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Ab Initio Methods for the Calculation of NMR Shielding and Indirect Spin–Spin Coupling Constants

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I. Introduction

Ab initio methods of quantum chemistry are presently routinely and successfully applied to the study of a vast range of problems of chemical interest. An important aspect of many of these studies is the calculation of the electric, magnetic, and optical properties associated with the responses of a molecular electronic system to perturbations such as externally applied electromagnetic fields and nuclear magnetic and electric moments. In recent years, efficient techniques have been developed for the ab initio calculation of such properties.

The molecular properties responsible for the generation of NMR spectra—that is, the nuclear magnetic shielding constants and the indirect nuclear spin—spin coupling constants—were identified and analyzed in terms of perturbation theory over 40 years ago by Ramsey. However, because of practical problems associated with the calculation of these properties, the early applications of ab initio methods to the study of NMR parameters were not particularly successful. In recent years, these obstacles have been overcome—partly as a result of a general improvement in ab initio techniques and computer technology, partly through the development of special methods and programs for the calculation of NMR properties. As a result, over the last 5—10 years, the calculation of NMR parameters by ab initio methods has developed into a useful and popular tool of computational quantum chemistry.

Hartree—Fock calculations of magnetic properties—difficult for small molecules only a few years ago—

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are today carried out routinely for large systems. Still, their accuracy is limited by the nature of the Hartree−Fock approximation and such calculations can no longer be said to represent the state of the art of ab initio theory for magnetic properties. Indeed, the most promising recent developments are now concerned with methods that go beyond the Hartree−Fock approximation, taking into account the often significant effects of electron correlation on such properties. However, it appears that despite the significant improvements observed in the efficiency of the calculations and the quality of the results, the recent methodological developments in the calculation of magnetic properties have not yet been thoroughly reviewed in the literature. The present review aims to fill this gap, concentrating on the recent developments of ab initio NMR theory and in particular on the methods that include correlation effects.

We begin this review with a short discussion of the effective NMR spin-Hamiltonian in section II. Next, in section III, we consider the evaluation of the NMR spin-Hamiltonian parameters from the exact electronic wave function (Ramsey's theory) and subsequently, in section IV, we describe the general principles for the calculation of NMR parameters from approximate wave functions. After a discussion of the electronic Hamiltonian and the gauge-origin problem in section V, we consider in section VI the evaluation of NMR parameters from the standard ab initio models. For each model, the basic equations needed for the calculation of magnetic properties are discussed, as are some aspects related to the practical implementation and application of the different methods. An important aspect of the calculation of shielding and spin−spin coupling constants, the choice of the atomic basis set, is discussed in section VII.

The next part of the present review is devoted to the discussion of the accuracy and reliability of the calculations—for the shieldings in section VIII and for the spin−spin coupling constants in section IX. Convergence of the properties with respect to the basis set and the correlation treatment is here analyzed. For both properties, we first discuss the highly accurate results obtained for small molecules and next consider the implications for larger molecules.

Two sections of this review are devoted to special topics. In section X, we discuss the calculation of some NMR-related properties, in particular spin−rotation constants and nuclear quadrupole-coupling constants. In section XI, we consider the importance of relativistic effects for NMR parameters.

From experimental data, it is usually difficult to extract the numerical value of a particular NMR parameter that corresponds to the calculated ab initio result for an isolated molecule at a fixed geometry. Therefore, to compare ab initio results directly with experiment, we must take into account the effects of molecular rotation and vibration. These rovibrational effects may be calculated from the geometry dependence of the NMR parameters and they determine the temperature dependence of the NMR parameters, as discussed in section XII. A related topic is the role of intermolecular forces and the influence of a solvent on the measured NMR parameters. Ab initio studies of these effects are now becoming feasible and selected methods and examples are discussed in section XIII. Moreover, NMR is becoming an increasingly important tool in the study of intermolecular interactions, and the ab initio calculations of NMR parameters of interacting species are hence becoming increasingly more common.

We shall try to avoid, as much as possible, overlap with other recent reviews. In the conference proceedings *Nuclear Magnetic Shieldings and Molecular Structure* edited by Tossell,[1] various ab initio methods are discussed. This volume summarizes well the theoretical developments up to 1992, containing a large number of reviews discussing practical applications of ab initio methods. This conference has been followed by two conferences held during 1998 in Smolenice (Slovakia) and Boston (United States), both devoted to the theoretical modeling of NMR parameters. Other reviews that have appeared lately are those by Chesnut,[2,3] Gauss,[4] de Dios,[5] Jameson,[6] and Fukui[7] for shielding constants; the review by Contreras and Facelli[8] for spin−spin coupling constants; and the reviews by Malkin et al.[9] and by Schreckenbach and Ziegler[10] on the application of density-functional theory to the calculation of NMR parameters. Some aspects of ab initio calculations of magnetic properties are discussed also in the *Encyclopedia of NMR*[11]—see, for example, the articles by Facelli, Hansen, Kutzelnigg, Lazzeretti, Pulay, Raynes, and Webb and coauthors. In addition, there are annual reviews in the NMR volumes of the Specialist Periodical Reports of the Royal Society of Chemistry. In recent years, the reviewers have been Jameson[12] for nuclear shieldings and Fukui[13] for spin−spin coupling constants.

