body and c is the speed of light. Interestingly, Einstein later showed that all physical laws remain unchanged under a Lorentz transformation (a series of mathematic transformations incorporating the Lorentz contraction). In order to understand the reason behind this invariance, Einstein proposed that we must not only analyze the laws of mechanics, but also our ideas of space and time.[1]

Relativistic effects, in the scope of special relativity, are defined as "differences in any measurable or observable properties that arise from the true velocity of light as opposed to the assumed infinite velocity."[3] The most important relativistic effect for understanding how classical mechanics must be altered is the dependence of mass on velocity. In relativistic theory, conservation of momentum is impossible unless mass is considered as a variable of velocity. Einstein's equation for the mass velocity correction is given in Figure 1 which includes the Lorentz contraction factor; as the velocity of an object approaches the speed of light, its mass (M_v) increases with respect to its rest mass (M_o). Here we see that the upper bound for the velocity of any particle is the speed of light, thus correcting the inherent flaw in classical mechanics.[2]

$$M_v = \frac{M_o}{\sqrt{1 - (v^2/c^2)}}$$

Figure 1. *Equation for relativistic mass.*[2]

As we see, relativistic effects become most important for objects that approach the speed of light. In addition to the mass correction, relativity is responsible for several other important phenomena. In classical mechanics, space and time are treated independently of one another. However, the theories of special relativity state that space and time are relative (i.e., not absolute) and demand that they be treated on the same basis.[2]

Another consequence of relativity is the equivalence of mass and energy as described by the famous equation $E=mc^2$. By using an interesting thought experiment for the transmission of a photon in a box, Einstein was able to derive an expression for the conversion of energy to mass, and vice versa.[2] Essentially, due to the large magnitude of the speed of light, a small amount of mass can be converted into enormous amounts of energy. The most compelling evidence is in radiative processes and the binding energy of nuclear reactions.[4]

In chemical phenomena, it is the mass-velocity correction that becomes most important is evaluating relativistic effects on experimental observations. In addition, the coupling of space and time become important in understanding computational approaches

to relativistic quantum mechanics. Another effect of relativity, known as spin-orbit coupling, will be described later.

Relativistic Effects in Chemistry

Chemical manifestations of relativity are typically studied or quantified in two ways: (1) the description of anomalous experimental trends in heavier elements via comparisons to lighter periodic analogs and, (2) the use of relativistic quantum mechanical techniques to quantify the degree to which these effects contribute to non-relativistic treatments. The latter method involves rigorous mathematical methodologies, such as the Dirac equation (Figure 2) and relativistic pseudopotentials, to perform calculations on atoms and molecules.[5]

$$\left\{ -ic\hbar\left(\alpha_x \frac{\partial}{\partial x} + \alpha_y \frac{\partial}{\partial y} + \alpha_z \frac{\partial}{\partial z} \right) + \beta mc^2 + V(x, y, z) \right\} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Figure 2. *The Dirac equation.*[5]

The time-dependent Schrödinger equation, as it turns out, is not a suitable framework for relativistic calculations since it treats time as a first-order partial derivative and the spatial coordinates as second-order partial derivatives, thus violating the requirement that space and time be treated equally.[5] The details of such equations will not be treated here, but in certain cases, outcomes of calculations will be provided to compare with non-relativistic treatments such as the Schrödinger equation. Nonetheless, the relativistic effects on a specific atomic or molecular property, P, are quantified as

$$\Delta_R P = P_{NR} - P_{R,}$$

where P_R and P_{NR} are obtained from relativistic and non-relativistic quantum theory, respectively.[6]

