Content: Electrostatic equilibrium in ground state molecules
ES 24 April 2018

Hellmann-Feynman theorem

1) A bit of (personal) history

Many textbooks of elementary chemistry do not know anything about the electrostatic equilibrium (Hellmann-Feyn-man electrostatic theorem) of ground state molecules. They mention electrostatic forces in the context of ionic (electrovalent) bonds in contrast to atom (covalent) bonds. The latter are thought of having nothing to do with electro-static forces - at least for non polar, neutral molecules like H2, N2, O2. The atoms are held together by electron-pair bonds, period.

This erroneous notion probably has its origin in the fact, that the result of the first computation of the covalent bond of the H2 molecule by Walter Heitler & Fritz London, Z.Physik.,44,455(June 1927) is far from a correct representation of the physical system (errors in dissociation energy -50%, in bond length + 16%): Slater has indicated, ". . . the Hell-mann-Feynman theorem has been less [useful]. The reason is that most molecular work has been done with very inaccurate approximations to molecular orbitals." (J. C. Slater, "Solid State and Molecular Theory", Wiley, 1975). Which is to say, the approximations of ψ are often insufficiently accurate models of the physical system (cit. D. Wal-lace, see below). It is very dangerous to derive a cause and effect description from such a crude calculation.

When W. Heitler, during his periodically held lecture "The chemical bond" at the University of Zurich (~1960), was asked specifically, he explained the cause of a "bond" between two H atoms by a rapid exchange of spin states - ↑↓ ↔ ↓↑ - of the two bonding electrons (hence, some (physicists) speak about "spin-valence", although interaction of spins has nothing to do here. However, the spins' orientation, antiparallel or parallel together with Pauli's principle decide whether a bond is formed. This is generally valid and not restricted to the Heitler-London ansatz).- My PhD students and myself, who were participating in the lecture, could not understand Heitler and so asked him, which physical law(s) were involved for creating a bond by just exchanging two (energy-)equivalent and indistinguishable spin states. Heitler was not able to give an answer, and said so [*this is already mentioned on page 460 of H-L's paper (1927): "Von einem wirklichen Verständnis dieses Sachverhaltes sind wir noch weit entfernt". It relates to the fact (in modern parlance!, not H-L), that two H-atoms, coming together, can interact in two ways: With a probability of 1/4 they attract each other and form a molecule with antiparallel ↑↓ spins of the electrons and a symmetric molecular wavefunc-tion (since the H2 molecule cannot radiate, having no dipole moment, no bond ever can be formed, unless a "third body" collides with the molecule in formation to dissipate bond energy as "heat" !); in 3/4 of the encounters parallel spins of the electrons force the population of a triplet configuration with two orbitals, one of them antisymmetric with a node of its molecular wavefunction between the protons, hence the H-atoms repel each other). This qualitative insight is the main, very important, contribution of H-L, at the time "unknown [even] to chemists"(?), as quoted in the paper. It is reported, that it came to Heitler, while dosing in bed. Then he called London and they wrote the paper together in one or two days and nights! It is interesting that Heitler repeated the statement of "not understanding" 1960, although between 1927 and 1960 much work has been done to clarify and "understand" this quantum mechanical behavior (perhaps, Heitler meant that only classical physics deserves the qualifier "understandable"? Regrettably, he did not clarify). Already in December 1927 F. London (alone!) worked on an improved discussion, published in Z.Physik,50(1928),51, and later a generalization of this problem (for his Habilitations-Schrift). It was certainly clear in 1928 when Pauli had published the proof of his principle with the complete theory of electron spin*].

Hence, the physicists in that lecture learned from Heitler that the chemical bond of H2 cannot be understood. I heard about this strange notion while giving a one week course to Gymnasium teachers together with a physics professor from Heitlers institute (1986). I had just finished deriving the electrostatic equilibrium between the attraction of the proton by the bonding electron distribution and the repulsion by the other proton in the H2 molecule when my physics colleague told the audience that bonding in H2 is not understandable! This gospel has spread and can still be read today, e.g. in one contribution to the (german) Wikipedia. BtW one of the hardest critics of the Heitler-London paper has been Wolfgang Pauli.

