

# Ab Initio Calculations of NMR Parameters for Diatomic Molecules

## An Exercise in Computational Chemistry

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The importance of computational chemistry in the undergraduate curriculum has been discussed in this *Journal* (1–3). The value to students of using commercial programs such as Gaussian to obtain results that may be compared to experiment was advanced early on by Mallinson and Peters (4), some years after the release of Gaussian 70. More recently, Duke and O’Leary illustrated the use of Gaussian as a teaching tool by working through a detailed example of how to carry out calculations on the hydrogen molecule (1). In 1996, an article by Williams et al. pointed out the advantages of working with Gaussian for Windows—for example, reasonable computation times on a PC (2). With the increasing availability, accessibility, and importance of programs such as Gaussian, computational exercises for undergraduates are timely<sup>1</sup> (5, 6) and practical. Martin’s paper on the integration of computational chemistry into the chemistry curriculum (3) demonstrates this.

Whereas Martin’s study focused on molecular mechanics, in this paper we present a computational quantum chemistry experiment for upper-year undergraduate students enrolled in a course on magnetic resonance or quantum chemistry that illustrates the connection between nuclear magnetic resonance (NMR) parameters and state-of-the-art ab initio calculations. In addition, the link between NMR parameters and hyperfine parameters available from high-resolution microwave spectra or molecular beam experiments is discussed. The exercise demonstrates that students can do relatively quick calculations and the results are comparable to highly accurate experimental data available in the literature.

Many scientists seem to be unaware of the relationship between spin–rotation constants (available from high-resolution microwave spectra or molecular beam experiments) and nuclear magnetic shielding tensors. This important relationship, which allows for a particularly meaningful comparison between experimental data and theoretical results, is not discussed in most standard physical chemistry or spectroscopy texts. Exceptions are pre-1980 books by Flygare (7), Ramsey (8), and Davies (9). In fact, most of the accurate absolute nuclear shielding scales in use today are based on spin–rotation data (10); the relationship between spin–rotation constants and nuclear shielding is therefore critical to our understanding of chemical shifts. Furthermore, few undergraduates are exposed to the idea that the magnetic shielding experienced by a nucleus depends on the orientation of the molecule in the applied magnetic field.

The following discussion and experiment will result in an awareness of the tensorial nature of NMR parameters such as nuclear magnetic shielding, an appreciation of the effects of basis sets in ab initio calculations, an awareness of the relatively simple relationship between the nuclear spin–rotation interaction and nuclear magnetic shielding in linear molecules,

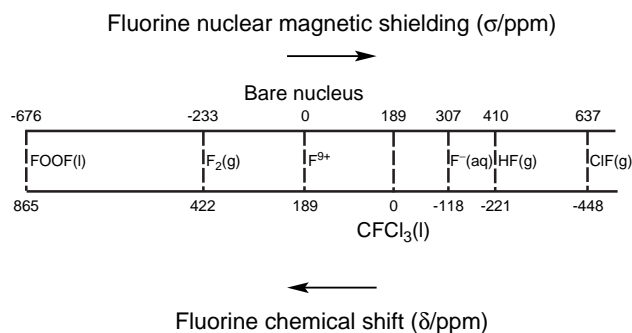


Figure 1. Fluorine nuclear magnetic shielding and chemical shift scales. The absolute shielding scale is referenced to the bare nucleus,  $F^{9+}$ , whereas the chemical shift scale is referenced to  $CFCl_3(l)$ . The data for HF,  $F_2$ , and ClF are for the gaseous state at zero pressure and 303 K (11, 30). Datum for liquid FOOF is from refs 11–13. The  $F^-(aq)$  value is a result of extrapolation to zero KF concentration (14).

and most practically, will provide undergraduates with hands-on experience in computational chemistry. A series of fluorine-containing diatomics is a good starting point for calculations because the computation time is relatively short, and reliable experimental data for isolated molecules in the gas phase are available.<sup>2</sup> In addition, the long history of efforts to interpret fluorine chemical shifts shows that molecules such as  $F_2$  and ClF will provide a stringent test of any computational method for calculating nuclear magnetic shieldings. The difference in magnetic shielding experienced by the fluorine nuclei in these two molecules represents a significant fraction of the total known range (about 1300 ppm) (11) of  $^{19}F$  chemical shifts in diamagnetic molecules (see Fig. 1).

This exercise is readily extended to consider calculated electric field gradients (EFGs) at nuclei. These are directly related to nuclear quadrupole coupling constants, which are available from a variety of NMR experiments or the hyperfine structure observed in the rotational spectra of molecules containing one or more quadrupolar nuclei.

### Theory and Background

#### NMR Parameters: Chemical Shifts and Nuclear Magnetic Shielding

Most upper-year undergraduates will be familiar with the concept of the isotropic chemical shift,  $\delta$ . It is defined in terms of the resonance frequencies,  $\nu$ , of the sample of interest and of a reference compound:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6 \quad (1)$$

The resonance frequency of a particular nucleus may be defined as

$$\nu = \frac{\gamma B_0}{2\pi} (1 - \sigma) \quad (2)$$

where  $\gamma$  is the magnetogyric ratio characteristic of a given isotope,  $B_0$  is the external applied magnetic field, and  $\sigma$  is the nuclear magnetic shielding constant particular to the chemical environment. Substitution of eq 2 into eq 1 gives the relationship between  $\sigma$  and  $\delta$ :

$$\delta = \frac{\sigma_{\text{ref}} - \sigma_{\text{sample}}}{1 - \sigma_{\text{ref}}} \quad (3)$$

If  $\sigma_{\text{ref}}$  is very small compared to unity, as is the case for fluorine, the above expression reduces to

$$\delta = \sigma_{\text{ref}} - \sigma_{\text{sample}} \quad (4)$$

where all quantities are in parts per million (ppm). Hence, in this approximation, the *shielding* scale is reversed compared to the *shift* scale, and has a different origin (see Fig. 1). The origin of the chemical shift scale is arbitrary; for example, TMS is chosen as  $\delta = 0$  ppm for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR, while  $\text{CFCl}_3(\ell)$  is usually the chemical shift reference for  $^{19}\text{F}$  NMR. In contrast, the origin of the shielding scale is defined by the resonance frequency of a bare nucleus.