We believe that none of the published reviews are similar in approach and scope to ours: most concentrate on the results; those that discuss the theory, do not have the character of a general review. Our purpose is to examine and compare the most important ab initio methods developed for the calculation of NMR parameters, analyzing their relative merits and deficiencies. Unlike semiempirical methods, the quality of ab initio calculations can be controlled, being determined by the particular level of theory chosen for the calculation. The recent progress in ab initio theory has made this systematic approach to the calculation of molecular properties applicable also to studies of shielding and spin−spin coupling constants, as we hope to demonstrate in the present review.

II. The NMR Spin-Hamiltonian Parameters

A. The NMR Spin Hamiltonian

The energy levels studied in NMR spectroscopy are the spin eigenstates of chemically bonded nuclei in the presence of an external magnetic field. The interactions of the magnetic moments of the NMR-active nuclei with the magnetic field are modified by the surrounding electrons of a closed-shell electronic system. Although these interactions are rather complicated, the main features of NMR spectra may be satisfactorily accounted for by the solution of the energy equation for a simple, effective spin-Hamiltonian where the electrons do not appear at all and where the nuclei are represented only by their intrinsic spins and their associated magnetic moments. Indeed, such an effective Hamiltonian may be written as[14]

$$H = -\sum_K \gamma_K \hbar \mathbf{B}^T (1 - \boldsymbol{\sigma}_K)\, \mathbf{I}_K + {}^1/_2 \sum_{K \neq L} \gamma_K \gamma_L \hbar^2 \mathbf{I}_K^T (\mathbf{D}_{KL} + \mathbf{K}_{KL}) \mathbf{I}_L \quad (1)$$

where γ_K are the nuclear magnetogyric ratios and $\mathbf{I}_K$ the nuclear spin operators, related to the nuclear magnetic dipole moments $\mathbf{M}_K$ as

$$\mathbf{M}_K = \gamma_K \hbar \mathbf{I}_K \quad (2)$$

In the spin Hamiltonian eq 1, we have introduced the nuclear magnetic shielding tensors $\boldsymbol{\sigma}_K$, which describe the magnetic shielding effects of the electrons; the classical dipolar interactions $\mathbf{D}_{KL}$, which describe the direct couplings of the nuclear magnetic dipole moments; and the reduced indirect nuclear spin−spin coupling tensors $\mathbf{K}_{KL}$, which describe the indirect couplings of the nuclear dipoles, mediated by the surrounding electrons. The NMR spin Hamiltonian is effective in the sense that its solutions reproduce the nuclear magnetic energy levels in a molecular system without reference to the electrons. We note that, in the (fictitious) absence of the surrounding electrons, the shielding constants and the indirect spin−spin coupling constants would vanish, leaving the NMR spectrum to be determined solely by the nuclear Zeeman term $-\mathbf{B}^T \cdot \mathbf{M}_K$ and by the direct dipolar couplings $\mathbf{M}_K^T \mathbf{D}_{KL} \mathbf{M}_L$.

For a rapidly tumbling molecule, we must carry out a rotational averaging of the spin Hamiltonian. It then turns out that the direct spin−spin coupling constants $\mathbf{D}_{KL}$ vanish but that the indirect couplings $\mathbf{K}_{KL}$ do not, their isotropic parts being responsible for the small, residual couplings between NMR-active nuclei observed in high-resolution experiments. For a rotating molecule in an isotropic medium, the NMR spin Hamiltonian may thus be written in the form

$$H_{\text{iso}} = -\sum_K \gamma_K \hbar (1 - \sigma_K)\, B I_{K_z} + {}^1/_2 \sum_{K \neq L} \gamma_K \gamma_L \hbar^2 K_{KL} \mathbf{I}_K \cdot \mathbf{I}_L \quad (3)$$

where the nuclear shielding constants σ_K and the reduced indirect nuclear spin−spin coupling constants K_{KL} are related to the corresponding tensors as

$$\sigma_K = {}^1/_3 Tr \boldsymbol{\sigma}_K \quad (4)$$

$$K_{KL} = {}^1/_3 Tr \mathbf{K}_{KL} \quad (5)$$

The effective spin Hamiltonian eq 3 contains all the information needed for an accurate representation of a high-resolution NMR spectrum, with the effects of the electronic system incorporated in the shieldings σ_K and in the indirect spin−spin couplings K_{KL}.

It should be noted that the NMR spin Hamiltonian is usually expressed not in terms of the reduced indirect spin−spin coupling tensors $\mathbf{K}_{KL}$ but rather in terms of the indirect spin−spin coupling tensors $\mathbf{J}_{KL}$, which are related to the reduced tensors as

$$\mathbf{J}_{KL} = h \frac{\gamma_K}{2\pi} \frac{\gamma_L}{2\pi} \mathbf{K}_{KL} \quad (6)$$

Since the reduced coupling tensors $\mathbf{K}_{KL}$ are independent of the nuclear magnetogyric ratios, they reflect more directly than do $\mathbf{J}_{KL}$ the role played by the electrons in setting up the coupling of the nuclei, allowing us more easily to compare the strengths of the couplings in different systems and isotopomers. However, in keeping with common usage, most of our discussion will be in terms of the coupling constants in the standard form eq 6.

