

- SHEET-1** **Index to Display-sheet contents**
- SHEET-2** **Abstract for this Poster Presentation**
- SHEET-3** **Calculated Energy Plots & Comments on the Excerpts from Reference-1**
of Abstract: *“Die magnetische Abschirmung von Protonen in Methylgruppen und aromatischen Ringen: Multipuls-NMR-Experimente an Molekulkristallen”*: Inaugural-Dissertation zur Erlangung der Doctorwürde der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität, Heidelberg. Vorgelect von Dipl.-Phys. Bernd Tesche aus Lüdenscheid, Tag der mündliche Prüfung 19-07-1995
- SHEET-4** **Plot of Energy Break ups for Claculation of Energy when the C-H bond-length is varied**
- SHEET-5** **Orbital Electron population for the maximum and minimum values of C-H bondlengths for the energy calculations on Methane molecule**
- SHEET-6** **A qualitattive trend assignment for the variation in the Shift tensor.**
- SHEET-7,8&9** **A graphical plot of the way the populations vary with the bond length in methane is displayed below**
- SHEET-10:** **Electron Population Trends: Graphical Plot**
- SHEET-11** **Clarifications and possibilites for expalining the trends in Chemical shift**
- SHEET-12** **OUTLOOK**

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION**VARIATION OF CHEMICAL SHIFTS WITH MOLECULAR
GEOMETRY THROUGH THE EQUILIBRIUM CORRESPONDING TO A
GEOMETRY OPTIMIZATION**

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When the Geometry Optimization for equilibrium (stable) geometry procedure is explained on the basis of the applicability of variation principle, then the molecule passes through a minimum of potential energy to recognize the most stable structure as corresponding to the minimum. For such a passage through a series of structures on both sides of the minimum energy, if the chemical shifts of the nuclei in the molecule are also calculated for the series of structures, would there be a possibility to recognize the characteristics of the stable structures? This is a pertinent question and since the Computational methods result in the Full Tensor element values (not merely the isotropic, trace value), it is probably worth the while looking into the above question, with the variation of the chemical shift tensor properties tracked through the series of structures encountered during the geometry optimization procedure.

For this perspective a beginning can be made with what ever effort is known in the literature to document the chemical shift dependence on the geometry parameters. Since the Solid State High Resolution NMR is gaining in importance in structure determination (small molecules, and polymeric macro molecules also of biologically relevant) a question of the variation of chemical shift with geometry, and explaining the trends on the basis of the electron population analysis would lead to a situation of using full tensor information similar to the way chemists these days interpret the isotropic liquid HR NMR spectra. In this context the consideration in the cited reference (1) for the trends of methyl group proton (isotropic and anisotropic part of the) chemical shift tensor can be viewed from the point of view of the available electronic structure information by the quantum chemical computation for the electron distribution within the molecule. The relevance of such considerations would be highlighted with regard to the HR Single Crystal PMR results as in cited reference (2).

REFERENCES:

1. *“Die magnetische Abschirmung von Protonen in Methylgruppen und aromatischen Ringen: Multipuls-NMR-Experimente an Molekulkristallen”*: Inaugural-Dissertation zur Erlangung der Doctorwürde der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität, Heidelberg. Vorgelegt von Dipl.-Phys. Bernd Tesche aus Lüdenscheid, Tag der mündliche Prüfung 19-07-1995
2. *“The proton nuclear magnetic shielding tensors in biphenyl: Experiment and Theory”*, Frank Schonborn, Heike Schmitt, Herbert Zimmermann, Ulrich Haeberlen, Clémence Corminboeuf, Gilbert Grossmann, Thomas Heine, J.Mag.Res. 175, (2005), 52-64.

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

The results of calculations on chemical shifts: from **reference 1** of Abstract.

The equilibrium C-H bond length in methane is **1.08 Å**. The variation of Chemical shift of the protons is linear **around this equilibrium** Geometry. The plot depicts this trend for **isotropic proton shift** and the **anisotropy** of the Chemical shift proton tensor.