Of course, it is anybody's free decision, to state that results e.g. from quantum chemistry are not understandable (assuming that (s)he has honestly studied the field) ... which provokes immediately the question: What do you mean by *understanding*? and then you get into the wasps nest of disagreeing schools of philosophers. Some of them might even go for your head if you don't share their belief.-

Quantum mechanics (QM) is a tool that was invented to explain experimental results. It is nothing more and nothing less than that. Therefore, it may also prevent humans to bash-in each others heads. It is very simple: Evolution has not foreseen humans to grasp phenomena not noticeable by their sense organs. Objects smaller than about 0.0001 meters cannot be perceived. Hence, they, e.g. ancient Greek philosophers, had to fantasize about a world with objects smaller than that. One of them - Democritos - stated that matter (the universe!) is made of *atoms* and *empty space*, and he included the soul (as part of the universe) as well.This provoked bash-ins by philosophers of a different view. The problem was, that neither had the means to look beyond human vision and thus prove his point. As soon as this was possible, to some degree, by the invention of the light microscope in the 17th century, the accumulated historical "wisdom" about the microscopic world collapsed, much to the indignation of the religious hierarchy which had pressed for faith in what this or that philosopher had preached. They either put a ban on the microscope or burned those having talked about things observed by its means not described in a holy book (take this with a grain of salt! but that was the fate of heretics). Fortunately, some survived the purges and continued to look into the world with enhanced sensors, telescopes, spectroscopes, and finally, all the wonderful scientific instruments we have now at our disposal. They uncovered a world which was entirely outside the language which we have learned for talking about our daily experiences and philosophies. A new language had to be invented to adequately describe the observed microscopic and cosmic phenomena. This language has a name: **Mathematics**. It is very old and has well served in the common world but is entirely open for new "words", "concepts", "ideas" and even new "syntax" and "grammar". With its help scientists have learned to "describe" precisely the phenomena for which our daily language has no words. *Niels Bohr* has invented the "*Correspondence Principle*" which helps to "understand" how the new mathematical language converges to our daily language when the dimensions of the objects of our interest merge into those we are used to. It appears that the evolution of the human brain and thus understanding the world in terms of everyday life is entirely hooked to the spatial and temporal dimensions we live in.
IMHO the atom of Democritos, celebrated as an epochal philosophical thought by classical philologists, is in fact trivial (except for the *empty space* which served as embedding "medium"): Either the material world can be subdivided ad infinitum or not (or, thirdly: This macroscopic view may not be meaningful). Unless there exist observations, measurements or phenomena predicted by one or the other hypotheses (and not by both), the two opinions are equivalent. The irony is, that the chemical "atom" of the nineteenth century was often identified as the atom of the Pre-Socratic philosophers. However, it had a short life: At the beginning of the twentieth century, *E. Rutherford* showed the atom to be composed (hence divisible, not a-tomic) of a tiny positively charged nucleus embedded in a low density cloud of negative charge from which electrons can be ejected. A couple of years earlier, nature revealed to *H. Becquerel* that some heavy atoms disintegrate spontaneously and produce a.o. the known element Helium. And the atoms demolition and that of its sub-, sub-sub- ... particles goes on, still using essentially Rutherfords technique of colliding "particles", now highly developed. Perhaps Democritos meant always the last not jet subdivided particle (or what remains, when the high energy physicists at CERN run out of power)? Certainly not! No Greek at the time of Democritos would have thought about complex valued "wavefunctions" in (empty) space and time (or a C*-algebra to describe them correctly). Don't take "wave" literally, it is a mathematical concept for accurately describing atomic

properties (not only densities of electron distributions!) and has *no* macroscopic analogue. Hence, the material world has become shadowy. Already in the chemical realm "atoms" cannot be described by words we use for everyday matter. Free atoms and even molecules (e.g. C60, not only electrons!) can form diffraction patterns behind a double slit or its modern analogs! "Empty space" is, perhaps, even more enigmatic: It can explode to create a universe of "matter" and "antimatter", which annihilate each other creating light quanta ... but not totally: The rest is the universe of "matter" of which we are a part and try to understand! Atomic "matter" (what is this? certainly not a macroscopic chunk of a pure chemical element but, perhaps, an atomic beam in vacuum and single, isolated molecules, like the fullerene C60 in a molecular beam) does not belong to the world in which we make, sell and buy material objects, hence their strange behavior. "Materialism" vanishes into thin air at the atomic dimension and even more so at its sub-sub divisions. Read e.g. Heinzwerner Preuss: "Materie ist nicht materiell", Vieweg 1997, or google for a vast literature about this topic (e.g. the "The Magic Mountain" by Thomas Mann)?