The main focus herein will be on the description of anomalous trends in heavier elements using relativistic theory. At this juncture, the question "Why are relativistic effects important in heavy elements?" may come to the forefront. In heavy atoms, the core electrons are subjected to a substantial electrostatic field due to the large nuclear

charge of the nucleus. As a result, they are pulled closer to the nucleus, are bound tighter, and are confined to smaller volumes of space.[2] Due to the Heisenberg uncertainty principle, restricting the electron to a smaller space results in a much higher radial velocity (sometimes comparable to c) since we cannot know both position and speed precisely. For example, the 1s electron in gold is estimated to move at nearly 60% of the speed of light. The speed of core 1s electrons in an element can be approximated by the following equation:

$$<v_r> = Z \cdot \alpha$$

Here, Z is the nuclear charge of the element and α is the fine structure constant in atomic units (~1/137). Since the speed of the 1s electron in gold moves at a considerable fraction of the speed of light, it is subject to relativistic effects and its mass depends on its velocity. Using the equation in Figure 1, the 1s electron of gold is calculated to be 25% heavier than its rest mass, thus imparting significantly more kinetic energy to the particle. In terms of the simplified equation for the Bohr radius ($a_0 = 4\pi\varepsilon_0\hbar^2/mZe^2$), there is a mass dependence in the denominator, thus causing the relativistic radius to be nearly 20% smaller than the non-relativistic one.[7]

Indeed, relativistic effects are most significant for electrons in orbitals that closely approach the nucleus. In heavy elements, the core electrons are most affected; both the inner s- and p-orbitals experience a direct relativistic orbital contraction and shrink in size. While this is most profound for the s-orbitals, the p-orbitals also shrink but to a lesser extent. In order to maintain orthogonality, the s- and p-orbitals of higher quantum number (valence orbitals) also experience a contraction, sometimes significant. Energetically, these orbitals become more stabilized. The effect on the d- and f-orbitals is quite different, however; the probability of these electrons approaching close to the nucleus is exceedingly small. In fact, due to s and p contraction, the d- and f-orbitals are more effectively screened and thus see an indirect relativistic orbital expansion. They expand radially and increase in energy, thus becoming more destabilized.[8]

In addition to orbital stabilization and destabilization, a subsequent coupling of orbital angular momentum and spin angular momentum occurs (except in s-orbitals that have no orbital angular momentum), as mentioned earlier. Spin-orbit coupling arises naturally from relativistic theory and allows for the mixing of electronic states that would

not normally mix in its absence.[2] As it turns out, in relativistic theory, *l* and *s* are no longer good quantum numbers. However, the quantum number *j*, describing the total angular momentum, is suitable, and is defined as[5]

$$j = \begin{cases} l + \tfrac{1}{2} \\ l - \tfrac{1}{2} \end{cases}$$

 The effect is observed to increase like Z^2 and is quite important for p-block elements, as well as the lanthanides and actinides.[6] For example, the coupling between $p_{1/2}$ and $p_{3/2}$ orbitals may result in splitting as high as a few electronvolts for valence electrons, sometimes on the order of bond energies.[7]

Relativistic Explanations for Periodic Phenomena and Anomalies

   The late 5d transition elements, 6p elements, and the lanthanides and actinides have been most thoroughly studied for relativistic effects. Among these, gold has received the most attention because it has many anomalous properties that can only be explained using relativity. A local maximum of relativistic effects occurs at gold that exceeds both coinage metals as well as their neighbors. As shown in Figure 3, an unusually large contraction of the 6s orbital occurs at gold due to the interaction of relativistic effects and shell structure effects.[9]
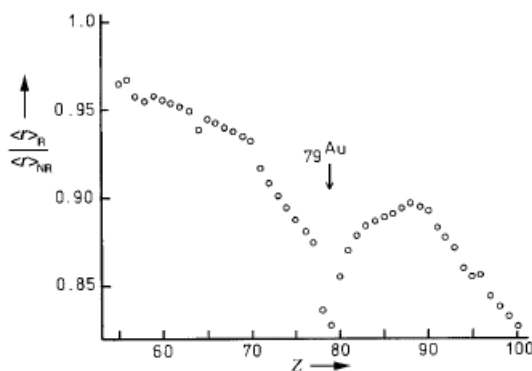

