Relativistic Effects in Structural Chemistry

Part 3 of my quest to remind math grads that physical reality exists and is worth thinking about occasionally

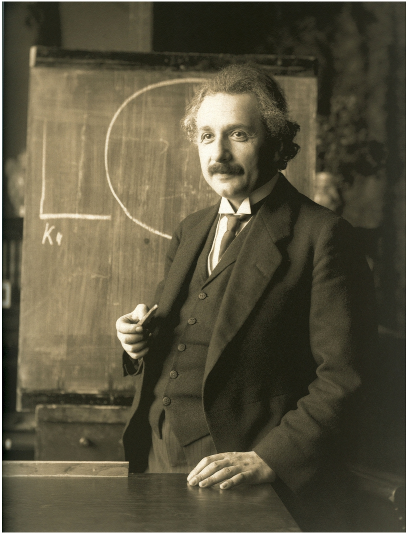
Gyu Eun Lee

December 5, 2018

Content

A return to practical concerns

Relativity! What is it good for?



- Left: famed Swiss patent officer Albert “Al” Einstein
- Introduced special relativity in 1905
- Introduced general relativity in 1915
- Proud honorary member of the Plumbers and Steamfitters Union
- Did some other neat stuff too

A return to practical concerns

Relativity! What is it good for?

Well-known modern applications of relativity:

- Global Positioning System (GPS)
- Cathode Ray Tubes (CRT)
- High-precision scientific measurements (e.g. electron microscopy)
- Using above applications to justify applications/impacts statements in grant proposals (!!!)[1]

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Most people can’t tell you how these devices work, or how relativity specifically factors into them.
But what if relativity were closer to home than you thought?

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A return to practical concerns

Three silly questions (answers in the back)

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- Why does mercury merc?
- How do car batteries work?

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- Why is gold yellow?
- Why does mercury merc?
- How do car batteries work?

We will see that relativity plays a key role in each of these!

High school chemistry

Atomic structure and orbitals

Basic constituents of an atom:

- A positively charged nucleus made of protons and neutrons.
  - Most of the mass of the atom, but very little of the volume.
- A collection of negatively charged electrons.
  - Can approximately be considered to be moving around the nucleus within certain regions called *orbitals*.

High school chemistry

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- m_s: The electron's internal spin (i.e. mumbo-jumbo). Two electrons (for the two spin states) can occupy any given orbital.

High school chemistry
Atomic structure and orbitals

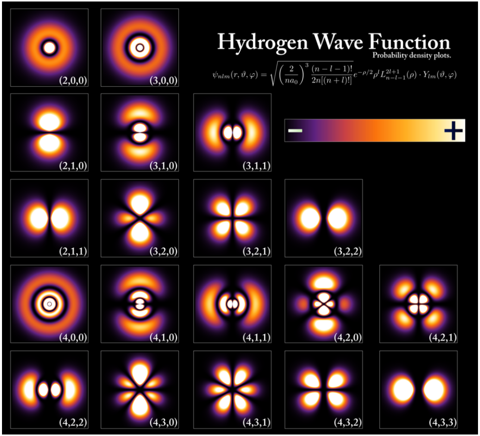

Figure: Plots of the wavefunction for an electron bound to a hydrogen atom for different values of (n, ℓ, m_ℓ).

High school chemistry

Atomic structure and orbitals

For historical reasons and convenience, the following notation is used to denote electron orbitals:

- $\ell = 0$ is called the *s* subshell, for “sharp.” Max electrons: 2.
- $\ell = 1$ is called the *p* subshell, for “principal.” Max electrons: 6.
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This is used to help denote an atom’s electron configuration.

- Neutral neon atom, ground state: $1s^2 2s^2 2p^6 = [Ne]$. (Two 1*s* electrons, two 2*s*, six 2*p*.)
- Phosphorus: $1s^2 2s^2 2p^6 3s^2 3p^3 = [Ne]3s^2 3p^3$. (All electrons in neon configuration, then valence subshells consisting of two 3*s*, three 3*p*.)

High school chemistry

Atomic structure and orbitals

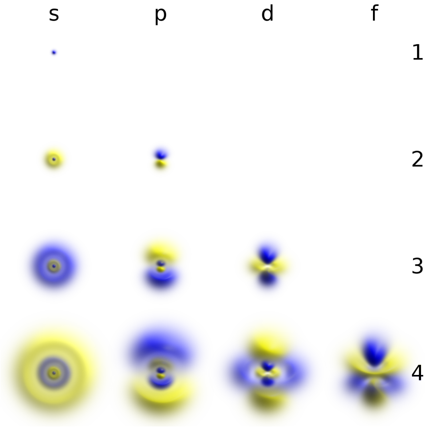

Figure: 3d visualizations of the shapes of the electrons clouds for various subshells, from $n = 1$ to $n = 4$.