So, perhaps, *understanding* now means, that we have learned to use and thus become accustomed to the tools of that mathematics which gives us answers in the realms of nature unknown to our sense organs. And, most importantly, a mathematics which can be falsified by experiment or observation and its inherent laws of logic. We also have to accept, that there are many layers of mathematical sophistication in any field. Quantum Mechanics has been proven to be (one of, or perhaps) the best, i.e. most accurate, physical theories known. Often its application is exceedingly difficult, and we have to be content with a rough approximation in order to obtain a mathematical result. But even that may be good enough to decide cases of disagreement and thus avoids to bash-in the heads of those with another opinion. More than 100 years of experimental chemistry has developed an operational language to describe and manipulate molecules. It is a very successful macroscopic language, but dealing with microscopic phenomena. Hence, it is essentially non mathematical (except for proofs built on symmetry incl. pattern recognition, i.e. distinguishing nonidentical molecules). Today, we have a good start for understanding its strange words and structure, using the mathematics of the molecular world.

Take e.g. the H2 molecule, again. It took about 40 years from the pioneering work of Heitler and London 1927 to 1964/68 and 1969 when its understanding was complete (spectroscopic observations and theory of many excited states still goes on!): W. Kołos and L. Wolniewicz were much improving the successful approach of James & Coolidge (1933, direct computation of molecular orbitals, not using atomic orbitals like Heitler-London!). They accurately predicted the spectrum of H2 and several other properties (of the ground and several excited states), among which its dissociation energy D into two H atoms from fundamental constants c,e,h,me,Mp, spin moments and some small corrections for relativity and quantum electrodynamics. Their solution gave a molecule a bit more stable than the most precise spectroscopic measurement to that day which contradicted the holy law of the *Variational Principle*. This

forced G. Herzberg 1969 to go back into his laboratory and correct his measurement by a closer examination of the ultraviolet absorption limit on the photographic record. He had overlooked a weak group of lines before he was confronted with the theoretical result! Including those and recomputing D led now to a difference between experiment and theory of less than +1 in 100'000 and with the correct sign. That was a triumph for Quantum Chemistry! The Hellmann-Feynman electrostatic equilibrium, which was badly at odds in the Heitler-London calculation, was finally established within experimental precision. This brought the real understanding of the covalent chemical bond (which Heitler, by his own words, could not understand). Now the easily comprehensible electrostatic equilibrium between opposite forces, repulsion of nuclei and attraction of each nucleus by an electron charge distribution, which has to be computed by Quantum Mechanics, was the main ingredient of the covalent bond in H2 (and generalization).

This told, it is a bizarre story that people still fight about which of two methods is better, *valence-bond* (Heitler-London, Slater, Pauling a.o.) or *molecular orbital* (Hund-Mulliken, Roothaan, Hückel, Hoffmann, Pople a.o.) theory of molecular structure. Both are badly off in their zeroth order attempt (which is the level of the qualitative VB and LCAO-MO languages of the research chemist!), identical(ly bad) in first order and almost within experimental error limits at a higher order of approximation. Today there exist other methods, equally good or better than the two protagonists, e.g. *Density Functional Theory* (Walter Kohn, making orbitals obsolete, eventually) and various codes for Car-Parrinello *Molecular Dynamics* (not as accurate but with a tremendous scope). Finally, the usefulness of these computational

chemistry tools depends on the trivial fact (but far from trivial methodology), whether they can be coded as efficient computer programs (especially for much larger molecules than H2, e.g. the protein Crambin with 644 nuclei $C_{202} H_{317} O_{64} N_{55} S_6$ and 2522 electrons, which has been computed with high precision by Frank Neese et al. 2013 with the ORCA code). Hence, no reason to bash-in somebody's head.

What IS an electron? Some say "it is a wave not a cloud" or "it's not a wave, it is a hard particle of some 0.01 attometers diameter (as measured in the Stanford LINAC)". - We just do not know because none of these descriptors from our macroscopic world have analogues in the microscopic realm. So, any fight about these words is for nothing! But, we can accurately *describe* electrons with Schrödinger's equation (including spin and quantum-electrodynamic subtleties) and its results is all we (can) know about them except a possible demolition into smaller "particles" (that is the accepted wisdom of 2017!).