An *absolute* shielding scale (10) is established when the nuclear magnetic shielding constant is known in at least one compound, the so-called primary reference. If the chemical shift for any other compound is known relative to this reference, its absolute shielding is also known. In this manner, an absolute shielding scale is established.

Nuclear magnetic shielding is a tensor quantity. Such a quantity is conveniently represented by a  $3 \times 3$  matrix:

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad (5)$$

where, in principle, all nine components are unique. In the *principal axis system* (PAS), the symmetric part of the shielding tensor becomes diagonal and its orientation with respect to the molecular axis system can be defined by three Euler angles. For a linear molecule, there are only two independent directions at a nucleus (parallel and perpendicular to the bond axis) and the shielding tensor simplifies to give

$$\sigma = \begin{bmatrix} \sigma_{\perp} & 0 & 0 \\ 0 & \sigma_{\perp} & 0 \\ 0 & 0 & \sigma_{\parallel} \end{bmatrix} \quad (6)$$

The average of the trace of the shielding tensor gives the isotropic shielding,  $\sigma_{\text{iso}}$ . Hence, for any nucleus in a linear molecule,

$$\sigma_{\text{iso}} = \frac{\sigma_{\parallel} + 2\sigma_{\perp}}{3} \quad (7)$$

The shielding parallel to the bond axis,  $\sigma_{\parallel}$ , is the shielding

experienced by a particular nucleus when the direction of the external applied magnetic field,  $B_0$ , is parallel to the bond axis. Similarly, the shielding perpendicular to the bond axis,  $\sigma_{\perp}$ , is the shielding experienced when  $B_0$  is perpendicular to the bond axis. The anisotropy or *span* (15) of the shielding tensor for a linear molecule is

$$\Omega = |\sigma_{\parallel} - \sigma_{\perp}| \quad (8)$$

In providing a theoretical basis for nuclear magnetic shielding, Ramsey (8, 16) decomposed the shielding into *diamagnetic*,  $\sigma^{\text{d}}$ , and *paramagnetic*,  $\sigma^{\text{p}}$ , terms:

$$\sigma = \sigma^{\text{d}} + \sigma^{\text{p}} \quad (9)$$

The diamagnetic contribution depends only on the ground electronic state of the molecule, whereas the paramagnetic contribution depends on a sum over excited states (8, 16–18); therefore the latter is the more difficult term to calculate. The expressions for  $\sigma^{\text{d}}$  and  $\sigma^{\text{p}}$  are

$$\sigma_{\alpha\beta}^{\text{d}} = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{e^2}{2m} \right) \left\langle 0 \left| \sum_k \frac{r_{k\alpha}^2 \delta_{\alpha\beta} - r_{k\alpha} r_{k\beta}}{r_k^3} \right| 0 \right\rangle \quad (10)$$

$$\sigma_{\alpha\beta}^{\text{p}} = - \left( \frac{\mu_0}{4\pi} \right) \left( \frac{e^2}{2m^2} \right) \times \sum_{n \neq 0} \left[ \frac{\langle 0 | \sum_k r_k^3 \hat{\ell}_{k\alpha} | n \rangle \langle n | \sum_k \hat{\ell}_{k\beta} | 0 \rangle + \langle 0 | \sum_k \hat{\ell}_{k\beta} | n \rangle \langle n | \sum_k r_k^3 \hat{\ell}_{k\alpha} | 0 \rangle}{\epsilon_n - \epsilon_0} \right] \quad (11)$$

Here,  $e$  is the charge of an electron,  $m$  is the mass of an electron,  $k$  indicates a sum over all electrons,  $n$  indicates a sum over excited singlet states,  $r_k$  is the position vector for electron  $k$ , and  $\hat{\ell}_k$  is the angular momentum operator with respect to the gauge origin. Equations 10 and 11 may be used to obtain any of the shielding tensor components by appropriate permutation of  $\alpha$  and  $\beta$  over  $x$ ,  $y$ , and  $z$ ;  $\delta_{\alpha\beta}$  is the Kronecker delta (8, 11, 19).

Although it is generally recognized that the precise partitioning of  $\sigma$  into  $\sigma^{\text{d}}$  and  $\sigma^{\text{p}}$  is somewhat arbitrary (20), the original formalism of Ramsey is particularly attractive because of the connection between  $\sigma^{\text{p}}$  and the perpendicular component of the spin–rotation tensor,  $C_{\perp}$ , in linear molecules. The calculation of  $\sigma^{\text{p}}$  using virtual states as in eq 11 may be circumvented if  $C_{\perp}$  is known. Ramsey (8, 16b) and Flygare (21–23) have shown that the perpendicular component of the shielding is simply related to  $C_{\perp}$  in the following manner:

$$\sigma_{\perp} \equiv \left( \frac{-m_{\text{p}} C_{\perp}}{2m g_{\text{N}} B} \right) + \sigma_{\text{atom}}^{\text{d}} \quad (12)$$

where  $m_{\text{p}}$  is the mass of a proton,  $m$  is the mass of an electron, and the nuclear  $g$ -factor,  $g_{\text{N}}$ , is defined as  $\gamma_{\text{N}} \hbar / \mu_{\text{N}}$  ( $\mu_{\text{N}}$  is the nuclear Bohr magneton). The molecular rotation constant,  $B$ , is equal to  $\hbar^2 / 8\pi^2 I$ , and  $\sigma_{\text{atom}}^{\text{d}}$  is the diamagnetic shielding for the free atom (24, 25). The paramagnetic component of the shielding along the bond axis is zero due to symmetry,<sup>3</sup> and  $\sigma_{\parallel}$  is given by eq 13.