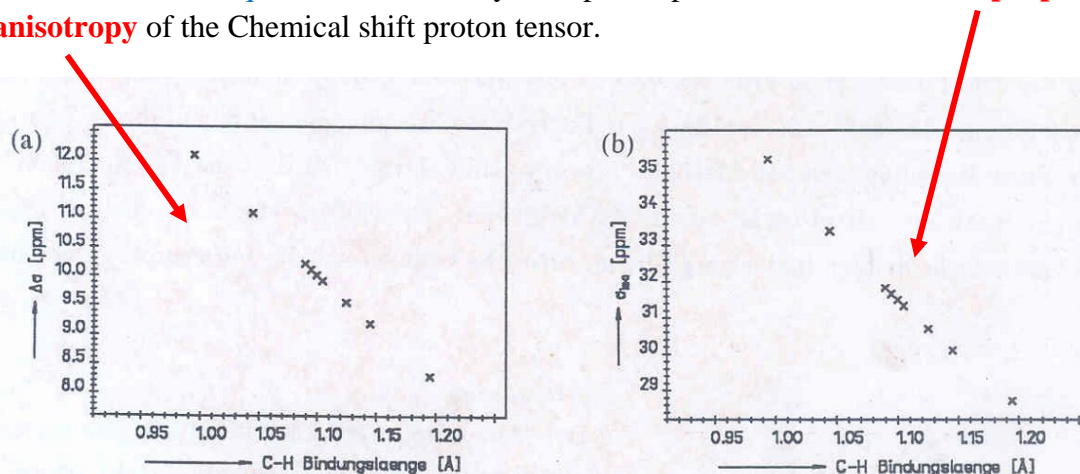
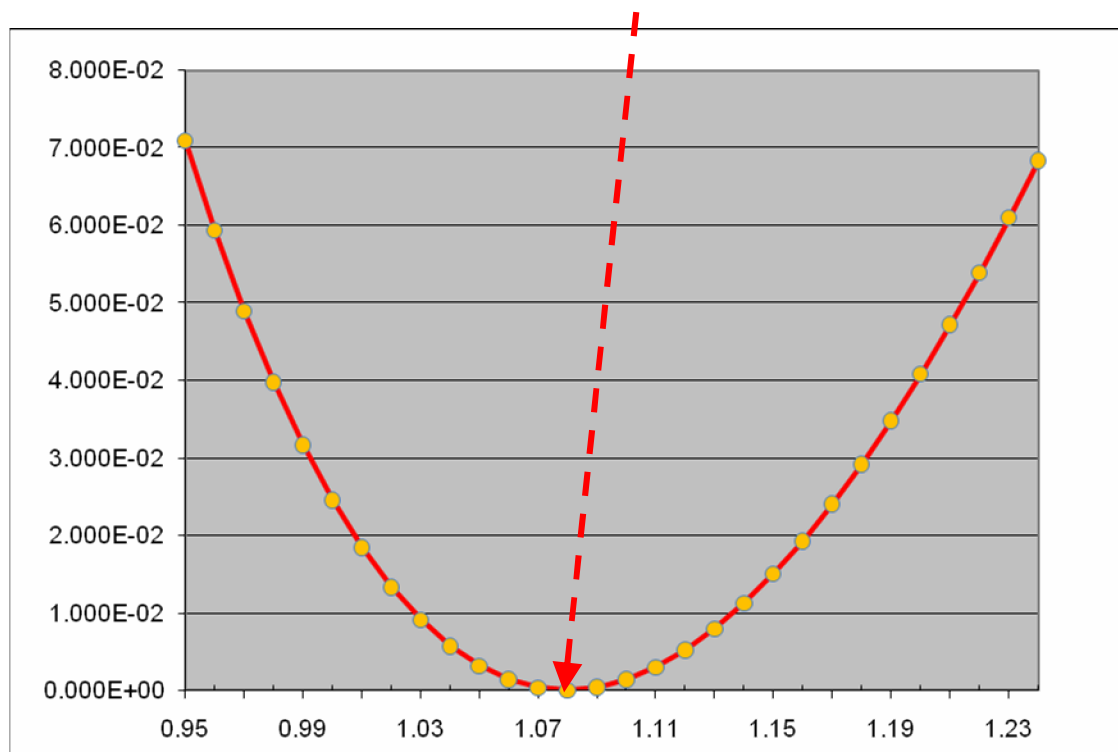
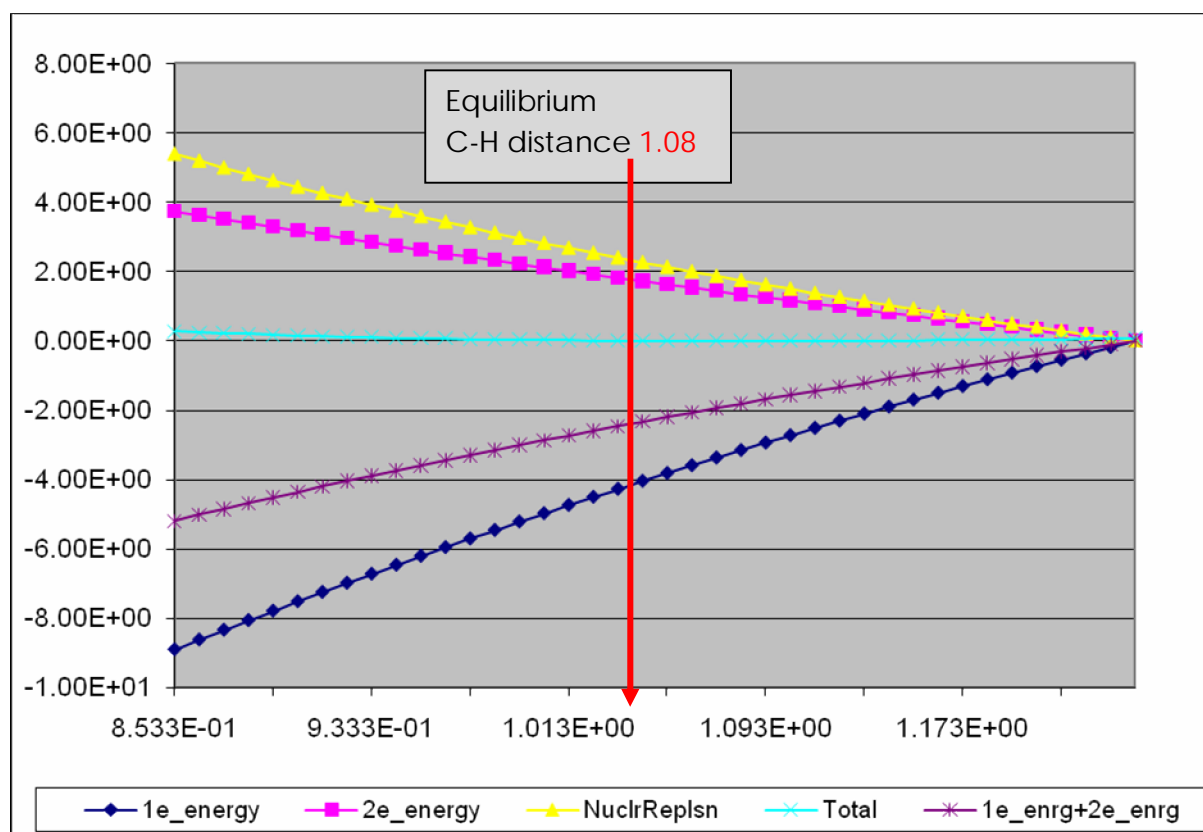