But, Schrödinger's equation is ill suited to describe a birthday cake, which is very easy for us ... that's the way with different languages.

But, we insist: What IS a piece of cake actually (this question may be meaningless, again)? Well, if you prefer to subdivide it instead of having fun eating it, you use the tools of chemistry to very subtly break it apart and finally end up with a vast number of distinguishable varieties of molecules, some of them well known (if you have eaten it, similar breakdown happens, only we have even more problems to analyze what remains). The left over molecules are describable, in general, by Schrödinger's equation or, if they are too large, by some simple approximation of it, like Kimball's model. However, it would be extremely difficult to reconstruct the cake exactly, using its constituting molecules ... the "soul" of the cake (the connectedness of its "parts", also, perhaps, the joy about its good taste) seems to have vanished unless we know the chemical pathways of the degradation. Hence, we should try to catch the soul - meaning all the complex structural details of interlaced molecules before we destroy the "cake". This will be the future of Chemistry and Physics. Smashing of atoms, nuclei, quarks, ... to ever smaller "entities" will probably not bring us nearer to *understanding* the world - IMHO. I know, that many particle or "high energy" physicists will not endorse that statement, naturally! And, I may be wrong!

Just get your own experience (free of charge!) with about 10 computational engines by login into the excellent WebMO suite. Many high school chemistry teachers talk about and teach the chemical bond and have never done an honest quantum chemical computation themselves. Often, they do not know, that their Smart-phone with the free *WebMO app* (IOS and Android) can do it in minutes! Very likely, some bright teeny will have found that App before his teacher, play with it, and then know much more about the chemical bond. Since *Chemistry is applied Quantum Mechanics*, there is no "understanding" without computing (of course, many chemists do not subscribe this statement, having comfortably settled in the era of Wilhelm Ostwald!). Chemistry teachers could do a lot, if they learned how to do modern QC computations, and then teach input and interpret output of them to their pupils. Instead, they preach

obsolete stuff from the twenties and thirties of last century when it took several months to Y. Sugiura, whom Heitler designated as "hard working dwarf", to compute a better approximation for H2 than H-L's results. (Such arrogance is hard to swallow: In every branch of Physics it is compulsory to show a good to excellent numerical prediction of experiment for the acceptance of a theory. As it turned out, H-L's idea that molecular wavefunctions can be computed by a zeroth order linear combination of atomic orbitals had to be abandoned, being just too inaccurate!). At that time numerical results of integrals over trial wavefunctions were obtained by hand and hand driven calculators, later, about 1952, by "human computers (usually badly payed female office clerks) using Marchants, Fridens, and Monroes, i.e. electrically driven desk calculators", main page [12]).

With a modern QC program as offered by the WebMO demo server, e.g. Gamess as engine, you may compute H2 in 0.7 s, using the following input file:

```
$CONTRL SCFTYP=RHF CCTYP=CCSD(T) RUNTYP=OPTIMIZE
  ISPHER=1 NUMGRD=.TRUE. ICHARG=0 MULT=1 COORD=UNIQUE $END
$STATPT NSTEP=100 $END
$BASIS GBASIS=CCT $END
 $DATA
H2_ccsd(T)
DNH 4

H 1 0.00000000 0.00000000 0.37000000
 $END
```

D(issociation energy) found: 4.6895 eV (=98.8 %), compared to the experimental value D=4.747 eV(=100%) and Heitler-London's estimated D=2.4 eV (=50.5 %), Sugiura's D=3.1 eV (=65.3%). The H-H distance is computed at 0.7427 Å, exp. 0.74144 Å (Re) and Heitler-London's 0.89 Å, Sugiura's 0.85 Å. You can check this by looking at input, above, and output Job 335 298 (Oct 20, 2017) of the demo servers archive.- With the same tools (G3MP2) you may compute formation enthalpies of molecules at standard [T, p] of some dozen atoms, e.g. benzene or SiF4 with error limits of about 0.5 kcal/mol (G3 and G4 methods of Pople et al. JCP 1998 to 2012) in a couple of minutes even on a Raspberry Pi !

Looking into German elementary chemical textbooks or German Wikipedia articles about the Chemical Bond, this writer finds himself in the wrong movie. Most of the authors of these texts quote Heitler-London's H2 and have never been enquiring into what theoretical and computational chemists do and know today, 90 years later, about this subject! That is very sad, because there are so many excellent theoretical and computational chemists in Germany and elsewhere.