Figure 3. *Ratio of relativistic and non-relativistic 6s-shell radii of elements 55-100.*[9]

   One of the most physically observable relativistic effects in gold is its yellow color. The 6s orbital of gold is stabilized by the relativistic contraction, resulting in the single electron ($[Xe]4f^{14}5d^{10}6s^1$) in the orbital being more tightly bound (consequences

on ionization and affinity will be discussed later). The 5d orbitals are totally filled and it is the 6s orbitals that constitute the Fermi-level. The energy splitting diagram thus shows that the 6s Fermi level is lower in gold than the 5s Fermi level in silver, resulting in band gap transition energies of 2.4eV and 3.5eV, respectively (Figure 4). The latter energy corresponds to the ultraviolet region of the spectrum, accounting for the color of silver, while the former corresponds to the blue region of the visible spectrum, accounting for the emission of the yellow wavelength in gold.[2]
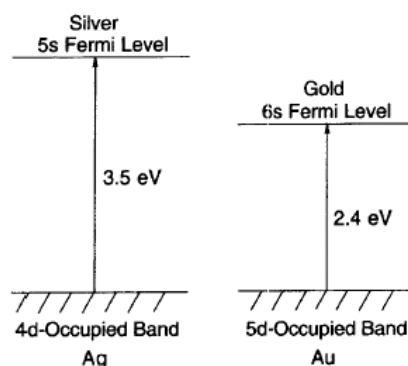

Figure 3. *Fermi-level energy diagram for silver and gold.[2]*

The stabilization of the 6s electron is also evident in the unusual ionization energy (IE) and electron affinity (EA) trends of the group 11 elements. As one proceeds down a given group in the periodic table, an observable decrease in IE is expected due to an increase in radius, and subsequently, the distancing of the outermost electron from the nucleus. While this trend is followed by many main-group elements, it is severely violated by group 11 elements, as shown in Figure 5. Calculations show that in the absence of relativistic effects, the expected trend is followed; however, relativistic effects significantly increase the IEs and EAs of the heavier group 11 atoms, making these energies higher than those of both silver and copper, clearly an anomalous trend. Using the electronegativity (EN) principles of Mulliken, EA = ½(IP+EA), the EN of gold may be estimated at 2.4, making it as electronegative as iodine (EN = 2.2) and a "pseudohalide."[6]

This trend toward a more tightly bound 6s electron is coupled with a tendency for the 5d electrons to be more loosely bound, allowing for the 5d orbitals and the 6s and 6d orbitals to take part in bonding, resulting in strong covalent bonds. For example, the

dissociation energies of Au_2, Ag_2 and Cu_2 are 2.29eV, 1.65eV, and 1.95eV, respectively.[10]
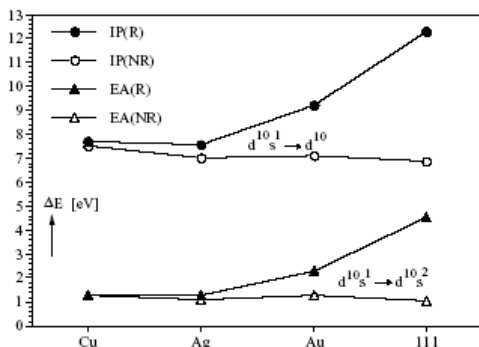

Figure 5. *Relativistic(R) and non-relativistic(NR) ionization potentials and electron affinities of group 11 atoms.*[6]