$$\sigma_{\parallel} = \sigma_{\parallel}^{\text{d}} \approx \sigma_{\text{atom}}^{\text{d}} \quad (13)$$

## On the Connection Between Nuclear Magnetic Shielding Tensors and Nuclear Spin–Rotation Tensors

When a molecule rotates, the motion of the nuclei and electrons generates magnetic fields proportional to the rotational angular momentum,  $\mathbf{J}$ . Of particular interest is the magnetic field generated in this way at the position of a nucleus that possesses a nuclear magnetic moment. The energy of interaction between the nuclear spin and this field may be written

$$\hat{H}_{IJ} = -\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{J} \quad (14)$$

where  $\mathbf{C}$  is, in general, a second-rank tensor. In the case of a linear molecule, only rotations of the molecular axis generate magnetic fields so there is only one unique component of the spin-rotation tensor,  $C_{\perp}$ .

The nuclear spin–rotation interaction perturbs rotational spectra and results in so-called hyperfine structure. Nuclear spin–rotation constants in diatomics are typically on the order of kilohertz. For example,  $C_{\perp} \approx 71$  kHz for  $^1\text{H}$  in HF and  $C_{\perp} \approx 305$  kHz for  $^{19}\text{F}$  in HF. The latter is one of the largest nuclear spin–rotation constants known. Given that the  $J = 0$  to  $J = 1$  rotational transition occurs at  $2B_0 \approx 1.25 \times 10^{12}$  Hz, it is clear that excellent resolution is necessary to observe hyperfine structure in rotational spectroscopy. Doppler broadening and pressure broadening obscure any hyperfine structure in conventional rotational spectroscopy. Molecular beam techniques have proven very useful in the observation of spin–rotation interactions (26, 27).

The key point is that spin–rotation tensors can be measured experimentally. Furthermore, these tensors are intimately related to the paramagnetic portion of the nuclear shielding tensor (eq 12). Accurate spin–rotation data available from these experiments yield shielding constants that should compare well with ab initio calculations. It is important to recognize that spin–rotation data are obtained for isolated molecules, and generally one does not have to be concerned with intermolecular effects when comparing experimental and theoretical results.

A rigorous comparison of experimentally determined shielding tensors with those calculated using a program such as Gaussian entails the consideration of rotational–vibrational corrections. Calculated values are typically for the equilibrium bond length (i.e., a rigid molecule), whereas experimental values are necessarily vibrationally averaged. These corrections were introduced by Buckingham (28) and discussed extensively by Hindermann and Cornwell (29) and Jameson (10). A particularly large correction is that for  $\text{F}_2(\text{g})$ ,  $-40$  ppm, whereas most corrections for small fluorine-containing molecules are an order of magnitude less (30). Details for carrying out such corrections are found in the Appendix, and excellent discussions are available in the original literature and review articles (10, 29, 30).

### NMR Parameters: Quadrupolar Coupling Constants

Another molecular property of interest in NMR is the electric field gradient (EFG) at a quadrupolar nucleus. A quadrupolar nucleus is one that has a nuclear spin greater than  $1/2$ ; the charge distribution within these nuclei is asymmetric, resulting in a nonzero nuclear quadrupole moment,  $Q$ . The quadrupolar coupling constant,  $C_Q$ , is defined as the

**Table 1. Accepted Quadrupole Moments**

Nuclide	$Q/\text{fm}^2$
$^7\text{Li}$	$-4.01$
$^{23}\text{Na}$	$10.06(20)$
$^{39}\text{K}$	$5.9(6)$
$^{35}\text{Cl}$	$-8.11(8)$

NOTE: From ref 31.

product of  $Q$  and the largest component of the electric field gradient,  $V_{zz}$ , at the nucleus:

$$C_Q = \frac{eQV_{zz}}{h} \quad (15)$$

where  $e$  is the charge of an electron and  $h$  is Planck's constant. Accepted values of nuclear quadrupole moments and their associated uncertainties are given in Table 1 (31).

In its principal axis system, the EFG is described by a second-rank tensor,  $\mathbf{V}$ :

$$\mathbf{V} = \begin{bmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{bmatrix} \quad (16)$$

$\mathbf{V}$  must satisfy Laplace's equation,  $\nabla^2 \mathbf{V} = 0$ , which, in the case of linear molecules (where axial symmetry exists), leads to  $\frac{1}{2}|V_{zz}| = |V_{xx}| = |V_{yy}|$ . We will use ab initio calculations to determine  $V_{zz}$  (also denoted  $eq_{zz}$ ), from which nuclear quadrupolar coupling constants may be calculated via eq 15. Although the EFG tensor is a first-order property dependent only upon the electronic ground state (7, 9, 25), reliable calculations require an accurate description of the electron distribution in the vicinity of the nucleus. Because Gaussian functions provide a poor description of charge distribution near a nucleus (17), large basis sets are required for reliable calculations of EFGs. Vibrational corrections analogous to those that may be carried out for shielding tensors may also be done for  $V_{zz}$  (see Appendix) (32).