Mo protons, mo problems

In which we sacrifice electrons to appease the gods

We now consider heavy atoms, i.e. atoms with large atomic numbers, which have lots of electrons.
Important but complicated question: How do electrons in different orbitals interact?

- Dominant forces: Coulomb force (electrostatic attraction/repulsion)

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- Electrons are attracted to the nucleus and repelled from each other
- Important consequence: electron shielding

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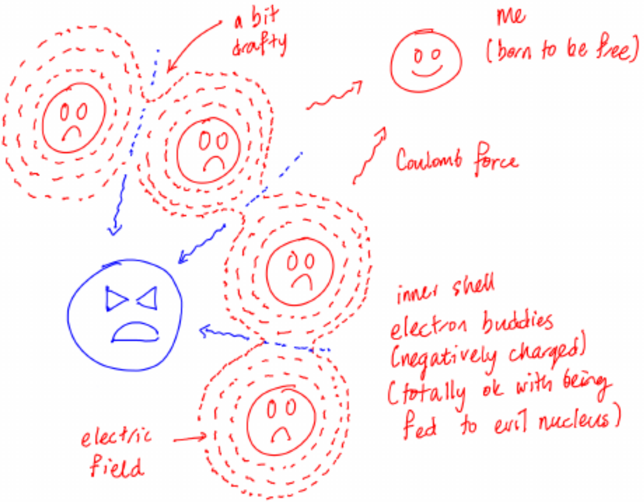

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In which we sacrifice electrons to appease the gods

Qualitative properties of electron shielding:

- Outer shell electrons are destabilized since they are shielded from nuclear attraction
  - In particular, outer shell electrons find it easier to move to higher energy orbitals

Mo protons, mo problems

Protip: for a slim and healthy look, run at the speed of light

- We take atomic units: electron mass, elementary charge, reduced Planck's constant, Coulomb's constant normalized $= 1$.
- With these units, speed of light is $c \approx 137$.

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Bohr hydrogenic atom model (nonrelativistic):

- Relatively massive nucleus of charge Z (corresponding to Z protons)
- Relatively massless electrons orbiting in classical trajectories within spherical shells, whose radii are quantized by the energy level of the electrons

Mo protons, mo problems

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Important facts:

- The radius of the 1*s* shell in the Bohr model is given by

$$r_{\text{Bohr}} \propto \frac{1}{Zm_e} = \frac{1}{Z}.$$

- The average radial velocity of an electron in the 1*s* subshell is given by

$$\langle v_r \rangle = Z.$$

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- Key observation: Since $c \approx 137$, and $Z = 1, 2, 3, \ldots$, a 1s electron reaches relativistically significant speeds!

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We now introduce relativity:

- An electron in motion experiences a relativistic mass correction which depends on its speed:

$$m_{e,\mathrm{rel}} = \frac{m_e}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{m_e}{\sqrt{1 - \frac{v^2}{137^2}}} = \gamma m_e.$$

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- Replacing v with the average velocity $\langle v_r \rangle = Z$ gives average relativistic factor:

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$$\gamma = \frac{1}{\sqrt{1-\frac{Z^2}{137^2}}}.$$

- Replacing m_e in the Bohr radius formula by $m_{e,\mathrm{rel}}$ gives a relativistic correction to the Bohr radius:

$$r_{\mathrm{Bohr,rel}} \propto \frac{1}{Zm_{e,\mathrm{rel}}} = \frac{1}{Zm_e}\frac{m_e}{m_{e,\mathrm{rel}}} = \frac{1}{\gamma Z}; \quad r_{\mathrm{Bohr,rel}} = \frac{r_{\mathrm{Bohr}}}{\gamma}.$$

Mo protons, mo problems

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Since $\gamma > 1$, $r_{\text{Bohr,rel}} < r_{\text{Bohr}}$: thus relativistic effects contract the 1*s* subshell. The strength of the relativistic correction γ depends on Z, the atomic number.

- $Z = 1$ (hydrogen): $\gamma \approx 1.000$, $\gamma^{-1} \approx 1.000$.
- $Z = 20$ (calcium): $\gamma \approx 1.011$, $\gamma^{-1} \approx 0.989$.