Aside from the properties of the metal, gold molecular compounds are also affected by relativity. In some instances, calculations show large bond contractions ($\Delta_R r_e$ > 0.3 Å) with gold-ligand bond lengths sometimes smaller than corresponding copper distances. As would be expected, contracted bond lengths are dependent upon the 6s orbital occupation of gold. For example, the interaction of Au^+ with electropositive ligands (Li, Na) result in M^+Au^- type compounds with large relativistic contractions, while the interaction with electronegative ligands yields Au^+X^- compounds with small contractions (Figure 6). Relativistic effects are also present in higher oxidation states of gold.[6]
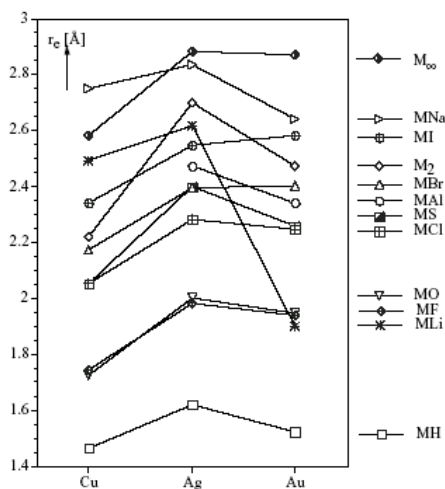

Figure 6. *Bond distance variations for diatomic Group 11 compounds.*[6]

Another interesting manifestation of relativity is attributed to the properties of mercury, both in its liquid metallic form and its stable ionic species. The 6s and 5d orbitals of mercury are totally filled in its electronic configuration. The enhanced stabilization of the two electrons in the 6s shell renders them quite inert; the result is a tightly bound pair of electron that is not easily shared in forming Hg-Hg bonds. In fact, mercury is the only metal that is monatomic in the gas phase. In its liquid form, mercury is also a poor conductor of electricity, an anomaly compared to its analogs.[11] Relativistic calculations of the Hg-Hg potential indicate that it has only 45% of the magnitude of a non-relativistic one.[7] In contrast, Cd_2 and Zn_2 are strongly bound; the formation of bonds in these two compounds is due to the relatively low promotion energy, $(ns^2)^1S \rightarrow (ns^1np^1)^1P$, compared to that to form Hg_2. The promotion energies for Zn and Cd are 5.8 eV and 5.4 eV, respectively, compared to 6.8 eV for Hg.[2]

An interesting consequence of the instability of Hg_2 is the unusual stability of the mercurous ion, Hg_2^{2+}, as evidenced by the existence of compounds such as Hg_2Cl_2. In contrast, the analogous Cd_2^{2+} and Zn_2^{2+} species are unstable. The relativistic stabilization of the 6s orbital favors the formation of Hg_2^{2+} which is isoelectronic with Au_2 and has a closed shell configuration. The stabilization of this orbital results in what has been called an "inert-pair" effect. The Cd_2^{2+} is also isoelectronic with Au_2, but the 5s orbital sees no relativistic stabilization. Thus, the promotion energy is low and the effort to remove electrons from the 5s orbital is considerably less, thus favoring the formation of Cd^{2+} and Zn^{2+} species.[11]

The inert-pair effect from relativistic stabilization has been mostly attributed to the valence observations in the heavy main group elements, particularly Tl, Pb, and Bi. In these elements, the energy required to remove electrons from the 6s orbital is considerably greater than from the 5s orbital in In, Sn, and Sb. Hence, the stable oxidation states for the heavier elements are Tl^+, Pb^{2+}, and Bi^{3+}, two less than the group number. In contrast, the stable oxidation state for the lighter group 3 elements (B, Al, Ga, In) is the trivalent state. The instability of the bonding in compounds such as Tl_2 and Pb_2 compared to the lighter analogs may be attributed to the ns-np splitting energy. In order to form these dimers, a promotion of the 6s electron to the 6p orbital is required; this splitting is unusually high for these elements, however, thus causing the instability.[2]