### Ab Initio Calculations: Nuclear Magnetic Shielding and EFG Tensors

In the Hartree–Fock approximation,<sup>4</sup> the wave function is that which represents the ground electronic configuration; this wave function is then optimized variationally. This approximation is reasonably good for closed-shell systems at the equilibrium geometry, such as for a series of diatomics. The Hartree–Fock equations are

$$\hat{F}\psi_i = \epsilon_i \psi_i; \quad i = 1, 2, \dots, N \quad (17)$$

$$\hat{F} = \hat{H}_{\text{core}} + \sum_{j=1}^N \left( 2\hat{J}_j - \hat{K}_j \right) \quad (18)$$

where  $\hat{F}$  is the Fock operator,  $\epsilon_i$  is the self-consistent field orbital energy for an electron in molecular orbital  $\psi_i$ ,  $\hat{H}_{\text{core}}$  is the one-electron operator for the core electrons,  $\hat{J}_j$  is the Coulomb

**Table 2. Minimal Basis Sets for Hydrogen through Chlorine**

Atom	Atomic orbitals	No. of AOs in Basis Set
H	1s	1
Li through F	1s 2s 2p	5
Na through Cl	1s 2s 2p 3s 3p	9

operator, and  $\hat{K}_j$  is the exchange operator. These equations are solved iteratively to reach a “self-consistent” solution. In most programs (e.g., Gaussian [33], Dalton [34], and ACES II [35]), the shielding tensor is not calculated using Ramsey’s equations, but equivalently by taking a second derivative of the energy (20, 36, 37):

$$\sigma_{\alpha\beta} = \left[ \frac{\partial^2 E}{\partial \mu_\alpha \partial B_\beta} \right]_{\mu, B=0} ; \quad \alpha, \beta = x, y, z \quad (19)$$

Here,  $E$  is the total electronic energy,  $\mu$  is the magnetic moment of the nucleus, and  $B$  is the external applied magnetic field. The molecular orbitals,  $\psi$ , used in the Hartree–Fock calculations are optimized linear combinations of *basis functions*. Students will be familiar with one of the simplest *basis sets*, the minimal basis set. This basis set is composed of the atomic orbitals (AOs) commonly used to describe electronic configurations in chemistry (Table 2). Thus, for a minimal basis set Hartree–Fock calculation on hydrogen fluoride, there will be 5 atomic orbitals on fluorine and a single atomic orbital on hydrogen. Any basis set that goes beyond the minimal basis set is called an *extended basis set*. Several good explanations of extended basis sets commonly used for calculations are found in refs 2, 17, and 38–41. Since Hartree–Fock theory is based on the variation theorem, in which a set of parameters are optimized to produce the minimum energy, a greater number of variational parameters will always yield a better (i.e., lower) estimate of the true energy of a system. The Hartree–Fock energy will always be greater than or equal to the true energy. For example, if a basis set such as 6-311++G(2d,2p) is used rather than the minimal basis set for a calculation on hydrogen fluoride, many more variational parameters are optimized in the process. The hydrogen atom will have  $3 + 1 + 1 = 5$  functions of the type “1s”, plus diffuse functions (indicated by the second “+”), plus two sets of p functions (indicated by “2p”). All the functions are Gaussians, as indicated by “G”. For the fluorine atom, six Gaussians are used for core orbitals, and  $3 + 1 + 1 = 5$  Gaussians of differing shapes for each of the valence orbitals. In addition, the fluorine will have a set of diffuse orbitals (indicated by the first “+”) and two sets of d functions. In the Hartree–Fock limit, a complete basis set is employed, which, in effect, entirely describes the molecular orbitals; a numerical solution will also give this limit. Of course, this “complete basis set” is not generally available, especially for large molecules.

The main shortcoming of the Hartree–Fock method is that it does not account for electron correlation effects. Thus, even in the limit of a complete basis set, the Hartree–Fock

energy will always be too large:

$$E_{\text{exact}} = E_{\text{Hartree-Fock}} + E_{\text{corr}} \quad (20)$$

where  $E_{\text{corr}}$  is the correlation energy and  $E_{\text{exact}}$  is the exact (nonrelativistic) energy. *Electron correlation* accounts for the fact that all electrons in a system interact with each other simultaneously (17, 42). For each electron, the Hartree–Fock method approximates the influence of the other electrons in the system by a fixed potential.

Clearly, this model cannot be entirely accurate, and for this reason, other computational methods were developed to include electron correlation. Some commonly used methods are Møller–Plesset perturbation theory (MP2, MP3, MP4SDQ), configuration interaction (CI) methods, multiconfigurational self-consistent field (MCSCF) theory, and the coupled cluster (CC) approximation (43). Density functional theory (DFT), which in principle includes electron correlation implicitly, may also be used to calculate NMR parameters (44–46). Any method that includes electron correlation should yield a more accurate result than Hartree–Fock theory. Helgaker et al. conclude that to accurately calculate nuclear magnetic shieldings, a basis set of triple-zeta quality or greater, with at least one set of polarization functions, must be used (37). However, qualitative features and trends in NMR parameters can be illustrated by much lower level calculations.

Depending on where the origin of the vector potential of the external applied magnetic field,  $B$ , is chosen (called the *gauge origin*), the calculated nuclear magnetic shieldings will differ (in the absence of a complete basis set). In the limit of a complete basis set, the choice of gauge origin is unimportant because shielding is a molecular property—it cannot depend on the choice of origin in a calculation. Since complete basis sets are not generally practical, methods have been proposed to circumvent the problem of gauge variance, including gauge-independent atomic orbitals (GIAOs) (47, 48), individual gauge origins for different localized molecular orbitals (IGLO) (20), and individual gauges for atoms in molecules (IGAIM) (49). The GIAO method uses a gauge factor in the atomic orbitals used in a calculation (36, 48); this is the method we will employ in the present calculations. Augspurger and Dykstra point out that when large basis sets are used, the range of the isotropic  $^{19}\text{F}$  shielding in HF as a result of moving the gauge origin over the length of the molecule is well within the limits of experimental uncertainty (50).