In experimental work, the numerical values of the shielding and indirect spin−spin coupling constants are determined so that the solutions of the nuclear spin equation with the effective Hamiltonian eq 3 reproduce, as accurately as possible, the observed NMR spectrum. The empirical spin-Hamiltonian parameters obtained in this way (i.e., by a fit to the observed spectrum) contain valuable information on the molecular system—structural information, information on the nature of the chemical bonding, and so on. Conversely, at a more fundamental level we should be able to determine the shielding constants and the indirect spin−spin constants ab initio from a knowledge of the molecular rovibronic state, in particular from a knowledge of the electronic wave function of the system as discussed in the present review.

1. Magnitudes of the NMR Interactions

At this point, it is useful to put things in perspective and to consider the magnitudes of the various quantities involved in generating an NMR spectrum. The magnitudes of the nuclear dipole moments $\mathbf{M}_K$ are of the order of 10^{-4} atomic units and a magnetic induction B of 10 T (available in magnetic resonance experiments) corresponds to 4.3×10^{-5} atomic units. Noting that the magnitudes of the direct dipolar couplings $\mathbf{D}_{KL}$ are of the order of 10^{-4} atomic units, we find that the NMR spectrum for a set of bare nuclei represents transitions of the order of 10^{-8} atomic units with multiplet splittings of the order of 10^{-13} atomic units. These direct interactions are indeed small compared with those responsible for chemical bonding, all of which are of the order of unity.

Tiny as the direct nuclear magnetic interactions are, the associated electronic effects are much smaller still. Indeed, we shall later establish the following estimates of the shieldings and spin−spin couplings of an NMR spectrum

$$|\sigma_K| \approx \alpha^2 \tag{7}$$

$$|K_{KL}| \approx \alpha^2 |D_{KL}| \approx \alpha^4 \tag{8}$$

where α is the fine-structure constant which is

$$\alpha \approx 1/137 \tag{9}$$

(we use atomic units throughout this review). These estimates indicate that the shieldings and indirect spin−spin couplings are 4 orders of magnitude smaller than the direct Zeeman and dipolar interactions, respectively. Clearly, the perturbations introduced in the electronic system by the NMR transitions are exceedingly small and we are thus justified in regarding the nuclear magnetic dipoles as sensitive probes of the molecular system. Moreover, the smallness of the effects permits the application of perturbation theory to the calculation of the NMR parameters from the electronic wave function.

B. Spin-Hamiltonian Parameters as Energy Derivatives

Accepting the adequacy of the spin-Hamiltonian approach, we shall now concentrate on relating the nuclear shielding and spin−spin coupling constants to quantities that are obtainable from the electronic wave function. For a compact representation of the electronic energy in the presence of an external magnetic field and nuclear magnetic moments, we expand the electronic energy in the magnetic induction $\mathbf{B}$ and in the nuclear moments $\mathbf{M}_K$ around zero field and zero magnetic moments

$$E(\mathbf{B},\mathbf{M}) = E_0 + {}^1\!/_2 \mathbf{B}^T \mathbf{E}^{(20)} \mathbf{B} + \sum_K \mathbf{B}^T \mathbf{E}_K^{(11)} \mathbf{M}_K + {}^1\!/_2 \sum_{K \neq L} \mathbf{M}_K^T \, \mathbf{E}_{KL}^{(02)} \mathbf{M}_L \tag{10}$$

using the following notation for total derivatives at the expansion point

$$\mathbf{E}^{(20)} = \left. \frac{\mathrm{d}^2 E(\mathbf{B},\mathbf{M})}{\mathrm{d}\mathbf{B}^2} \right|_{\mathbf{B}=0,\mathbf{M}=0} \tag{11}$$

$$\mathbf{E}_K^{(11)} = \left. \frac{\mathrm{d}^2 E(\mathbf{B},\mathbf{M})}{\mathrm{d}\mathbf{B} \, \mathrm{d}\mathbf{M}_K} \right|_{\mathbf{B}=0,\mathbf{M}=0} \tag{12}$$

$$\mathbf{E}_{KL}^{(02)} = \left. \frac{\mathrm{d}^2 E(\mathbf{B},\mathbf{M})}{\mathrm{d}\mathbf{M}_K \, \mathrm{d}\mathbf{M}_L} \right|_{\mathbf{B}=0,\mathbf{M}=0} \tag{13}$$

In these expressions, we refer collectively to the magnetic moments by $\mathbf{M} = \{\mathbf{M}_K\}$. For closed-shell systems, the first-order terms vanish identically (vide infra) and have therefore not been included in the expansion of $E(\mathbf{B},\mathbf{M})$ in eq 10. Also, higher than second-order terms may be neglected due to the smallness of the perturbations. For a rigid, nonrotating molecule, the simple expression eq 10 therefore gives an accurate representation of the electronic energy in the presence of an external magnetic field and magnetic nuclei.

Comparing the expansion eq 10 with the NMR spin-Hamiltonian in eq 1, we identify the $\mathbf{E}_K^{(11)}$ with the nuclear shielding tensors and $\mathbf{E}_{KL}^{(20)}$ with the spin−spin coupling tensors:

$$\boldsymbol{\sigma}_K = \mathbf{E}_K^{(11)} + \mathbf{1} \tag{14}$$

$$\mathbf{K}_{KL} = \mathbf{E}_{KL}^{(02)} - \mathbf{D}_{KL} \tag{15}$$

The $\mathbf{E}^{(20)}$ tensor represents the molecular magnetizability and does not enter the spin-Hamiltonian. We note that the absence of first-order terms in the expansion of the closed-shell energy as well as the smallness of higher-order terms serve as a justification of the effective spin Hamiltonian eq 1, where only terms bilinear in the external field and in the nuclear magnetic moments appear.

