OVERVIEW AND DIRECTIONS FOR THE FUTURE

CYNTHIA J. JAMESON
University of Illinois at Chicago
Department of Chemistry M/C-111
Chicago, Illinois 60680

ABSTRACT. A brief summary of the lectures and discussions is given, with some questions for the future.

1. Overview of the Conference

This is the first conference on nuclear magnetic shielding. It brings together a good mix of theoreticians and experimentalists, all of whom are interested in this magnetic tensor property. This quantity is so sensitive to the electronic environment that sites which can not be distinguished from each other by any other measurement can be easily distinguished by the differences in their NMR shielding. The precision with which such measurements can be carried out allow determinations not only of molecular structure but even detection of subtle changes in geometry such as alteration of bond lengths and bond angles and changes in the number and closeness of neighboring molecules. A few of the questions that have been answered by measurements and calculations of magnetic shielding are: Is the system disordered, averaging dynamically, or does it have small domains of particular well-ordered structures? What is the distribution of molecules in the cavities of a microporous solid? What is the number of bridging oxygen atoms around a phosphorus, aluminum, or silicon atom in a network? Is the molecular structure and geometry proposed on the basis of other evidence correct?

In this conference the nuclear shielding in a broad continuum of systems has been studied, ranging from the one extreme wing of small molecular systems having well-known geometries such as CO, to the other extreme wing comprising of complex systems and networks, some of unknown structure. A variety of theoretical approaches have been used: Post-Hartree-Fock, e.g., SOLO, SOPPA, MC-IGLO, coupled Hartree-Fock or RPA using local origins (IGLO, LORG, GIAO) or using a common origin, Geertsen's gauge invariant method, approximate methods employing a mean excitation energy, and empirical correlations. On the one hand, the largest basis sets and second order electron correlation corrections are being applied to some small molecules such as N_2, CO, HCN. On the other hand, in complex systems, the unit for which the shielding is measured is an extended network of atoms (an aluminosilicate crystallite or a semiconductor alloy) rather than a single molecule having a fixed number of atoms. For these the interpretation is still at the empirical and semi-empirical stages, employing mean excitation energies and qualitative concepts such as ionicity, bond polarity, cation/anion radii. Alternatively, high-quality *ab initio* calculations on model systems to emulate the essential characteristics of the real complex system have been reported here. Examples are the IGLO calculations on the SiO_4^{4-} fragment to simulate the geometry dependence of observed ^{29}Si chemical shifts in polycrystalline silicates (Wolff) and the modeling of the different ^{19}F environments of ^{19}F-labeled phenylalanine in various proteins by using electric field and

J. A. Tossell (ed.), Nuclear Magnetic Shieldings and Molecular Structure, 557–560.

electric field gradient derivatives of ^{19}F shielding together with the electric fields generated by point charges representing the electrostatic effects within the protein (Dykstra and Oldfield).

What are some important lessons we can take home from the conference? The damping of errors from incomplete cancellation of long-range contributions due to basis set inadequacies by the use of local origin methods has been well-established. The GIAO method (Pulay, Chesnut), the IGLO method (Kutzelnigg), and the LORG method (Hansen and Bouman) all can provide results of experimental quality or near-experimental quality in the same classes of systems. The first and second row calculations have offered may success stories, but it is quite clear that large basis sets are necessary to obtain near experimental quality results in most cases. When modest basis sets are used in all methods, GIAO appears to do a little better, although an across-the-board comparison with a large number of molecules has yet to be done in the same way that has been done for the LORG vs IGLO comparison. It is now possible to obtain experimental accuracy in many classes of nuclear shieldings, especially for ^{13}C, although a few pathological cases still pose over ten ppm discrepancies (CO, HCN). When a saturated basis set is used the common-origin conventional CHF results (Lazzeretti, Raynes) are indistinguishable from the local-origin results. The gauge origin dependence of shielding calculations is basis-set dependent. (Geertsen, Oddershede). That is, it is not possible to determine that a basis set is saturated simply because the results for a given gauge origin no longer change as the basis set is further improved. A locally-dense basis set may be very useful when only a small number of shieldings are to be calculated in a large molecule (Chesnut). Shielding density maps and current density maps provide stunning visual aids for deriving physical intuition and first-principles understanding of shielding and magnetizability (Lazzeretti, Keith).