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- $Z = 57$ (lanthanum): $\gamma \approx 1.100$, $\gamma^{-1} \approx 0.910$.
  - Correction strength exceeds 10% for first time.

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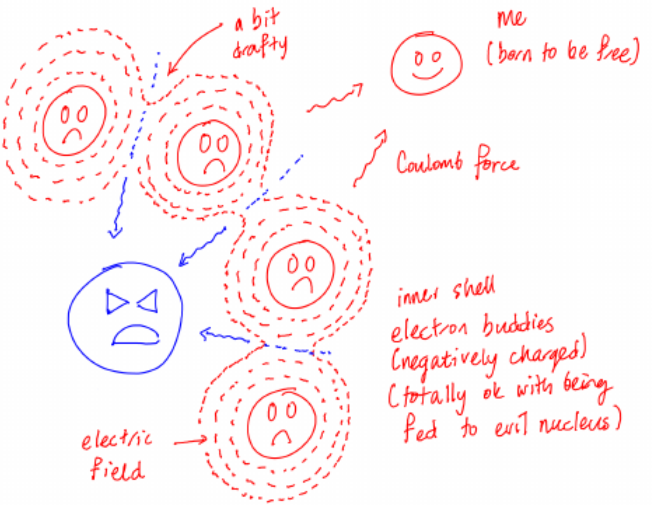
  - Correction strength exceeds 10% for first time.
- $Z = 79$ (gold): $\gamma = 1.224$, $\gamma^{-1} \approx 0.817$.
  - 1*s* shell radius contracts nearly 20% due to relativity.

Similarly, the other *s* subshells experience a relativistic contraction. The *p* subshells do as well, but the effect is less pronounced.

Mo protons, mo problems

Relativity, ritual sacrifice, and you



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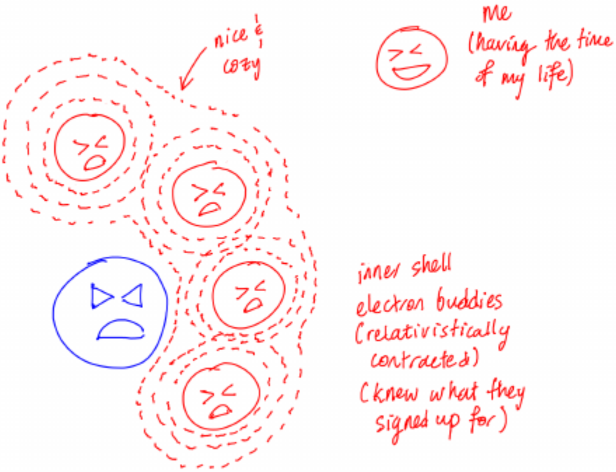

Mo protons, mo problems

Relativity, ritual sacrifice, and you

Practical effects of relativity on valence shells:

- Relativistic contraction stabilizes valence *s* and *p* shells
- Stronger electron shielding destabilizes valence *d* and *f* shells

Mo protons, mo problems

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Practical effects of relativity on valence shells:

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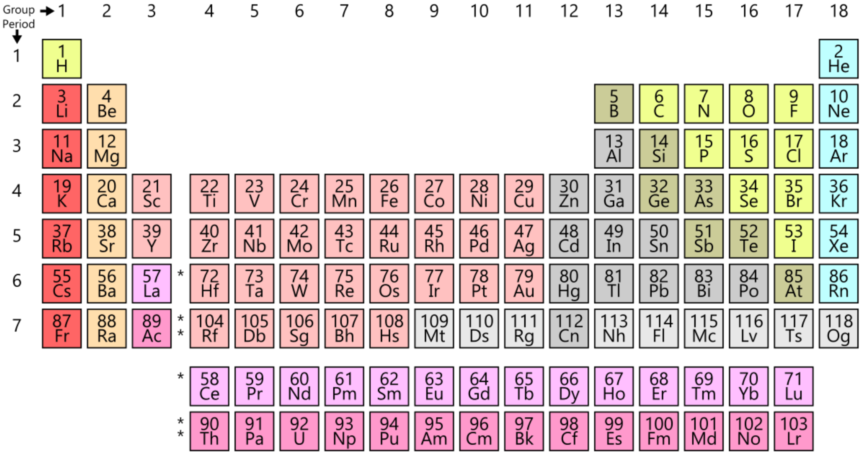
Effects are most pronounced in period 6 of the periodic table:

- 6*s* shell tends to be stabilized
- 5*d* shell tends to be destabilized

Answers to selected exercises

Periodic table (for reference)



Group → 1 Period ↓	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Answers to selected exercises

Why is gold yellow?