Abbildung 6.1: *Ab-initio* Berechnungen der ^1H -CV-Tensoren in Methan für verschiedene C-H-Bindungslängen. Man erkennt die starke Abhängigkeit von (a) $\Delta\sigma$ und (b) $\sigma_{i,so}$ von der C-H-Bindungslänge. Es wurde die Full LORG Methode mit dem Basissatz 4-31G(2d2p) verwendet.

The Calculation of energy as a function of geometry: C-H bond lengths varied from **0.95 to 1.23 Å**. **Energy minimum at 1.08 Å**.



VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION
EXPLORING THE ENERGY BREAK UPS RESULTING IN THE MINIMUM ENERGY OF THE MOLECULE



The Various interaction energies between the nuclei and electrons in the molecule consists of the categories indicated in the Graph above

The total energy has magnitude of the order of 10^{-2} whereas the individual contributions above are of the order of 1-10. The total energy above depicted by the **line** looks almost a straight line whereas in actuality it would be a parabolic curve with minimum as shown in the graph of previous page. The contributions in energy breakups are all displaying a monotonically increasing or decreasing linear trend, but only the sum (total energy) has the display of minimum. The individual contributions above probably can be shown to have a correlation with the linear trend of the chemical shift tensor parameters? These individual contributions are essentially electron-nuclear and electron-electron interactions. As a result of the variation in the C-H bond length, the electron distributions determined by the occupied molecular orbital show varying trend this in turn results in the variation in the interaction energies. The **variations** in the categorized **break up energies** have monotonically varying **linear trend**; thus the electron populations in the molecular orbital/atomic centers could have also such a trend and **this probably would provide a handle to explain the trends in the chemical shift variations while the total energy goes through a minimum at the equilibrium geometry. This means electron population analysis**

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATIONfit for **1e_energ+2e_energ**

$$y = -0.0009x^2 + 0.1683x - 5.3336 \quad R^2 = 1$$

fit for **1e_energ**

$$y = 0.228x - 8.7905 \quad R^2 = 0.9961$$

$$y = -0.0014x^2 + 0.2847x - 9.1879 \quad R^2 = 1$$

$$y = 5E-06x^3 - 0.0017x^2 + 0.2898x - 9.2063 \quad R^2 = 1$$

These are the equations to which the trend lines in the graph (for break up energies) could be fitted. From the coefficients it is evident that the lines are predominantly linear.

The above energies are the result of single point energy calculations (STO 3G) calculated by setting the C-H bond lengths to be from **0.86328518 Å** to **1.1532851 Å**

The following are the results for electron population trends as the C-H bond length is changed in Methane

ForSTO3G_SinglePoint_C-H = 0.86328518

The electron configuration for atomic carbon is $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

1	C1	S	1.99183	1.99084
2	C1	S	1.12918	0.83921
3	C1	P(X)	1.17264	1.19183
4	C1	P(Y)	1.17264	1.19183
5	C1	P(Z)	1.17264	1.19183
6	H2	S	0.84027	0.89862
7	H3	S	0.84027	0.89862
8	H4	S	0.84027	0.89862
9	H5	S	0.84027	0.89862

When the bond length is small compared to equilibrium value of 1.08 Å, The electron charges from the Hydrogen (1S) have been distributed into the Carbon (2S,2P(x),2P(y),2P(z)) orbital