Shielding anisotropies provide more complete information than σ_{iso}. There are many examples of systems exhibiting very nearly the same σ_{iso} but very different individual components. (Mason). σ_{iso} being the same offers no clear indication of unchanging electronic environment of the nucleus. Complete experimental shielding tensors [three principal values plus the Euler angles orienting the principal axis system (PAS) of the shielding tensor with respect to the molecular frame] have been obtained unequivocally and accurately in isolated spin pairs (AX systems) by making use of the dipolar tensor (Wasylishen) and in systems of up to 24 ^{13}C nuclei in one molecule, by using ingenious experimental techniques (Grant). *Ab initio* calculations of the shielding tensor are nearly indispensable in obtaining shielding tensor information. Assignment of the PAS seems to be good even when the basis set may not be of sufficient quality to reproduce the individual tensor components, provided the individual σ_{ii} values are sufficiently different from each other.

It is very important to do temperature-dependent experiments because dynamic averaging may give the wrong tensor components (Mason, Kirkpatrick). There is a change in the tensor with physical state/environment. In the condensed phase there may be a) intermolecular effects on the structure of the molecule and the σ tensor reflects this change in geometry (Farrar), b) intermolecular shielding (Jameson), c) hydrogen-bonding (Hansen), or d) electric field effects (Oldfield, Dykstra). The shielding tensor and the molecular structure in solution can both be obtained but (Warning!) in a multi-parameter fit to experiments it is always important to look at the table of correlation coefficients. If the parameters are highly correlated then a unique fit is not obtained. It is important to use more than one set of boundary conditions (new experiments (Farrar).

The dependence of nuclear shieldings on molecular geometry has been a focus point of several papers (Schleyer, Kutzelnigg, Jameson, Raynes, Chesnut, Barfield). For calculating the shielding at the equilibrium geometry, one needs accurate bond lengths

and angles because the shielding depends sensitively on these. It is better yet to do vibrational averaging over the nuclear shielding surfaces. This averaging is especially important for comparison with the experimental shielding when the potential energy surface is fairly flat while the shielding surface is not. Rovibrational averaging is also important for the interpretation of the temperature-dependence of the shielding in the isolated molecule and for the interpretation of isotope shifts (such as ^{15}N shielding in ND_3 relative to NH_3).

The intermolecular nuclear shielding surface has a minimum that occurs below the shielding of the infinitely separated molecules (Jameson, Kutzelnigg) and is employed in the interpretation of the density dependence of shielding in the gas phase and of the chemical shifts observed in physisorption. The effects of external electric fields and electric field gradients on shielding can be large and of either sign. (Dykstra, Raynes) These can be used in the interpretation of long-range intermolecular and intramolecular effects on σ (Jameson, Oldfield).

Electron correlation is important for shielding in multiple-bonded systems, especially when lone pairs are also involved (the $n\rightarrow\pi^*$ transitions) and when nearly degenerate or low-lying excited states are involved. For these systems it is necessary to use post-Hartree-Fock methods such as SOPPA (Oddershede), SOLO (Hansen), MC-IGLO (Kutzelnigg). Lone pairs by themselves do not make electron correlation contributions significant; systems with lone pairs can generally be brought into agreement with experiment by saturating the basis set. How large are the actual contributions from electron correlation can not be determined correctly if the basis set is not saturated because part of the difference between the results of a correlated calculation and a calculation at the CHF level may be due to an inadequate basis set. Nevertheless, where correlation effects are known to be significant, it makes sense to do correlated calculations even with a modestly large basis set, specially if basis set errors are damped out by the use of local origins. There appears to be no effects of correlation in ^1H shielding. The sign of the electron correlation effect on shielding is positive for σ_{iso} in most cases, that is, the CHF-level result is usually too deshielded and correlation corrections are positively shielding. Correlation also generally increases $(\sigma_{\parallel} - \sigma_{\perp})$. There are exceptions, for example, in F_2 correlation makes σ_{iso} more deshielded. For molecules whose electronic ground state cannot be properly described by a single Slater determinant (such as ONNO, O_3,SO_2, NSF, HN=NH) it is important not to use a CHF-level calculation of the shielding for comparison with experiment. Molecules of this type are good candidates for MCSCF calculations.