From the point of view of molecular electronic-structure theory, the shielding constants eq 14 and the indirect spin−spin coupling constants eq 15 are particular examples of molecular properties. When a molecular electronic system is modified by a perturbation $\mathbf{x}$, its total energy changes:

$$E\,(\mathbf{x}) = E^{(0)} + \mathbf{E}^{(1)} \mathbf{x} + \frac{1}{2} \mathbf{x}^T \mathbf{E}^{(2)} \mathbf{x} + ... \tag{16}$$

The coefficients of this expansion are characteristic of the molecular system in a given quantum state and are known as molecular properties. When the perturbation is static (that is, time-independent, as for the NMR properties studied here for a homogeneous magnetic field), the molecular properties may be calculated by differentiation:

$$\mathbf{E}^{(1)} = \left. \frac{\mathrm{d}E}{\mathrm{d}\mathbf{x}} \right|_{\mathbf{x}=0} \tag{17}$$

$$\mathbf{E}^{(2)} = \left. \frac{\mathrm{d}^2 E}{\mathrm{d}\mathbf{x}^2} \right|_{\mathbf{x}=0} \tag{18}$$

For time-dependent properties, however, a more general approach must be considered, see for instance ref 15.

We have now established the following program for the a priori generation of an NMR spectrum. First, the nuclear shielding constants and the indirect spin−spin coupling constants are evaluated ab initio as the derivatives of the electronic energy with respect to the magnetic induction **B** and the nuclear magnetic moments $\mathbf{M}_K$. Next, we solve the effective spin Hamiltonian equation and generate the NMR spectrum from its solutions in the usual way. Computationally, the crucial step of this program is the calculation of the spin-Hamiltonian parameters as derivatives of the electronic energy—in the following sections, we shall discuss the techniques developed for their evaluation in more detail. At present, it is sufficient to note that we have reduced the ab initio evaluation of NMR shielding and coupling constants to a special case of the more general problem of evaluating total derivatives of molecular electronic energies, for which efficient techniques have been developed over the last two decades.[16,17] We should add, however, that the proposed two-step program for the a priori generation of an NMR spectrum is a simplified one in the sense that rotational and vibrational effects have been ignored. We shall return to a discussion of rovibrational effects in section XII.

III. NMR Parameters for Exact States

Having identified the NMR spin-Hamiltonian parameters as the rovibrationally averaged derivatives of the electronic energy, we shall now consider the evaluation of these derivatives. In this section, we consider the evaluation of the nuclear shielding tensors and the indirect spin−spin coupling tensors for exact states. In the subsequent sections, we go on to consider the evaluation of the same parameters for approximate electronic wave functions.

A. First- and Second-Order Molecular Properties for Exact States

In nondegenerate time-independent perturbation theory,[18] we have the following expressions for first- and second-order molecular properties

$$\frac{\mathrm{d}E(\mathbf{x})}{\mathrm{d}x_i} = \left\langle 0\left|\frac{\mathrm{d}H}{\mathrm{d}x_i}\right|0\right\rangle \tag{19}$$

$$\frac{\mathrm{d}^2E(\mathbf{x})}{\mathrm{d}x_i\,\mathrm{d}x_j} = \left\langle 0\left|\frac{\mathrm{d}^2H}{\mathrm{d}x_i\,\mathrm{d}x_j}\right|0\right\rangle - 2\sum_{n\neq 0}\frac{\left\langle 0\left|\frac{\mathrm{d}H}{\mathrm{d}x_i}\right|n\right\rangle\left\langle n\left|\frac{\mathrm{d}H}{\mathrm{d}x_j}\right|0\right\rangle}{E_n - E_0} \tag{20}$$

where the derivatives are taken at $\mathbf{x} = 0$, (e.g., zero field and zero magnetic moments), and the factor of 2 in the sum-over-states term reflects the use of a Taylor series rather than a power series expansion of the energy. The first derivative or the first-order property eq 19 is simply the expectation value of the first-order Hamiltonian (the Hellmann−Feynman theorem) and requires only a knowledge of the unperturbed reference state $|0\rangle$. The second derivative or the second-order property eq 20 contains an expectation-value term analogous to the first-order properties but also a sum-over-states contribution from each excited state $|n\rangle$ of energy E_n. For magnetic properties, the expectation-value contribution to the second-order property is known as the diamagnetic part, the sum-over-states contribution is referred to as the paramagnetic part.

To arrive at explicit expressions for the nuclear shielding and spin−spin coupling constants, we must consider the form of the electronic Hamiltonian. In particular, we must determine its dependence on the magnetic induction **B** and on the nuclear magnetic moments $\mathbf{M}_K$.