Unlike nuclear magnetic shielding, the electric field gradient is a first-order property (it does not depend explicitly on virtual orbitals [11]); however, electron correlation effects are important for EFG tensor calculations, as they are for the magnetic shielding calculations discussed above. Visscher et al. discuss the effects of basis set size and electron correlation on EFG calculations and present relativistic calculations of the EFGs at the nuclei in the hydrogen halides (51). Bacskey and Buckingham’s paper considers the effect of several electron-correlated methods on the nuclear quadrupole coupling constants in the alkali halides (52).

Several informative articles dealing with the calculation of nuclear magnetic shielding and other magnetic properties can be found in the *Encyclopedia of Computational Chemistry* (53) and the *Encyclopedia of NMR* (54).



## Interpretation of Fluorine Chemical Shifts— A Brief History

Shortly after the publication of Ramsey's equations (16), a note on fluorine chemical shifts appeared (55), comparing hydrogen fluoride and the fluorine molecule. The paramagnetic part of the shielding is described as arising from an imbalance of  $p$  electrons about the fluorine nucleus. In the spherically symmetric fluoride ion, the imbalance is zero, and thus  $\sigma^P$  is also zero. In a partially ionic molecule such as hydrogen fluoride, the paramagnetic term becomes nonzero as a result of the deviation from spherical symmetry about F. In the covalently bound  $F_2$  molecule, the paramagnetic term is even larger, and negative. Between the extremes of the fluoride ion and the fluorine molecule, the chemical shift of the fluorine nucleus in binary fluorides is almost linearly dependent on the electronegativity of the atom bonded to fluorine. In 1964, Jameson and Gutowsky (56) showed that for atoms other than hydrogen, the paramagnetic part of the chemical shielding must be the dominant factor in determining  $\sigma_{\text{total}}$ . Shortly thereafter, Kolker and Karplus compared calculated values of  $\sigma^P$  with results from experimental spin-rotation data (57). Agreement was good for light atoms such as H and Li. However, discrepancies were evident for heavier atoms such as fluorine, highlighting the difficulty associated with calculating  $\sigma^P$ . At the same time, Baker et al. (58) determined the total fluorine nuclear magnetic shieldings for HF and  $F_2$  by employing experimental fluorine nuclear spin-rotation data for the paramagnetic contribution, and calculated values for the diamagnetic contribution. We will adopt this strategy for the present exercises.

Chemical shifts do not depend directly on electron density or electronegativity (20, 59). Chlorine monofluoride in particular is often cited as a molecule that does not exhibit the "expected" fluorine shift based on naive electron density arguments (59–61). Figure 1 clearly shows that such arguments, which are traditionally used to justify proton NMR shifts in undergraduate courses, are insufficient and incorrect. Often it is the HOMO–LUMO gap, represented by the denominator in eq 11, that is responsible for variations in chemical shifts (59, 62, 63). Interpretations of the apparently anomalous fluorine shift in ClF appeared in the literature as early as 1966 (60) and as recently as 1998 (61, 64). The seemingly unusual fluorine shielding in ClF has been explained by considering the paramagnetic term alone. It is left as an exercise for the student to consult the literature for an explanation. The paper by Wiberg et al. provides an informative comparison of the fluorine shielding in  $F_2$  vs ClF (61).

We emphasize that the present exercise is an uncompromising test of computational methods owing to the large range of the fluorine shifts and, more importantly, to the availability of accurate experimental spin-rotation tensors for  $^{19}\text{F}$  in several diatomic molecules, which permits direct comparison between experiment and theory.

## The "Experiment"

To illustrate the results of the experiment, we chose the following series of fluorine-containing diatomics: HF, LiF, NaF, KF, ClF, and  $F_2$ . Of course, other molecules may be studied, provided reliable experimental spin-rotation data

**Table 3. Equilibrium Bond Lengths Employed in ab Initio Calculations**

Molecule	Equilibrium Bond Length/ $\text{\AA}^a$
LiF	1.563884
NaF	1.9259648
KF	2.1714777
ClF	1.6283323
HF	0.91682
$F_2$	1.41193

<sup>a</sup>From refs 66, 67. Uncertainties can be found in the original references.

(65) and spectroscopic constants (66) and suitable basis sets are available. Because very accurate experimental equilibrium bond lengths are available for these molecules (67, 68), they are used in our calculations; however, geometries may also be optimized within the ab initio calculation. The bond lengths employed in our calculations are shown in Table 3.