ForSTO3G_SinglePoint_C-H =1.1532851

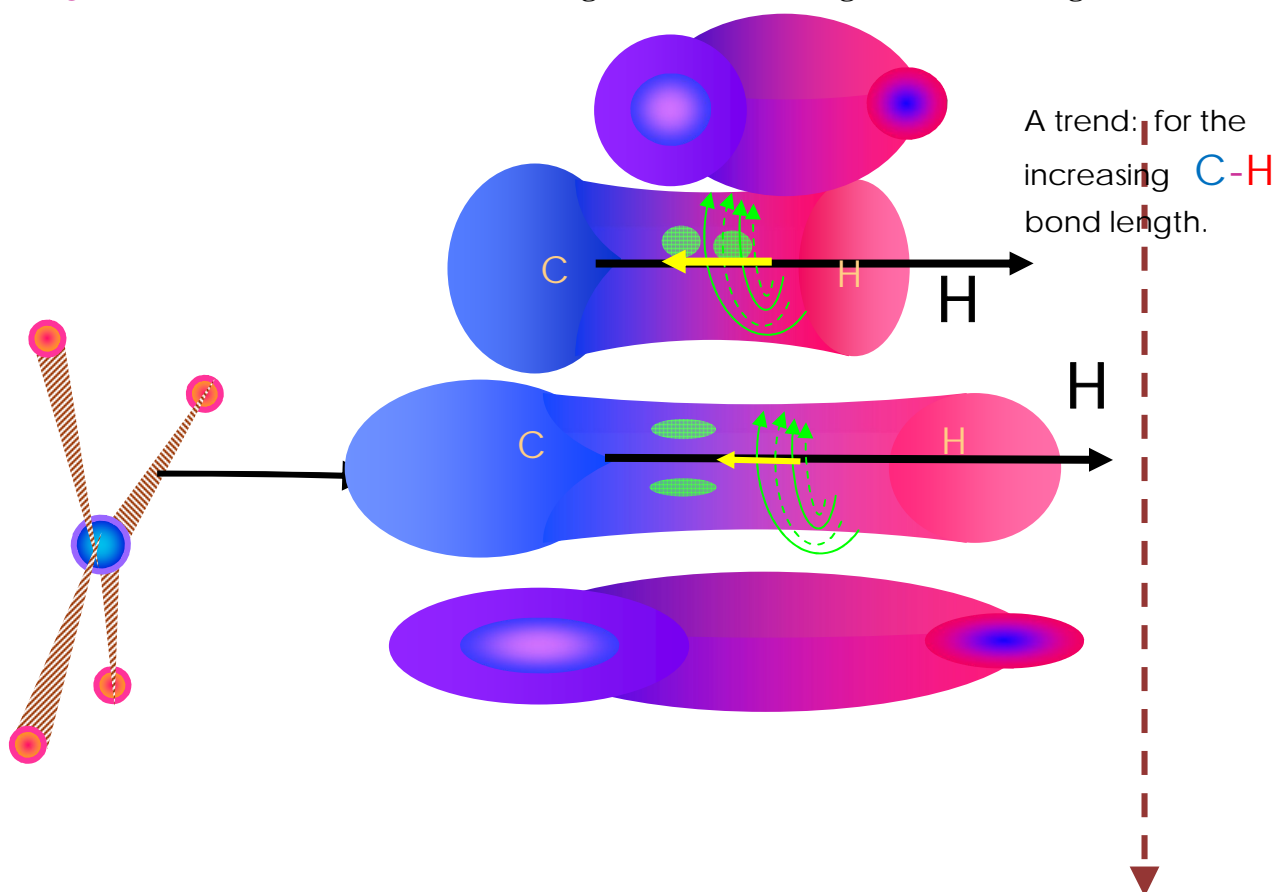
1	C1	S	1.99237	1.98497
2	C1	S	1.21797	1.05156
3	C1	P(X)	0.99460	1.01904
4	C1	P(Y)	0.99460	1.01904
5	C1	P(Z)	0.99460	1.01904
6	H2	S	0.97659	0.95147
7	H3	S	0.97659	0.95147
8	H4	S	0.97659	0.95147
9	H5	S	0.97659	0.95147

When the bond length is longer compared to equilibrium value of 1.08 Å, The electron charges from the Hydrogen (1S) have been distributed into the Carbon (2S) orbital and the other orbital populations are almost as if it is in the atomic state.

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

If such a trend in the population (electron charge in the atomic centers) can be evaluated, then from the geometry parameters the corresponding orbital (with its charge density) can be indicating the trends for the induced fields arising due to the charge circulations induced by the external magnetic fields. This in turn provides the estimation of the contribution to anisotropy and isotropic values of the shifts from each of the orbital by the appropriate symmetries in the molecules. Each population of orbital can be assigned an anisotropy and isotropy contribution which can be duly summed up to compare with the total values for the respective quantities. Illustration follows:

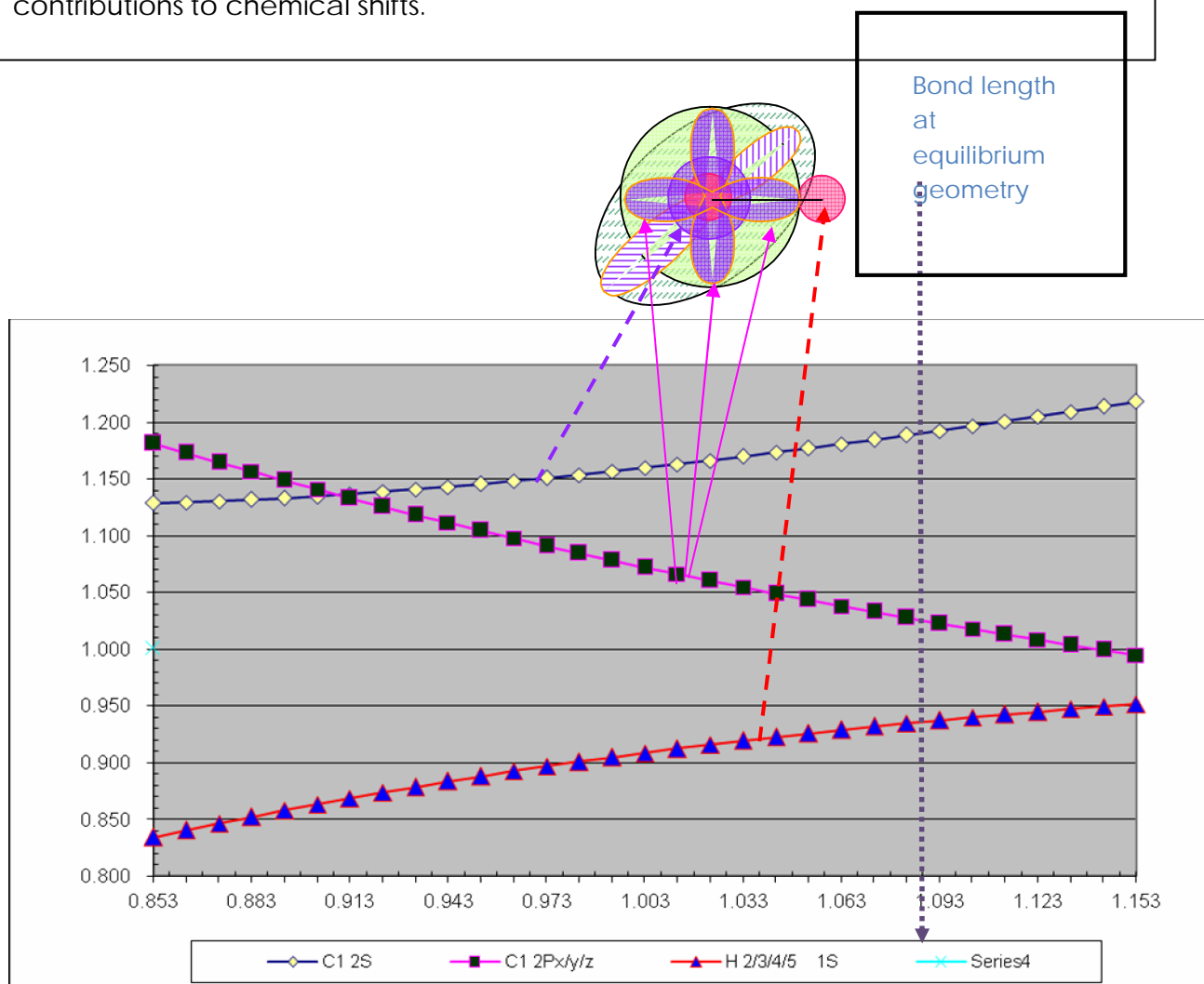
A Qualitative trend assessment: the change in C-H bond length and the changes in the induced fields.



With the depiction above and combining the charge distribution/electron populations, and with the designation of the directions of current circulations, the induced field trends at the proton site can be envisaged.

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

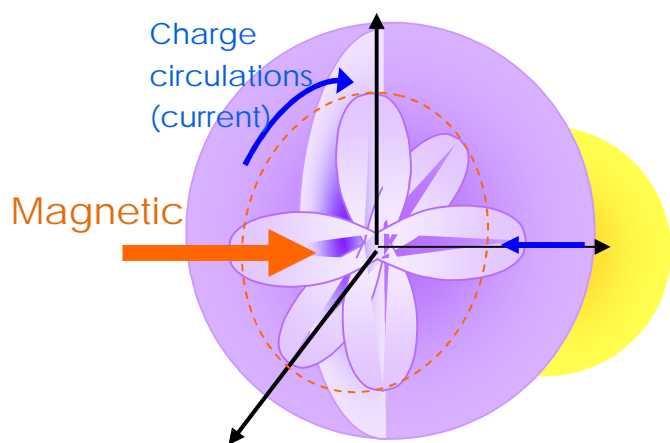
The Population at two different-H bond length values was tabulated in an earlier sheet. **A graphical plot of the way the populations vary with the bond length in methane is displayed below.** It is possible to recognize the monotonic variation trends rather than the trend governed by the variation principle for the energy of the molecule. Such recognition of the electron charge variation at the orbital of different atomic centers in a molecule and further estimating the induced fields from the charge circulations is the basis for calculating atom and bond susceptibility. With the susceptibility values with a magnetic dipole model the chemical shift changes can be estimated. The ab-initio/semi empirical quantum chemical methods calculate the chemical shift changes by similar formalisms. Susceptibility combined with magnetic dipole model is the basis for calculating neighbor group contributions and intermolecular contributions to chemical shifts.



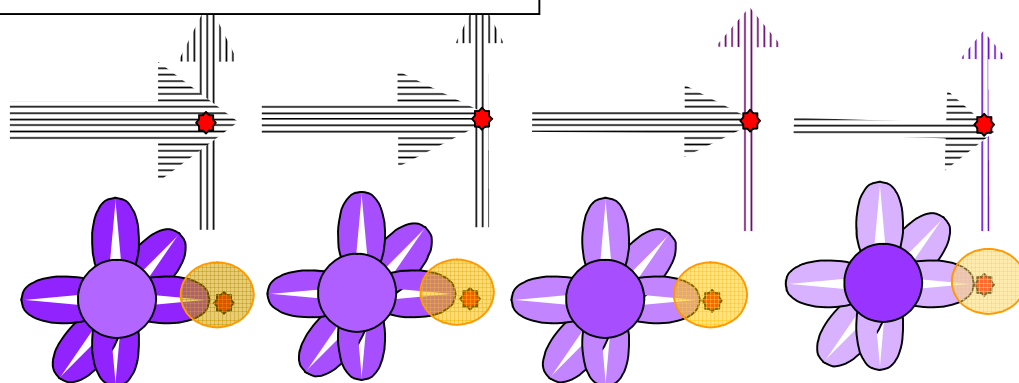
VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

Increasing Charge in the Hydrogen 's' orbital would increase the isotropic shift value at the proton. And, decreasing charge would result in decreasing isotropic shift.