B. The Molecular Electronic Hamiltonian

Let us consider the electronic Hamiltonian as modified by the presence of a homogeneous external magnetic field **B** and nuclear magnetic moments $\mathbf{M}_K$. The electrons interact with these perturbations: (1) because of the orbital motion of the electrons and (2) because of the permanent magnetic moments of the electrons

$$\mathbf{m}_i = -g\mu_B\mathbf{s}_i = -\mathbf{s}_i \tag{21}$$

where we have set the electron g factor equal to 2 and the Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} \tag{22}$$

is equal to $^1/_2$ in atomic units. In the presence of these magnetic perturbations, the nonrelativistic molecular electronic Hamiltonian may in atomic units be written in the form

$$H(\mathbf{B},\mathbf{M}) = {}^1/_2\sum_i \pi_i^2 - \sum_i \mathbf{m}_i\cdot\mathbf{B}^{\mathrm{tot}}(\mathbf{r}_i) - \sum_{iK}\frac{Z_K}{r_{iK}} + {}^1/_2\sum_{i\neq j}\frac{1}{r_{ij}} + {}^1/_2\sum_{K\neq L}\frac{Z_KZ_L}{R_{KL}} - \sum_K \mathbf{M}_K\cdot\mathbf{B}^{\mathrm{tot}}(\mathbf{R}_K) + \sum_{K>L}\mathbf{M}_K^T\mathbf{D}_{KL}\mathbf{M}_L \tag{23}$$

We have here introduced the operators for the kinetic momentum

$$\boldsymbol{\pi}_i = -i\nabla_i + \mathbf{A}^{\mathrm{tot}}(\mathbf{r}_i) \tag{24}$$

where $\mathbf{A}^{\mathrm{tot}}(\mathbf{r}_i)$ is the vector potential at the position of electron i, constructed such that its curl reproduces the magnetic induction $\mathbf{B}^{\mathrm{tot}}(\mathbf{r}_i)$ arising from the external field and the NMR active nuclei:

$$\mathbf{B}^{\mathrm{tot}}(\mathbf{r}_i) = \nabla_i \times \mathbf{A}^{\mathrm{tot}}(\mathbf{r}_i) \tag{25}$$

For an electronic system in the presence of a static magnetic field **B** and nuclear moments $\mathbf{M}_K$, the vector potential and the magnetic induction may each be decomposed into one contribution from the external field and one contribution from each nucleus

$$\mathbf{A}^{\mathrm{tot}}(\mathbf{r}_i) = \mathbf{A}_O(\mathbf{r}_i) + \sum_K \mathbf{A}_K(\mathbf{r}_i) \tag{26}$$

$$\mathbf{B}^{\mathrm{tot}}(\mathbf{r}_i) = \mathbf{B} + \sum_K \mathbf{B}_K(\mathbf{r}_i) \tag{27}$$

where, for each contribution, the relation between the magnetic induction and the vector potential is given as for the total potential and field in eq 25. From eqs 23−25, we note that the orbital motion of the electron is coupled to the vector potential and its spin to the induction. In the following, we shall consider first the contributions to the Hamiltonian from the external field **B** and next the contributions from the nuclei $\mathbf{M}_K$.

For a homogeneous, external magnetic field represented by a constant magnetic-induction vector **B**, the associated vector potential $\mathbf{A}_O(\mathbf{r}_i)$ may for instance be written in the form

$$\mathbf{A}_O(\mathbf{r}_i) = {}^1/_2\mathbf{B} \times \mathbf{r}_{iO} \tag{28}$$

where the subscript O indicates that the vector potential vanishes at the origin of the vector potential **O**, known as the gauge origin. It is important to realize that, although the vector potential depends on the choice of the origin **O**, the physical field as represented by the induction **B** does not, as is easily appreciated from the expression eq 25. As we shall discuss later, except for atoms, there exists no unique, natural gauge origin for the external vector potential. This ambiguity in the choice of gauge origin has important implications for the approximate evaluation of all properties associated with the application of an external magnetic field, for example nuclear shielding constants. In particular, although the molecular magnetic properties calculated from the exact wave function do not in any way depend on our (arbitrary) choice of gauge origin, such gauge invariance is not automatically ensured for properties calculated from approximate wave functions,[19] unless special precautions are taken as discussed in section V.B.

Let us now consider the contributions to the Hamiltonian from the nuclear magnetic dipole moment $\mathbf{M}_K$. The vector potential associated with the nucleus may for example be written as

$$\mathbf{A}_K(\mathbf{r}_i) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_{iK}}{{r_{iK}}^3} \tag{29}$$

where α is given in eq 9. Unlike for the external vector potential $\mathbf{A}_O(\mathbf{r}_i)$, there exists for the nuclear vector potential $\mathbf{A}_K(\mathbf{r}_i)$ a preferred gauge origin: the position of the nucleus. There are therefore no problems associated with the choice of gauge origin for the calculation of perturbations arising from the introduction of nuclei with nonzero magnetic moments. Note that the vector potential eq 29 assumes (like all terms in the Hamiltonian eq 23) a point-charge model for the nuclei. If a more elaborate nuclear charge distribution is assumed, then the vector potential eq 29 must be modified accordingly.

The vector potential $\mathbf{A}_K(\mathbf{r}_i)$ interacts with the orbital motion of the electrons, see eq 24. The interaction with the spin of the electrons is mediated by the Zeeman term in eq 23, for which we need the magnetic induction associated with the potential eq 29. Taking the curl of the vector potential, we obtain

$$\mathbf{B}_K(\mathbf{r}_i) = -\alpha^2 \frac{{r_{iK}}^2\mathbf{1} - 3\mathbf{r}_{iK}\mathbf{r}_{iK}^T}{{r_{iK}}^5}\mathbf{M}_K + \frac{8\pi\alpha^2}{3}\delta(\mathbf{r}_{iK})\mathbf{M}_K \tag{30}$$

where, as we shall discuss shortly, the first term gives rise to the dipole−dipole interaction between the electrons and the nucleus, and the last term is responsible for the Fermi-contact interaction of the electrons with the nucleus.