To carry out an ab initio calculation of the shielding and EFG tensors simultaneously, the *NMR* and *Prop* keywords are required in Gaussian 94/98. The Gaussian 94 input file for ClF, shown below without the basis set, for a calculation of the NMR properties of ClF at the RHF level with the 6-311++G(2d,2p) basis set, is representative of what is required for this exercise.

```
#p RHF/Gen NMR Prop
chlorine monofluoride with 6-311++G(2d,2p)
0 1
Cl
F 1 1.6283323
```

*RHF* indicates that a spin-restricted Hartree–Fock calculation will be done and *Gen* indicates that the basis sets to be used will follow the **Z** matrix in the input file. Note that the default method for calculating shielding tensors is the GIAO method. For a more complete explanation of Gaussian input files and **Z** matrices, see Duke and O'Leary (1) and Foresman and Frisch (40). Electron-correlation methods may be used for calculating EFGs by altering the RHF entry; Gaussian 98 (69) can include electron correlation by calculating nuclear shielding at the MP2 level of theory, whereas Gaussian 94 can only calculate nuclear shielding using Hartree–Fock and DFT methods. Small basis sets are available within the Gaussian suite of programs; however, larger basis sets must be appended to the input file. The Web site at <http://www.emsl.pnl.gov:2080/forms/basisform.html> is the source of the basis set files used for this exercise.<sup>5</sup>

The results at the RHF/6-311++G(2d,2p) level are presented here as an example of what students should expect. When the calculation is complete (43 s CPU time for  $F_2$  on an IBM RISC/6000 workstation, or a few minutes CPU time on a PC), the desired information is found in the log file. Shielding tensor results are found under the heading "GIAO Magnetic shielding tensor"; an example of the output is given below. Both the isotropic value and the anisotropy are redundant pieces of information. Notice that the tensors are in the

form given in eq 6; they are in their principal axis system.<sup>6</sup> Hence, in the case of ClF, the non-vibrationally-corrected values for the fluorine shielding tensor at the indicated level of theory are  $\sigma_{||} = 493$  ppm and  $\sigma_{\perp} = 792$  ppm.

GIAO Magnetic shielding tensor (ppm):

```

1 Cl Isotropic = -418.2789 Anisotropy = 2357.8584
  XX= -1204.2317  YX=      .0000  ZX=      .0000
  XY=      .0000  YY= -1204.2317  ZY=      .0000
  XZ=      .0000  YZ=      .0000  ZZ= 1153.6267
Eigenvalues: -1204.2317 -1204.2317 1153.6267
2 F Isotropic = 692.4638 Anisotropy = 149.5039
  XX=  792.1331  YX=      .0000  ZX=      .0000
  XY=      .0000  YY=  792.1331  ZY=      .0000
  XZ=      .0000  YZ=      .0000  ZZ=  493.1253
Eigenvalues:  493.1253  792.1331  792.1331

```

EFG results are found under the heading “Electric Field Gradient—(tensor representation)—Eigenvalues”. It is important to use this set of EFG data; there are many other forms given in the Gaussian output. An example of the desired output is given below for ClF. Note that the ab initio results given by Gaussian are in atomic units and that the EFG eigenvalues generated by Gaussian 94/98 are the negatives of those more commonly defined and used. To convert the EFG from atomic units to  $\text{Vm}^{-2}$ , values must be multiplied by  $9.7177 \times 10^{21} \text{ Vm}^{-2}$  per au (70). Hence, the value of  $V_{zz}$  to be employed in eq 15 for ClF is  $7.618755 \times 9.7177 \times 10^{21} \text{ Vm}^{-2} = 7.4036 \times 10^{22} \text{ Vm}^{-2}$ .

Center	Electric Field Gradient (tensor representation)		
	Eigenvalues		
1 Atom	-7.618755	3.809377	3.809377
2 Atom	-4.519642	2.259821	2.259821

Vibrational effects, while important for researchers in this area, may be ignored for the present purposes (see Appendix). The magnitudes of the corrections for the series of molecules in this experiment were less than ca. 10 ppm for  $\sigma_{\perp}$  (except for  $\text{F}_2$ ), and from ca. 0.002 MHz (Li) to ca. 0.19 MHz (Cl) for the quadrupole coupling constants. The corrections to  $C_Q$  in particular are very small when compared to  $C_Q$  itself.

Table 4 shows the experimental spin-rotation constants, paramagnetic contributions to shielding, and quadrupole coupling constants (7, 71–74).

The results of the fluorine shielding calculations are shown in Table 5.  $\sigma_{\text{iso}}$  (calcd),  $\sigma_{\perp}$  (calcd), and  $\sigma_{||}$  (calcd) are simply the vibrationally corrected values from the ab initio calculations.  $\sigma_{\perp}$  (exptl) is given by combining eqs 12 and 13:

$$\sigma_{\perp}(\text{exptl}) = \frac{-m_p C_{\perp}}{2m_N B} + \sigma_{||}(\text{calcd}) \quad (21)$$

and  $\sigma_{\text{iso}}$  (exptl) is given by

$$\sigma_{\text{iso}}(\text{exptl}) = \frac{2\sigma_{\perp}(\text{exptl}) + \sigma_{||}(\text{calcd})}{3} \quad (22)$$

The experimental and calculated quadrupole coupling constants are shown in Table 6. Both calculated shieldings and EFGs are in qualitative agreement with the experimental data. RHF calculations with the 6-31G(d) basis set were not as consistently in agreement with experimental data. However,

**Table 4. Experimental Quadrupole Coupling Constants, Spin-Rotation Constants, and Paramagnetic Shieldings for Some Fluorine-Containing Diatomics**

Molecule	Ref	$C_Q/\text{MHz}^a$	$C_{\perp}/\text{kHz (F)}^a$	$\sigma^p/\text{ppm (F)}$
$^7\text{LiF}$	71	0.420792 (Li)	32.9550	-142.5
$^{23}\text{NaF}$	72	-8.4393 (Na)	2.2	-29.3
$^{39}\text{KF}$	73	-7.981013 (K)	10.8325	-225.5
$^{35}\text{ClF}$	74	-145.78211 (Cl)	-22.67	255.8
HF	7	—	284	-78.4
$\text{F}_2$	7	—	157	-1038.9

<sup>a</sup>Uncertainties can be found in the original references.