There are many unanswered questions in shieldings involving 3rd row and below in the Periodic Table, especially for transition metal nuclei, for which there are no absolute shielding scales, no gas phase data; geometries are unknown in solution, and the basis sets are largely untested. While the agreement between calculated shielding differences and observed chemical shifts are good (Nakatsuji), this good agreement may be fortuitous, since the shielding calculations are shown not to be converged when larger basis sets are used (Ellis). For these it is important to (a) do basis set studies, (b) also calculate the shielding of ligand atoms for which there are absolute shielding scales and comparison with the experiment can actually be made, and (c) do geometry studies, especially for complex ions where the geometries in solution are not necessarily the same as in the crystalline state, and the theoretical optimized geometry may be sensitive to the counter ions.

2. Directions for the Future

As theorists begin to do calculations for nuclei beyond the 1st and 2nd rows of the Periodic Table, new problems arise:

(1) Basis sets have not been optimized for shielding calculations in 3rd and 4th row atoms; basis set studies are needed. Computation becomes more time and disk-space demanding and it becomes even more important to make sure the CHF - level calculations are converged with respect to basis sets.

(2) Relativistic effects begin to become important. How to do relativistic calculations? Prof. Kutzelnigg led the discussion on this topic and several comments and suggestions were made which can serve as starting points for future work. There is no exact relativistic many-electron Hamiltonian; it is only defined to order c^{-2} (c = velocity of light); singularities appear beyond c^{-2}. This means that we are really speaking of doing calculations only to order c^{-2}. One can do relativistic Hartree-Fock with 4-component spinors but even quantum electrodynamics exact theory cannot go beyond two electrons. So how do we proceed? We can consider deriving a fully relativistic theory with 4-component spinors using a coupled Hartree-Fock scheme, IGLO-version for example. One could do perturbation theory based on the Breit-Pauli Hamiltonian. The most important contribution comes from the spin-orbit coupling terms contributing to the paramagnetic shielding.

(3) Absolute shielding scales are not available. In the first place we no longer have an identity relating the spin rotation tensor and σ^p in relativistic systems, therefore cannot derive an accurate absolute shielding scale this way. I can suggest the following: Find a linear molecule. — A measure of $(\sigma_{\parallel} - \sigma_{\perp})$ can provide, together with the theoretical $\sigma_{\parallel}^{d}$, the absolute shielding tensor components. Make chemical shift measurements of this molecule (and others) in the gas phase relative to the commonly used reference substance for this nucleus. With this, all the measured chemical shifts can be converted to absolute shielding.

(4) We need more gas phase data for more accurate comparisons of calculations with experiments. We need this even for 1st and 2nd row atoms for example. ^{35}Cl, ^{33}S, ^{29}Si. We also need to carry out vibrational averaging before comparing *ab initio* numbers with experiments since theoretical results are becoming accurate to this level.

5) We need methods of dealing with complex systems which are not yet tractable by *ab initio* methods. We can do high quality *ab initio* calculations on model systems or fragments which emulate the essential characteristics of the real system. This helps to sort out various effects such as charge polarization effects (electric field effects), geometry - dependence (T-O-T angle, etc.), coordination-number-dependence. At the same time we need to think of new clever ways of modelling these complex systems.

(6) We need correlated calculations at higher levels than have already been done. Presently there are several approaches in use: CI, MCSCF (Daborn and Handy, Yeager and Jorgensen), SOPPA (Oddershede), SOLO (Hansen and Bouman), MBPT (Saika), MBPT(2)-GIAO (Gauss), and MC-IGLO (Wülle and Kutzelnigg). These methods have a tendency to overshoot the correlation effects. We can correct for this by using more sophisticated methods, MP4, MCSCF-CC, for example. Since the local origin methods owe their success to removing error terms in the long-range contributions, we can use correlated calculations to improve the long-range contributions. The local correlation effects which are not obtained in a not-saturated basis set might be improved by using locally-dense basis sets in connection with one of the various correlated calculation techniques.

The next conference on this subject will undoubtedly bring new results and understanding along these lines and much more that we do not yet foresee at this time.