Finally, we get to the point:

2) Hellmann-Feynman Theorem

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Forces in Molecules
R. P. Feynman
Phys. Rev. 56, 340 – Published 15 August 1939
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Abstract:

Formulas have been developed to calculate the forces in a molecular system directly,
rather than indirectly through the agency of energy. This permits an independent calcu-
lation of the slope of the curves of energy vs. position of the nuclei, and may thus
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increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.

R. P. Feynman develops in his paper what is now called *"Electrostatic Theorem"*, a special case of the *General Hellmann-Feynman Theorems (see D. Wallace).* We only apply this special, electrostatic, theorem.

The chemists' traditional education imprints the notion that two neighbor nuclei, bonded in a molecule, are kept "together" just by the bonding electrons between them (electron pair bond or "stick"). This is wrong and should not be taught anymore. A nucleus, stationary in a molecule or extended structure, is kept at its position by the electrostatic attraction of **all** electrons, i.e. the electron distribution of the entire molecule or crystal, and the repulsion by **all** other nuclei of that structure (assumed well separated from other structures, for simplicity). This holds true for all matter from the borderline cases of pure "covalent" or "metallic" to pure "ionic" varieties. It is made clear in the paper by Feynman. Its corollary is, that all forces which could move a nucleus in (or out of) the molecular skeleton, vectorially add up to zero in a ground state molecule at (thermal) equilibrium. If the contrary were true, we had a perfect *perpetuum mobile,* like the Heitler-London H2 molecule.
[*I want to make clear, that both, W. Heitler and F. London, have been first-rate physicists. The aim of the paper, mentioned at the beginning, was not to compute accurate dissociation energy and bond length but to "understand" the interaction of two neutral atoms, eventually forming a "chemical bond". At the time, the Pauli principle was stated (1925), but its proof and the physics of the electron spin were only clarified by Pauli in 1928, after H-L's paper! The most unwieldy integral to be evaluated for the H2 problem is the electrostatic repulsion of the two electrons. H-L only estimated an upper bound for this using an approximation similar to Kimball's model (!) replacing a spherical charge distribution for the ellipsoidal one. The latter was evaluated correctly in the same year, 1927, by Y. Sugiura, who thus was able to appreciably improve H-L's results, though not highly recognized by Heitler, as mentioned above.*]

Acknowledgment: Some historical remarks from a preprint of Buhm Soon Park (2010), "Computational Imperatives in Quantum Chemistry"

Applications

Compute LiH and show Hellmann-Feynman electrostatic equilibrium

```
(* LiH on x-axis; with polarization, Li-cloud at x=0 *)
(* 4 Variables: 1 Li (ecc from center of P), 2 H (Q from center of R),
3 Li-cloud (P),  4 H-cloud (R), Z=3 inserted *)
Clear[d12, d13, d14, d23, d24, d34, ecc, P, R, Q, func];
c2 = {k1 → 1.02480344, k2 → 1.232443643, s1 → 0.27877144, s2 → 0.28887416};
```

Computation

```
T = k2 * 2.25 / R^2 + k1 * 2.25 / P^2;
d12 = P + R + Q - ecc;
d13 = ecc;
d14 = P + R - ecc;
d23 = P + R + Q;
d24 = Q;
d34 = P + R;

Vee = 3 * s2 / R + 3 * s1 / P + 4 / d34;
Vnn = 3 / d12;
Vne = -3 * (3 - (d13 / P)^2) / P - 6 / d14 - (3 - (d24 / R)^2) / R - 2 / d23;

func = T + Vee + Vnn + Vne /. c2;
(* arbitrary center positions on x-axis, 4 variables *)
t = FindMinimum[func, {R, 2.2}, {P, 0.5},
    {Q, 0.5}, {ecc, 0.012}, {Method → "Newton", MaxIterations → 500}]
```

```
{-8.027595381, {R → 1.986878512, P → 0.5610518732, Q → 0.4514616982, ecc → 0.01765291548}}
```

```
u = t[[2]];
```