**Table 5. Experimental and Vibrationally Corrected ab Initio Fluorine Nuclear Magnetic Shielding Constants for Some Fluorine-Containing Diatomics**

Molecule	Shielding Constant/ppm				
	$\sigma_{\text{iso}}$		$\sigma_{\perp}$		$\sigma_{  }$
	calcd	exptl	calcd	exptl	
$^7\text{LiF}$	390	386	345	339	481
$^{23}\text{NaF}$	460	463	448	454	483
$^{39}\text{KF}$	350	335	282	260	485
HF	404	429	366	403	482
$\text{F}_2$	-204	-204	-551	-550	488
$^{35}\text{ClF}$	689	664	787	749	493

Note: RHF/6-311++G(2d,2p) calculations.

**Table 6. Nuclear Quadrupole Coupling Constants for Some Fluorine-Containing Diatomics**

Molecule	$C_Q/\text{MHz}$		Difference (%)
	Calcd <sup>a</sup>	Exptl (Ref)	
$^7\text{LiF}$	0.42707 (Li)	0.420792 (71)	1.5
$^{23}\text{NaF}$	-9.3049 (Na)	-8.4393 (72)	-10
$^{39}\text{KF}$	-8.84286 (K)	-7.981013 (73)	-11
$^{35}\text{ClF}$	-145.379 (Cl)	-145.78211 (74)	0.3

<sup>a</sup>Vibrationally corrected, ab initio RHF/6-311++G(2d,2p) calculations.

even with this basis set qualitatively correct results may be obtained for both shieldings and EFGs; the trends are reproduced. Calculations of the electric field gradient using MP2, MP3, and MP4SDQ methods did not show a systematic improvement over the RHF/6-311++G(2d,2p) results for this series of molecules, a reminder that the error due to an incomplete basis set should be more of a concern than the relatively small effects of electron correlation.

## Implementation of the Exercise in the University Curriculum

This exercise was implemented with success as an assignment in a combined 4th-year undergraduate and 1st-year graduate course, Magnetic Resonance, in the Department of Chemistry at Dalhousie University in Halifax, Canada. Nine students with varying backgrounds in NMR and quantum

chemistry completed the assignment. Some students had only learned about NMR in 2nd- and 3rd-year organic chemistry courses, whereas others were working on graduate studies in solid-state NMR. Before the assignment was done, regular course lectures on the fundamentals of nuclear magnetic shielding and quadrupolar interactions were given. A special lecture aimed at giving the students a thorough understanding of the assignment and the implications of the results was also presented. This lecture focused on the topics discussed in this paper: namely, the relationship between the spin-rotation tensor and the nuclear magnetic shielding tensor, and some theoretical and practical aspects of carrying out ab initio calculations of NMR parameters. The students were given the following list of questions and a copy of this manuscript.

1. For all six molecules in the paper (HF, LiF, NaF, KF, F<sub>2</sub>, ClF), determine the experimental paramagnetic fluorine shielding from the experimental spin-rotation data. Use equations and constants given in the paper.
2. For all six molecules, carry out ab initio (RHF) calculations of the shielding tensors (keyword: NMR) and electric field gradient tensors (keyword: Prop). Use a Pople-type basis set of the type 6-31G\* or 6-311G\*\* etc. For one of the six molecules, compare the results of the calculations for three different basis sets.
3. Using equations in the paper, the experimental data, and the calculated data,
  - (i) compare the fluorine shielding constants perpendicular to the bond ( $\sigma_{\perp}$ ) for the calculated and experimental results.
  - (ii) compare the isotropic fluorine shielding constants for the calculated and experimental results; discuss.
4. Referring to the vibrationally corrected results given in the paper, discuss the importance of these corrections.
5. For the electric field gradient tensors, determine the quadrupolar coupling constant from the equations given in the paper and discuss the results.
6. What is the main cause of the difference in isotropic fluorine chemical shifts between F<sup>-</sup> and F<sub>2</sub>?

## Reactions and Comments of the Students

Many of the students had never done ab initio calculations before. Both Gaussian 98 and Gaussian for Windows were used by the students without any serious difficulties. Students commented that this assignment “definitely” gave them a better understanding of the origins of NMR parameters. Most agreed that valuable hands-on experience in carrying out quantum chemical calculations was gained by doing the exercise; some explained that, of course, this assignment only gave them a small sampling of the power of computational chemistry. It is hoped then, that this assignment will encourage further study into this area.

Students agreed that the experiment fit in well with the course lectures. Some students specifically pointed out the value of combined experimental and theoretical approaches to determining the final shielding tensors. It was encouraging to learn that this assignment was a welcome change from

traditional assignments. One student suggested carrying out a more extensive study of the basis-set dependence of the calculated parameters; of course such a procedure could easily be incorporated into the assignment. For example, it was found that potassium fluoride gives particularly poor results when a small (i.e., 6-31G\*) basis set is used.

## Conclusions

This discussion and quantum chemical experiment illustrate that ab initio calculations that take very little time can be used at the undergraduate level to reproduce experimental spectroscopic data from the literature. Of central importance to this exercise are the tensorial nature of nuclear magnetic shielding and the relatively simple but little-recognized relationship between  $\sigma^p$  and  $C_{\perp}$  in linear molecules. Work in quantum chemistry and NMR continues to exploit the increasing reliability and accuracy of ab initio calculations of NMR parameters (46, 63, 75, 76), highlighting the importance of exposing undergraduates to the underlying ideas as well as the practical considerations associated with these areas. The implementation of the exercise into the curriculum at Dalhousie University proved to be very successful.