In our discussion in this section, we have adopted for the vector potentials the Coulomb gauge—that is, the vector potentials are chosen to be divergence free:

$$\nabla\cdot\mathbf{A} = 0 \tag{31}$$

In nonrelativistic calculations, this is by far the most common choice of gauge for the vector potentials, although other choices have also been considered. In particular, we mention here the calculations in the Landau gauge presented by Ferraro et al.[20] The requirements for gauge invariance in the Landau gauge have been discussed by Lazzeretti et al.,[21] whereas Woliński, Hinton, and Pulay have discussed some computational aspects.[22] Still, this choice of gauge has not become widespread in quantum-chemical calculations. For the remainder of this review, we shall assume the use of the Coulomb gauge.

The Hamiltonian eq 23 is the correct nonrelativistic operator for electrons in the presence of an homogeneous external field and point-charge nuclei. Upon expansion of the kinetic-momentum operator with the vector potential in the form eq 26, it is seen to contain terms that are linear and bilinear in **B** and $\mathbf{M}_K$. Differentiation of eq 23 with respect to **B** and $\mathbf{M}_K$ then yields the perturbation operators to be used in the general expression eq 20 for the calculation of nuclear shieldings and spin−spin coupling constants.

C. The First-Order (Paramagnetic) Interaction Terms

Having set up the electronic Hamiltonian, let us now extract the interaction terms that this operator gives rise to, beginning with the first-order terms. Differentiating the Hamiltonian eq 23 with respect to the magnetic induction **B** at zero field and zero magnetic moments, we obtain

$$\frac{\mathrm{d}H}{\mathrm{d}\mathbf{B}} = \mathbf{h}_B^{\mathrm{orb}} + \mathbf{h}_B^{\mathrm{spn}} \tag{32}$$

where

$$\mathbf{h}_B^{\mathrm{orb}} = {}^1/_2\sum_i \mathbf{l}_{iO} \tag{33}$$

$$\mathbf{h}_B^{\mathrm{spn}} = -\sum_i \mathbf{m}_i = \sum_i \mathbf{s}_i \tag{34}$$

The first term couples the external field to the orbital motion of the electron by means of the orbital angular-momentum operator

$$\mathbf{l}_{iO} = -\mathrm{i}\mathbf{r}_{iO} \times \nabla_i \tag{35}$$

whereas the second term couples the field to the spin angular-momentum operator eq 21. Thus, the first-order coupling of the electrons with **B** depends on the orbital and spin angular momentum of the electron—with double weight on the spin contribution—and is known as the Zeeman interaction.

Let us next consider the first-order interaction of the electrons with the nuclear magnetic moments. Differentiating the Hamiltonian eq 23 with respect to the magnetic moments at zero field and zero magnetic moments, we obtain the hyperfine operators

$$\frac{\mathrm{d}H}{\mathrm{d}\mathbf{M}_K} = \mathbf{h}_K^{\mathrm{pso}} + \mathbf{h}_K^{\mathrm{sd}} + \mathbf{h}_K^{\mathrm{fc}} \tag{36}$$

There are three distinct interactions: one involving the orbital motion of the electron and two involving the electron spin. Thus, the paramagnetic spin—orbit (PSO) operator or the orbital hyperfine operator

$$\mathbf{h}_K^{\mathrm{pso}} = \alpha^2 \sum_i \frac{\mathbf{l}_{iK}}{r_{iK}{}^3} \tag{37}$$

couples the nuclear magnetic moments to the orbital motion of the electrons whereas the spin—dipole (SD) operator

$$\mathbf{h}_K^{\mathrm{sd}} = \alpha^2 \sum_i \frac{r_{iK}{}^2 \mathbf{m}_i - 3(\mathbf{m}_i \cdot \mathbf{r}_{iK})\mathbf{r}_{iK}}{r_{iK}{}^5} \tag{38}$$

and the Fermi-contact (FC) operator

$$\mathbf{h}_K^{\mathrm{fc}} = -\frac{8\pi\alpha^2}{3} \sum_i \delta(\mathbf{r}_{iK})\mathbf{m}_i \tag{39}$$

couple the nuclear magnetic moments to the spin of the electron. When multiplied by the nuclear magnetic moment, the spin—dipole operator represents the classical interaction between two magnetic dipoles. The FC operator represents the direct interaction of the dipole moment of the electron with the source of the nuclear magnetic field and makes a contribution only when the electron is at the nucleus. As we shall discuss later, the FC interaction is usually the dominant mechanism for coupling nuclear spins.