Plots of result

```
plot1 = Graphics[{Circle[{0, 0}, P], Disk[{ecc, 0}, 0.05], Circle[{P + R, 0}, R],
    Disk[{P + R + Q, 0}, 0.05], {Dashing[{0.01, 0.01}], Circle[{P + R, 0}, Q],
     {Circle[{0, 0}, ecc]}}}] /. u;
plot1a = Graphics[{Arrow[{{P + R, 0}, {P + R + Q / 2, Q Sin[π / 3]}}],
    Arrow[{{P + R, 0}, {P + R - R / 2, R Sin[π / 3]}}], Arrow[{{0, 0}, {P / 2, P Sin[π / 3]}}],
    Text["Q", {P + R + Q / 2 + 0.05, (Q + 0.1) Sin[π / 3]}], Text["R",
     {P + R - Q / 2 - 0.05, (Q + 0.4) Sin[π / 3]}], Text["P", {P / 2 + 0.1, (P + 0.1) Sin[π / 3]}],
    Text["H+", {P + R + Q + 0.2, 0.1}], Text["Li+3", {-0.25, 0.1}]}] /. u;

Show[plot1, plot1a,
 {AspectRatio -> Automatic, PlotRange -> All, Axes -> True, AxesLabel → {x, y},
  PlotLabel → Style[Framed["LiH x,y plane with nuclei"], 16], Frame -> True}]
```
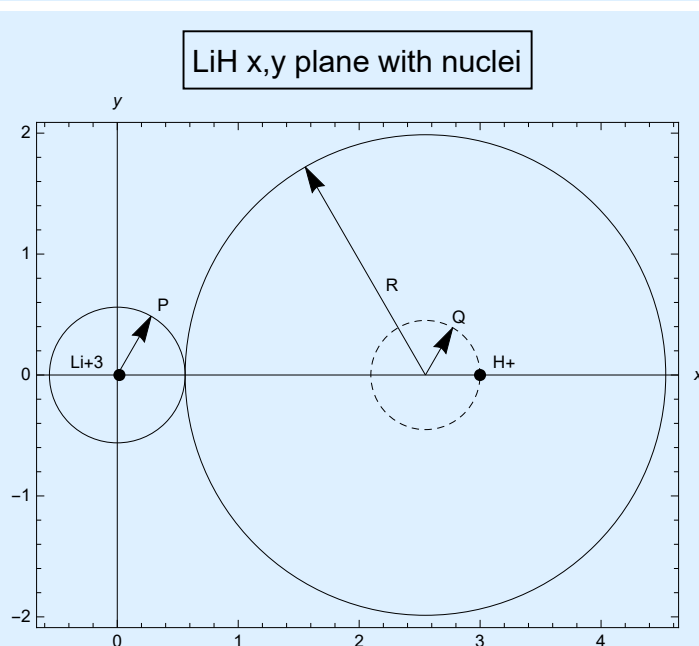
```
plot2 = Graphics[{Circle[{0, 0}, P], Disk[{ecc, 0}, 0.01], Circle[{P + R, 0}, R],
      Disk[{P + R + Q, 0}, 0.03], {Dashing[{0.002, 0.002}], Circle[{0, 0}, ecc]}}] /. u;
plot2a = Graphics[{Arrow[{{0.1, -0.1}, {ecc, 0}}], Text["Eccentricity of Li+3", {0.25, -0.1}],
      Arrow[{{0, 0}, {P / 2, P Sin[π / 3]}}], Text["P", {P / 2 + 0.02, (P + 0.02) Sin[π / 3]}]}] /. u;
Show[plot2, plot2a, {AspectRatio -> Automatic, Axes -> True,
   PlotRange → {{-0.6, 1}, {-0.6, 0.6}}, PlotLabel →
    Style[Framed["Li(+3)1s2, left cloud, magnified"], 16], Frame -> True, ImageSize → 600}]
```