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## Notes

1. The Nobel Prize in Chemistry for 1998 was awarded to John Pople and Walter Kohn, both computational chemists.
2. Spin-rotation data are also available for numerous diatomics containing chlorine. See: Gee, M.; Wasylishen, R. E.; Laaksonen, A. *J. Phys. Chem. A* **1999**, *103*, 10805–10812.
3. For a molecule in a  $^1\Sigma$  ground state, the eigenvalue of  $\hat{L}_z$  is zero.
4. See ref 17 (Chapter 9) for an overview of the calculation of electronic structure.
5. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352. Funding is by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.
6. This is not the case in general; however, for diatomic molecules the tensors are always given in their PAS by Gaussian.

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## Appendix. Optional Exercise—Vibrational Corrections

Accurate ab initio results must be vibrationally corrected for useful comparison with experimental data (see, for example, Fig. 2 of ref 19). This is because real molecules vibrate, whereas ab initio calculations are generally carried out on a rigid, isolated molecule at the equilibrium bond length,  $r_e$ . Figure 2 shows a representation of the potential well of a typical anharmonic oscillator (Morse function). What is important to notice is that the equilibrium bond length is less than the effective bond length for a vibrating molecule. For a molecule in the  $v = 0$  state, the apparent bond length is larger than  $r_e$  owing to the anharmonicity of the oscillator. As a result, ab initio results must be corrected for this. (Conversely, the experimental data may be “reverse-corrected” to  $r_e$ .) Buckingham (28) first pointed out that vibrational corrections may be impor-

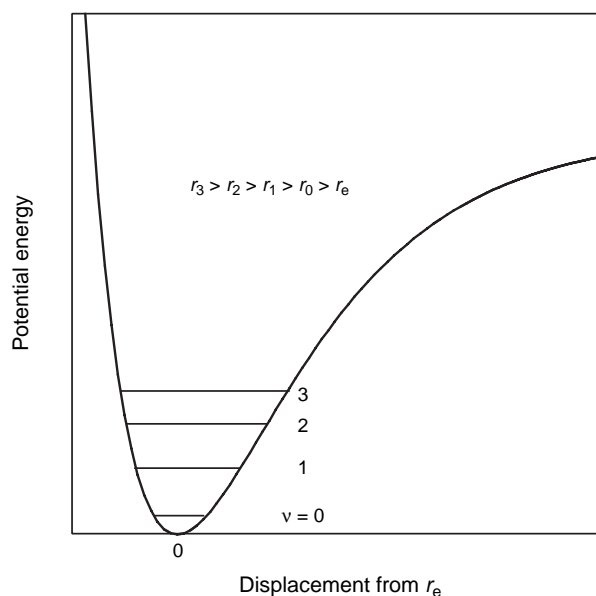


Figure 2. Schematic representation of a Morse potential for a diatomic molecule. The internuclear distance depends on which vibrational states are occupied, whereas the equilibrium bond length is a fixed value defined by the minimum in the potential.

tant when studying chemical shifts. The expression used for the corrected shielding value is (28, 77, 78)

$$\langle \sigma \rangle^T = \sigma^e + f(T) \left( \frac{d\sigma}{dr} \right)_e + g(T) \left( \frac{d^2\sigma}{dr^2} \right)_e \quad (\text{A1})$$

where  $\sigma_e$  is the ab initio value at  $r_e$ , and  $f(T)$  and  $g(T)$  are defined as

$$f(T) = \frac{3h}{16\pi^2 r_e \mu c \omega_e} \left( 1 + \frac{\alpha_e \omega_e}{6B_e^2} \right) \coth \left( \frac{hc\omega_e}{2kT} \right) + \frac{kT}{2\pi^2 r_e \mu c^2 \omega_e^2} \quad (\text{A2})$$

$$g(T) = \frac{h}{16\pi^2 \mu c \omega_e} \coth \left( \frac{hc\omega_e}{2kT} \right) \quad (\text{A3})$$

Here,  $B_e$ ,  $\omega_e$ , and  $\alpha_e$  are the molecular spectroscopic constants and  $\mu$  is the reduced mass (79).

The expression used for correcting EFG tensor components is (80)

$$V_{zz}^{\text{corr}} = \frac{B_e}{\omega_e} \left[ 3 \left( 1 + \frac{\alpha_e \omega_e}{6B_e^2} \right) \left( \frac{\partial V_{zz}}{\partial \xi} \right)_{\xi=0} + \left( \frac{\partial^2 V_{zz}}{\partial \xi^2} \right)_{\xi=0} \right] \quad (\text{A4})$$

**Table A1. Spectroscopic Constants for Some Fluorine-Containing Diatomics**

Molecule <sup>a</sup>	$\omega_e / \text{cm}^{-1}$	$B_e / \text{cm}^{-1}$	$\alpha_e / \text{cm}^{-1}$
<sup>7</sup> LiF	910.34	1.345276	0.0202868
<sup>23</sup> NaF	536	0.43690127	0.00455869
<sup>39</sup> KF	428	0.279937413	0.002335038
HF	4138.32	20.9557	0.798
F <sub>2</sub>	916.64	0.89019	0.013847
<sup>35</sup> ClF	793.2	0.516508	0.004358

<sup>a</sup>Refs 66 and 67; ref 7 for <sup>35</sup>ClF.

for  $V_{zz}$ , where  $\xi = (r - r_e)/r_e$ . The partial derivatives in eqs A1 and A4 may be estimated by calculating the appropriate quantity at  $r = r_e \pm 0.5\%$ . Use of a spreadsheet renders the correction process trivial. The spectroscopic constants are found in the literature; Table A1 shows the required constants for the fluorine-containing diatomics discussed. One particularly useful source of spectroscopic constants is the NIST Web site (67).