Let us briefly investigate the effect of the first-order operators on a closed-shell wave function. From a consideration of the form of the operators, we find that

$$\frac{\mathrm{d}H}{\mathrm{d}\mathbf{B}}\left|0\right\rangle = \begin{array}{l} \mathbf{h}_B^{\mathrm{orb}}|0\rangle \leftarrow \text{imaginary singlet} \\ + \mathbf{h}_B^{\mathrm{spn}}|0\rangle \leftarrow \text{vanishes} \end{array} \tag{40}$$

since

$$\sum_i \mathbf{m}_i|0\rangle = -\sum_i \mathbf{s}_i|0\rangle = -\mathbf{S}|0\rangle = 0 \tag{41}$$

for closed-shell states with total spin zero. For the hyperfine interactions, we obtain

$$\frac{\mathrm{d}H}{\mathrm{d}\mathbf{M}_K}\left|0\right\rangle = \begin{array}{l} \mathbf{h}_K^{\mathrm{pso}}|0\rangle \leftarrow \text{imaginary singlet} \\ + \mathbf{h}_K^{\mathrm{sd}}|0\rangle \leftarrow \text{real triplet} \\ + \mathbf{h}_K^{\mathrm{fc}}|0\rangle \leftarrow \text{real triplet} \end{array} \tag{42}$$

which is a combination of imaginary singlet and triplet wave functions.

At this point, let us comment on the first-order magnetic properties of closed-shell systems. It has already been noted that in the expansion of the closed-shell energy eq 10, the first-order terms, which represent the permanent magnetic moment of the molecule $\mathbf{M}_{\mathrm{mol}}$ and the hyperfine coupling tensors $\mathbf{A}_K$ of the nuclei, vanish:

$$\mathbf{M}_{\mathrm{mol}} = -\left\langle 0 \middle| \frac{\mathrm{d}H}{\mathrm{d}\mathbf{B}} \middle| 0 \right\rangle = 0 \tag{43}$$

$$\mathbf{A}_K = \left\langle 0 \middle| \frac{\mathrm{d}H}{\mathrm{d}\mathbf{M}_K} \middle| 0 \right\rangle = 0 \tag{44}$$

The reason that these terms vanish is now seen to be the absence of real singlet components in the operators eqs 40 and 42. The orbital operators do not contribute since closed-shell expectation values of imaginary Hermitian operators vanish (the orbital angular momentum is quenched) and the spin operators do not contribute since their effect is to generate a wave function of triplet spin. For open-shell states, in contrast, the permanent magnetic moment and the hyperfine coupling tensor do not vanish and are in fact responsible for the dominant magnetic interactions of such systems.

D. The Second-Order (Diamagnetic) Interaction Terms

The second-order interaction terms, which contribute to the diamagnetic parts of the magnetic properties eq 20, are obtained by differentiating the Hamiltonian eq 23 twice with respect to the perturbations at zero field and zero magnetic moments. We obtain

$$\frac{\mathrm{d}^2 H}{\mathrm{d}\mathbf{B}\,\mathrm{d}\mathbf{M}_K} = -\mathbf{1} + \mathbf{h}_{BK}^{\mathrm{dia}} \tag{45}$$

$$\frac{\mathrm{d}^2 H}{\mathrm{d}\mathbf{M}_K\,\mathrm{d}\mathbf{M}_L} = \mathbf{D}_{KL} + \mathbf{h}_{KL}^{\mathrm{dso}} \tag{46}$$

where the diamagnetic electronic operators are given by

$$\mathbf{h}_{BK}^{\mathrm{dia}} = \frac{\alpha^2}{2} \sum_i \frac{(\mathbf{r}_{iO} \cdot \mathbf{r}_{iK})\mathbf{1} - \mathbf{r}_{iK}\mathbf{r}_{iO}^T}{r_{iK}{}^3} \tag{47}$$

$$\mathbf{h}_{KL}^{\mathrm{dso}} = \frac{\alpha^4}{2} \sum_i \frac{(\mathbf{r}_{iK} \cdot \mathbf{r}_{iL})\mathbf{1} - \mathbf{r}_{iK}\mathbf{r}_{iL}^T}{r_{iK}{}^3 r_{iL}{}^3} \tag{48}$$

Noting that $\alpha^2 \approx 5.32 \times 10^{-5}$, we see that each operator contains a leading term that involves the nuclei only and a much smaller correction term that represents a diamagnetic interaction with the electrons. The nuclear contribution to the shielding operator eq 45 arises from differentiation of the nuclear Zeeman interaction in the Hamiltonian eq 23, whereas the nuclear contribution to the spin−spin operator eq 46 represents the classical dipolar interaction between two magnetic dipoles. The operator eq 48 is known as the diamagnetic spin−orbit (DSO) operator.

E. Ramsey's Expressions

Substituting the expressions for the interaction operators discussed in the preceding two sections into the general expression for second-order properties eq 20, we obtain Ramsey's expressions[23,24] for the nuclear shielding tensor and the nuclear spin−spin coupling tensor:

$$\boldsymbol{\sigma}_K = \langle 0|\mathbf{h}_{BK}^{\mathrm{dia}}|0\rangle - 2\sum_{n_S\neq 0}\frac{\langle 0|\mathbf{h}_B^{\mathrm{orb}}|n_S\rangle\langle n_S|(\mathbf{h}_K^{\mathrm{pso}})^T|0\rangle}{E_{n_S}-E_0} \tag{49}$$