- Color = wavelengths of reflected light
- Reflected light = all light not absorbed
- When atoms absorb photons, their valence electrons shift orbitals to account for higher energy
  - There are only finitely many orbitals, each with fixed energy, therefore a given atom can only absorb photons of certain energies
- Object appears yellow if object absorbs blue light (blue light is complementary to yellow light)
- Real question: Why does gold absorb blue light?

Answers to selected exercises

Why is gold yellow?

- Gold ($Z = 79, \gamma \approx 1.224$) configuration: $[Au] = [Xe]4f^{14}5d^{10}6s^{1}$
- Most energetically favored energy transition is a 5*d*-6*s* transition
  - 6*s* orbital stabilized, 5*d* orbital destabilized $\implies$ 5*d*-6*s* transition requires less energy
- Precise energy needed turns out to be 2.4 eV, corresponding to light of wavelength 516 nm (blue light)

Answers to selected exercises

Why is gold yellow?

For comparison:

- Silver ($Z = 47$, $\gamma \approx 1.065$) configuration: $[Ag] = [Kr]5s^1 4d^{10}$.
- Same group as $[Au]$, much weaker relativistic effects
- Most energetically favored energy transition is $4d$-$5s$; weaker relativistic effects $\Longrightarrow$ transition requires more energy than in Au
- $4d - 5s$ transition requires an energy of 3.7 eV, which corresponds to 335 nm (ultraviolet light).
- Consequently silver (along with several other metals) reflects most visible light
- On a related note, silver is commonly used as the reflective coating in mirrors

Answers to selected exercises

Why does mercury merc?

- Mercury: atomic number 80, electron configuration $[Hg] = [Xe]4f^{14}5d^{10}6s^{2}$.
- Mercury has low melting point, electrical conductivity, and is relatively nonreactive (especially compared with neighboring elements)
- These properties summarized by: bonding forces between mercury atoms are unusually weak. Why?

Answers to selected exercises

Why does mercury merc?

- $[Hg] = [Xe]4f^{14}5d^{10}6s^2$ is an unusual configuration
  - Consists entirely of completely filled subshells, like a noble gas
  - Such configurations resist the addition and removal of electrons
  - $\Longrightarrow$ *Hg*-*Hg* bonds are already hard to form from the electron configuration alone

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- Outermost electrons (most relevant to bonding) in this configuration are the $6s^2$ electrons
  - $6s$ shell is relativistically stabilized, hence the $6s$ electrons resist being shared
  - $\implies$ *Hg*-*Hg* bonds even harder to form due to relativistic effects

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  - $\implies$ *Hg*-*Hg* bonds even harder to form due to relativistic effects
- Therefore *Hg*-*Hg* bonds are abnormally weak, contributing to low melting point & other unusual properties

Answers to selected exercises

How do car batteries work?

- Lead: atomic number 82, electron configuration $[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$
- Most automobile batteries are 6-cell lead-acid batteries
- Lead-acid battery reaction relies on the strong oxidation properties of the reactant $Pb(IV)O_2$
  - i.e. $Pb(IV)O_2$ accepts additional electrons extremely well
- Question: Why is $Pb(IV)O_2$ so willing to accept additional electrons?

Answers to selected exercises

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Answers to selected exercises

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- $Pb(IV)O_2$ is in an oxidation state $\Longrightarrow$ already pretty good at accepting electrons
- $Pb(IV)$ atom in $Pb(IV)O_2$ has an unfilled $6s$ shell, which is relativistically stabilized
  - $\Longrightarrow$ filling this shell is energetically favored
  - $\Longrightarrow$ reinforces already high oxidation strength of $Pb(IV)O_2$

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- Typical single lead-acid battery cell: electromotive force of $\approx 2.11\ V$. Numerical simulations of this reaction:
  - Relativistic model predicts an average electromotive force of $\approx 2.13\ V$
  - Nonrelativistic model predicts an average electromotive force of $0.39\ V$

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  - Relativistic model predicts an average electromotive force of $\approx 2.13\ V$
  - Nonrelativistic model predicts an average electromotive force of $0.39\ V$
- Thus relativity accounts for over 80% of the electromotive force in a lead-acid battery $\Longrightarrow$ cars start due to relativity

Closing I

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