Relativistic effects have also been attributed to the differences in electronic configuration between Pt and Pd which are $[Xe]5d^9 6s^1$ and $[Kr]4d^{10}$, respectively. The stabilization of the 6s orbital due to the mass-velocity correction causes the Pt atom have a $^3D_3$ ground state in contrast to the $^1S_0$ ground state of Pd. The $^3D_3$-$^1S_0$ splitting is 6140cm^{-1}, while the $^1S_0$-$^3D_3$ splitting is 6564cm^{-1} for Pd.[11] Stabilization of the same orbital also accounts for differences in the dimers, Pd$_2$ and Pt$_2$. The $^1\Sigma^+_g$ state of Pt$_2$ leads to a shorter, stronger bond (2.45 Å) as compared to the same state in Pd$_2$ (2.87 Å) due to predominant π^2_g and $1\sigma^2_g 1\sigma^2_u$ configurations, respectively (a consequence of the differing ground states of the atoms). In general, Pt$_2$ bond lengths are shorter than those in Pd$_2$ for many electronic states of the dimers. The difference in electronic and spectroscopic states of the two dimers is attributable to spin-orbit effects which will be described later.[11]

An interesting point to note is the effect that the 4f electrons play in many of the observed anomalies. The incomplete screening of the 4f electrons has been attributed to what has been called the lanthanide contraction. Due to the compact nature of these orbitals, their electrons do a poor job screening the nuclear charge; hence, the 6s and 5p orbitals feel a significant fraction of this charge and subsequent non-relativistic contraction and stabilization.[5] The degree to which the 4f orbitals and relativistic effects account for the lanthanide contraction and the stabilization of the 6s orbital has been the subject of many studies.[12,13] While it is true that the sub-structure effects of the 4f orbitals do indeed cause the 6s orbital to be stabilized, it is the relativistic effect that causes the 4f orbitals to considerably expand, thus resulting in a poorer screening of the nuclear charge. Hence, the 6s electrons spend more time close to the nuclear and are subjected to enhanced relativistic effects. Calculations by Pitzer et al. have shown that nearly 30% of the lanthanide contraction may be attributable to relativistic effects.[2]

The second most significant relativistic effect, aside from the mass-velocity correction, is the spin-orbit coupling which tends to complicate electronic spectra and can also manifest itself in bond strengths and other phenomena. Spin orbit coupling increases dramatically with increasing nuclear charge and for a given quantum shell decreases as p>d>f.[5] In the case of the group 14 elements, spin orbit coupling of the $^3P_0$ and $^3P_2$ spin states increases significantly going down the group, as shown in Figure 7.

Energy Terms for Fourth Group Elements (Electronvolts)

element X	ionization potential	X₂ bond D_0	spin-orbit $^3P_2 - ^3P_0$
C	11.26	6.1	0.005
Si	8.15	3.2	.03
Ge	7.88	2.8	.17
Sn	7.34	2.0	.42
Pb	7.42	1.0	1.32

Figure 7. *$^3P_0$ and $^3P_2$ spin-orbit coupling for group 11 atoms.*[10]

The spin-orbit energy is relatively small compared to chemical bond energy for the pre-Pb atoms, but is larger than the dissociation energy(D_e) in Pb_2, thus accounting for the relatively weak Pb-Pb bond.[10] This trend in decreasing dissociation energy is also observed in the halogens. As one proceeds from F_2 to At_2, calculations show a relativistic destabilization of the dihalogen bond, resulting in increased bond lengths and lower D_e values. The cause is an increase in the spin-orbit splitting between the $p_{1/2}$ and $p_{3/2}$ orbitals in the heavier halogens, thus making the formation of pure π and σ bonds unfavorable.[14] As was mentioned earlier, the electronic and spectroscopic states of Pt_2 and Pd_2 are quite different. Spin-orbit splittings for Pt_2 are much larger than Pd_2, as would be expected. For example, the spin-orbit splitting for $^3\Gamma_u(5u) \rightarrow ^3\Gamma_u(3u)$ of Pt_2 and Pd_2 is 15,192 cm^{-1} and 5214 cm^{-1}, respectively.[2]