LEFT:- The previous sheet consisted of the trend plot for the variation of electron population at the atomic centers of methane. When the C-H fragment is under purview, the relevant orbitals of Carbon and Hydrogen atom are depicted in the diagram on the **left side**. Since the Charges are delocalized it may be possible to envisage a spherically symmetric charge cloud around the Hydrogen nucleus which would contribute to isotropic shift values. On the other hand, the



Below:- The set of 'p' orbital, all the three taken together may have a spherical symmetry about the carbon atom center. Then at the hydrogen nucleus it would contribute to anisotropy in chemical shift. A decreasing electron charge in the set of p orbital would show up as a decreasing anisotropy of the proton. Increasing charge density in the carbon 's' orbital would result in increasing anisotropy at the proton. These two competing factors have to be taken proper note of by the population changes in 's' and 'p' orbital of carbon.

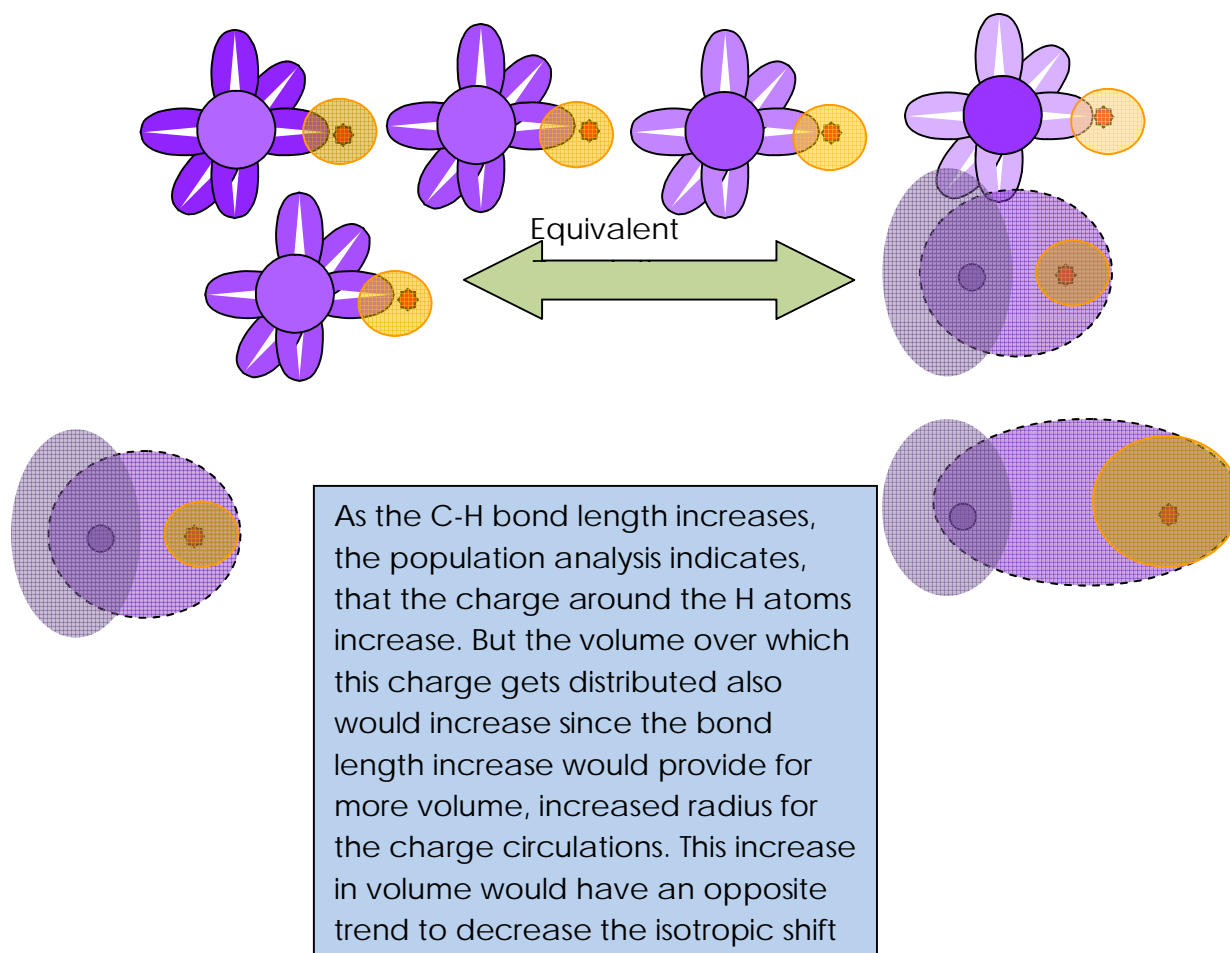


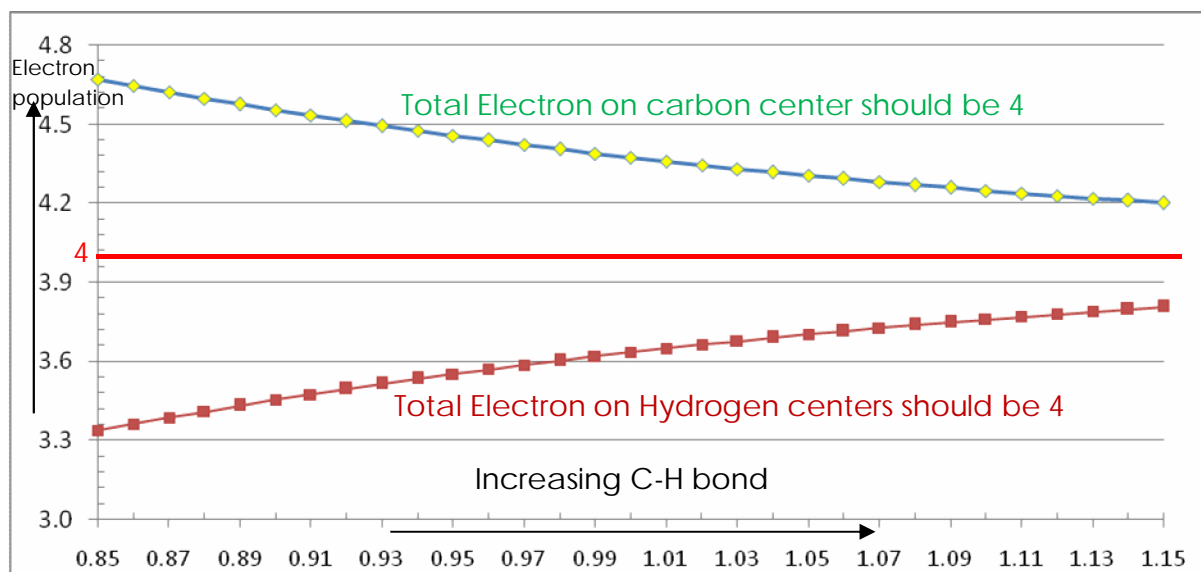
VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

With the discussion for the break up for the chemical shift contributions in the previous page, combining it with the actual population variations calculated and plotted in the earlier sheet, it would be possible to arrive at a rationalization as follows:- Carbon 's' orbital population and one of the 'p' orbital results in a near constant value for the electron population through the variation in bond length. This would mean that the anisotropy value should remain constant. But taking the fact that there are 3 p orbital contributing to the decreasing trend for the anisotropy, the net result would be that the anisotropy decreases with increasing bond length.