Li(+3)1s2, left cloud, magnified
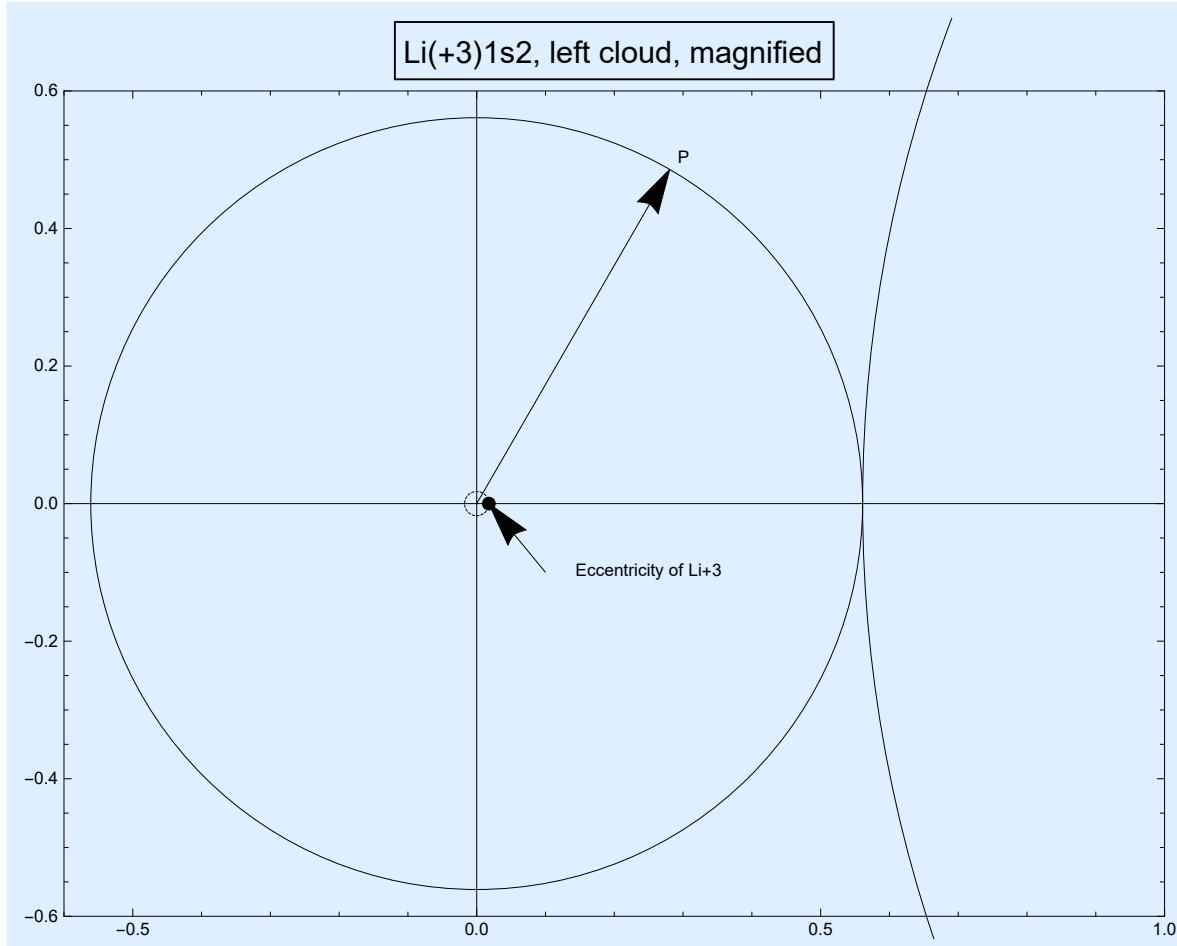
Hellman-Feynman force analysis for LiH:

```
(* Forces on Li(+3) in ± x direction connecting the two nuclei *)
f1 = -6 * ecc / P^3 /. u (* eccentricity of Li(+3) in its 1s2 cloud *)
```

−0.5997339609

```
f2 = -3 / d12^2 /. u   (* repulsion by proton *)
```

−0.33742865

```
f3 = +6 / d14^2 /. u   (* attraction of Li(+3) by outer 2e cloud *)
```

0.9371626109

Hellmann-Feynman vector sum on Li(+3):

```
sumf = f1 + f2 + f3
```

$5.440092821 \times 10^{-15}$

```
(* Forces on H+ *)
g1 = -2 * Q / R^3 /. u (* eccentricity of H+ in outer cloud *)
```

-0.1151163386

```
g2 =  3 / d12^2 /. u   (* repulsion by Li(+3) *)
```

0.33742865

```
g3 = -2 / d23^2 /. u   (* attraction by 1s2 cloud *)
```

-0.2223123114

Hellmann-Feynman vector sum on H(+):

```
sumg = g1 + g2 + g3
```

$-8.326672685 \times 10^{-16}$

Virial theorem

```
(Vnn + Vee + Vne) / T /. u /. c2 (* Virial ratio *)
```

$-2.$

The complete Tutorial 9 can be called here

Summary of Tutorial 9
Hellmann – Feynman theorems
A bit of (personal) history
Applications