More dramatic effects of spin-orbit coupling are observed in electronic transition spectra, where many transitions that are not allowed in non-relativistic theory become observable. For example, in non-relativistic theory, the transition in mercury corresponding to $^3P_1 \rightarrow ^1S_0$ is a "spin-forbidden" transition. However, this transition is intense and readily observable at 2537 Å and is overwhelming evidence that spin alone is not a good quantum number in heavy elements, but is coupled.[10] A further example is the relativistic versus non-relativistic picture of the molecular orbital energy levels in OsO_4 (Figure 8). The relativistic calculations based on the tetrahedral molecule show a much greater degree of energy level splitting based on the availability of non-integer J values.[5]
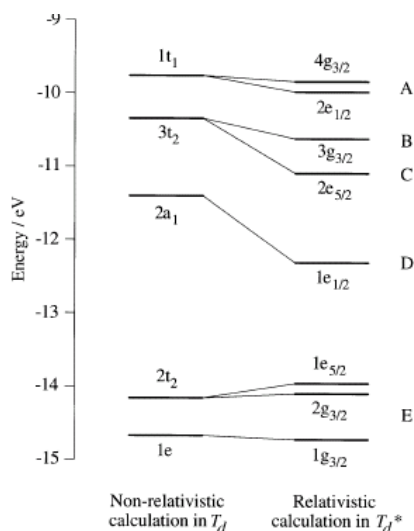
Figure 8. *Relativistic and non-relativistic molecular orbital energy levels for OsO₄.*[5]

Studies on the effects of relativity have by no means been limited to just individual heavy atoms and simple diatomic molecules. Relativistic calculations have been used to study the adsorption of CO and hydrocarbons on Ni, Pd and Pt surfaces[8,15], organometallic complexes containing lanthanides and actinides[5,16], and the complicated electronic spectra of the UO_2^{2+} and NpO_2^+ ions[17,18], just to name a few. Relativistic effects in the early actinides are particularly interesting due to the challenges in eliciting the degree to which the 5f electrons participate in chemical bonding, in addition to making the calculations much more difficult.[19]

References

1. Feynman, R. P. *Feynman Lectures on Physics*; Addison-Wesley, New York, 1970.
2. Balasubramanian, K. *Relativistic Effects in Chemistry, Part A: Theory and Techniques*; Wiley Interscience: New York, 1997.
3. Balasubramanian, K. *J. Phys. Chem.* **1989**, *93*, 6585-6596.
4. Choppin, G.; Liljenzin, J. O.; Rydberg, J. *Radiochemistry and Nuclear Chemistry*; Butterworth-Heinemann: Oxford, 1995.
5. Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1996**, 1-11.
6. Schwerdfeger, P. *Heteroatom Chem.* **2002**, *13*, 578-584.
7. Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276-281.
8. Bond, G. C. *J. Mol. Catal. A: Chem.* **2000**, 156, 1-20.
9. Pyykkö, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 3573-3578.
10. Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271-276.

11. Balasubramanian, K. *Relativistic Effects in Chemistry, Part B: Applications*; Wiley Interscience: New York, 1997.
12. Küchle, W.; Dolg, M.; Stoll, H. *J. Phys. Chem. A* **1997**, *101*, 7128-7133.
13. Seth, M.; Dolg, M.; Fulde, P.; Schwerdtfeger, P. *J. Am. Chem. Soc.* **1995**, *117*, 6597-6598.
14. Visscher, L.; Dyall, K. G. *J. Chem. Phys.* **1996**, *104*, 9040-9046.
15. Pacchioni, G.; Chung, S.-C.; Krüger, S.; Rösch, N. *Surface Sci.* **1997**, *392*, 173-184.
16. Kaltsoyannis, N. *Chem. Soc. Rev.* **2003**, *32*, 9-16.
17. Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*: 6880-6886.
18. Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* **2000**, *104*, 4064-4068.
19. Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719-741.