It seems that, understandably, there is the trend towards reduced bonding (sharing of electrons) as the bond length increases. Then, considering the possibility of a spherical charge distribution around proton due to electrons from carbon as well as hydrogen atoms in the bonded case, and the charge cloud due to only the single electron of Hydrogen in the non bonded case, the decrease in isotropic shift value would only indicate that the spherical charge cloud around proton is of greater density in the bonded case than in the non bonded case of trend towards increasing bond length.

Thus such population analysis can explain the shift trends and also it is possible to get clues for the situation of electronic molecular structures.



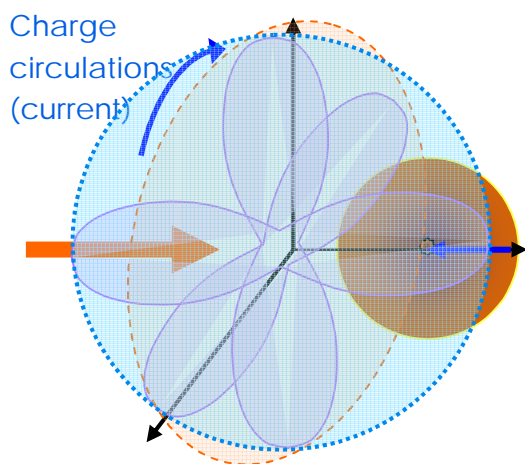
VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION

Above is the trend for the Variation of Total Electron (population) in Carbon atom and Hydrogen atoms of Methane: A combination of the equivalent description on the basis of the calculated populations seem to be convincing the trends of Chemical shift values with geometry parameters.

In methane there are 4 hydrogen atoms and each hydrogen atom should have one electron. Thus each of the hydrogen 1s orbital should be having 1 electron and hence 4 hydrogen atom 1s orbital population must account for 4 electrons. The carbon 1s has two electrons and for the variation in bond lengths, at all values the 1s population was seen to be closely two and hence were not included in the graph above. the carbon $2s^2$, $2p_z^1$, $2p_x^1$, $2p_y^0$ electron configuration requires 4 electron population in the carbon orbital. As can be seen from the graph, when bond lengths are smaller than the equilibrium value, then the electron population is more than 4 on the carbon atom, and less than 4 when summed up for the four hydrogen atoms. The total of carbon and hydrogen populations adds up to invariably 8 at all bond lengths.

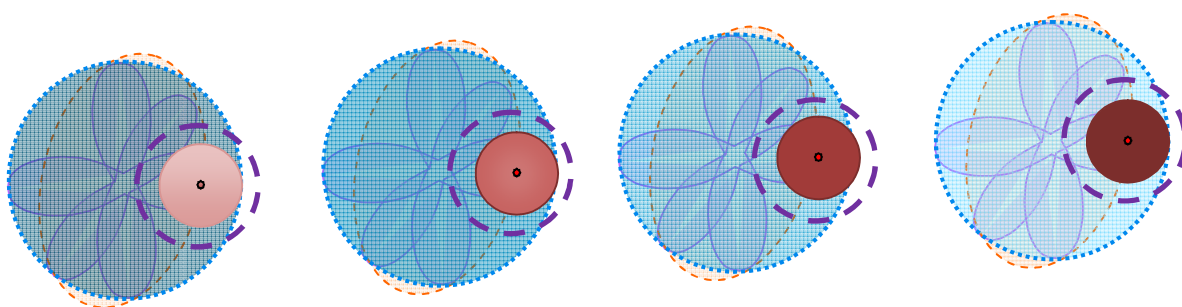
As the bond lengths increase the situation can be described as weaker bonding, and the populations for hydrogen and carbon reach the atomic values of 4.

This monotonic trend of variation is in conformity with the trends for the variation of chemical shifts with bond lengths as in Sheet-2. However, the isotropic shielding of proton seems to be decreasing with increasing bond length: contrary to the trend expected when the electron population increases on Hydrogen atom with increase in bond-length!



For the remark on the trends of chemical shift variations and population in Hydrogen 1s orbital with bond-distances, a picture on the left could be convincing if one tries to account for the orbital extensions for the sp^3 Hybrids, and the spherical symmetry of the three

The population in the three carbon p-orbital is equal; as per the tetrahedral symmetry requirements (sp^3 situation) and as per the graph on Sheet-7, the population of each of the p-orbital decreases from 1.17 to 0.99 for the bond-length range. The hydrogen 1s orbital population trend is to get increased population from 0.84 to 0.97. The decrease in population of carbon p-orbital is by 0.2 and the increase in Hydrogen s-orbital is by 0.13. Thus within the pink line marked region, there would be a net decrease in electron and



Thus trying to consider the chemical shifts in terms of populations and magnetic dipole model might have suggestions to optimally choose the theoretical method appropriate and the kind of electronic structure and the bonding situations in detail.

<http://cat.inist.fr/?aModele=afficheN&cpsid=13406670> Chemical shift driven geometry optimization

Author(s) :WITTER Raiker ; PRIESS Wolfram ; STERNBERG Ulrich ;

Abstract: A new method for refinement of 3D molecular structures by geometry optimization is presented.

VARIATION OF CHEMICAL SHIFTS..... GEOMETRY OPTIMIZATION**A COMMENT ON THE CHEMICAL-SHIFT DRIVEN GEOMETRY OPTIMIZATIONS**

During the geometry optimization using the energy minimizing criteria, the optimization is carried out by calculating the gradients for energy changes with the coordinates of atoms. At this stage, at any stage of iteration, the corrections could be determined also by calculating the chemical shifts of nuclei for that geometry and compare it with the input of required values of chemical shifts (could be experimental value) and find the error/deviations from the target geometry and incorporate this also as a criterion as much as including the NOE distances as constraints in the bio-molecules. Such procedures called “Chemical shift driven geometry optimization” have been found effective for determining bio-molecular structures. The current procedures, incorporating a magnetic dipole model on the basis of the charge density changes inferred from population analysis, would provide in certain contexts convenient spectral analysis criteria for molecular structure determination. Thus this would be an approach of the “ring current effect” at the much more micro level of atoms and orbital in a molecule.

OUTLOOK

It is pertinent to begin with this author’s publication in Indian Journal of Physics: [http://ugc-inno-
nehu.com/IJP_Vol79_Sept2009_pages985to989.pdf](http://ugc-inno-
nehu.com/IJP_Vol79_Sept2009_pages985to989.pdf)

[http://ugc-inno-
nehu.com/IJP_Vol79_Sept2009_pages985to989.pdf](http://ugc-inno-
nehu.com/IJP_Vol79_Sept2009_pages985to989.pdf)

The title of this article is:

Magnetized materials: contributions inside Lorentz ellipsoids

There in it

has been pointed out that the role of HR PMR in Solids is significant in determining the boundaries for the Lorentz Sphere, termed as Inner (semi micro) Volume Element [IVE] in the material medium. A magnetic dipole model could enable a discrete summation of contributions from within this IVE to the Shielding factors of proton. If the entire set of discrete molecular units within the IVE, considered as a cluster of molecules, can be subjected to a Quantum Chemical Calculation to determine the Proton chemical shift at the centre of the molecule, then the magnetic dipole model would not be necessary. This would be like calculating intra molecular chemical shift values considering the cluster of molecules as a single supra molecular entity. It is precisely such an approach which has been reported in the Reference No. 2 of the Abstract to this poster presentation. However, in this JMR paper on page 59 it has been pointed out a scaling becomes necessary after the Quantum Chemical Calculation as reconciliation with the Magnetic Dipole model approaches for the macroscopic considerations. Hence a micro level magnetic dipole approach seems warranted to discern how exactly such a scaling becomes necessary. More over such are the approaches with the ring current shifts which is important even in the macro molecules of biological significance:

http://www.geocities.com/inboxnehu_sa/nmrs2005_icmrbs.html The orientations and packing of aromatic rings in Tryptophan residues of proteins also is evident from the publication by the research group of Pinak Chakrabarti, in Acta Crystallographica Section D Biological Crystallography (1999) D55, 1421-1427.

Thus the methods indicated herein could be of insightful results for further investigations.