$$\mathbf{K}_{KL} = \langle 0|\mathbf{h}_{KL}^{\mathrm{dso}}|0\rangle - 2\sum_{n_S\neq 0}\frac{\langle 0|\mathbf{h}_K^{\mathrm{pso}}|n_S\rangle\langle n_S|(\mathbf{h}_L^{\mathrm{pso}})^T|0\rangle}{E_{n_S}-E_0} - 2\sum_{n_T}\frac{\langle 0|\mathbf{h}_K^{\mathrm{sd}}+\mathbf{h}_K^{\mathrm{fc}}|n_T\rangle\langle n_T|(\mathbf{h}_L^{\mathrm{sd}})^T+(\mathbf{h}_L^{\mathrm{fc}})^T|0\rangle}{E_{n_T}-E_0} \tag{50}$$

where $|n_S\rangle$ denotes a singlet excited state and $|n_T\rangle$ a triplet excited state. Both expressions contain a diamagnetic part, which corresponds to an expectation value of the unperturbed state, and a paramagnetic part, which represents the relaxation of the wave function in response to the external perturbations. There is, however, an interesting difference between the two properties. For the shieldings, there are no spin contributions at all. For the nuclear spin−spin coupling constants, in contrast, the purely paramagnetic spin contributions are usually by far the most important, although the orbital contributions may also be significant and in rare cases dominate.

For an isolated atom in a ^1S state, there is no paramagnetic contribution to the isotropic shielding if the gauge origin is chosen to be the atom. The shielding may then be written in the simplified form

$$\sigma_K = \frac{\alpha^2}{3}\left\langle 0\left|\frac{1}{r}\right|0\right\rangle \tag{51}$$

known as the Lamb expression. For an atomic system, therefore, the shielding constant is always positive. The reason for this simplification is that, for a spherically symmetric atomic system, the wave function is an eigenfunction of the angular momentum operator and therefore of the orbital Zeeman operator, making the paramagnetic contribution to the shielding vanish. For molecules, the paramagnetic contribution may in some cases be even larger than the diamagnetic one, leading to a negative shielding constant (deshielding).

The indirect spin−spin coupling constant given in eq 50 may be decomposed into several contributions: the diamagnetic DSO and paramagnetic PSO contributions arise from the orbital motion of the electrons; the FC, SD, and mixed SD−FC contributions originate from the spin of the electron. The FC operator uncouples spin-paired electrons at one nucleus, allowing these electrons to interact with the magnetic dipoles of neighboring nuclei. The resulting FC contribution to the coupling is often, and in particular for one-bond couplings, by far the dominant contribution to the indirect spin−spin coupling constants. Of the remaining contributions, the DSO contribution is usually the smallest one. The mixed SD−FC term does not contribute to the isotropic coupling constant, but may be important for the anisotropy of the coupling.

IV. Variational Perturbation Theory for Approximate Calculations of NMR Parameters

Although conceptually important in that they elucidate the different physical mechanisms at work, the Ramsey expressions eqs 49 and 50 are not useful for practical calculations since they require an explicit representation of the excited states. In practice, such a representation can be obtained only for model systems and we must therefore approach the calculation of the NMR spin-Hamiltonian parameters in a different manner. Thus, for the practical calculation of the spin-Hamiltonian parameters, we shall return to the expressions eqs 14 and 15 and develop these for the energy functionals of approximate electronic wave functions.

The principles underlying the calculation of NMR parameters are independent of the wave function model chosen for a particular calculation and their understanding is relevant and useful for the application of existing methods as well as for further development. In this section, we present the general theoretical framework within which NMR parameters are calculated: variational perturbation theory.[17,25]

A. Numerical versus Analytical Differentiation

Since the NMR spin-Hamiltonian parameters are obtained as derivatives of the electronic energy, we should be able to extract these parameters by carrying out a simple numerical differentiation of the electronic energy. This can be achieved by repeating the calculations with a redefined one-electron Hamiltonian that includes a contribution from the perturbing operator multiplied by a (small) parameter representing the finite value of the perturbation. Numerical differentiation of the calculated energies with respect to that parameter then yields the energy derivatives. Equivalently, a mixed second derivative of the energy may be obtained by numerical differentiation of the average value of the operator describing one of the perturbations with respect to the parameter representing the finite value of the other perturbation.[26,27] This approach is known as the finite-field (FF) or finite-perturbation (FP) method. The main advantage of this approach for calculating polarizabilities, for example, is that practically no programming is required to obtain the results. However, there are several reasons why a numerical scheme is not practical for the calculation of NMR parameters, making the analytical approach, where the derivatives are calculated directly from analytically derived expressions, the preferred one.

First, the calculations in the presence of the magnetic field or the nuclear magnetic moments are more complicated than in the absence of these perturbations since the wave function is no longer real-valued or no longer a pure singlet (see section III.C). In the presence of a magnetic perturbation, therefore, the standard programs developed for the calculation of wave functions and energies in the absence of perturbations can no longer be used. The FP approach thus requires substantial development of code for the optimization of energies and wave functions.

Second, numerical differentiation is an inherently unstable technique, in particular for higher-order derivatives. To calculate properties with high numerical precision, strict convergence criteria must be applied and, for higher-order properties, it may frequently be impossible to calculate the properties with any degree of reliability by numerical differentiation. These problems for higher-order properties may partially be solved by calculating the properties by FP calculations on first- and second-order properties, as has been done for shielding polarizabilities.[28]

Third, numerical differentiation will usually be less efficient than techniques developed for the direct calculation of properties from analytical expressions.

Fourth, numerical differentiation will usually require the optimization of the wave function and the energy in a symmetry lower than that of the unperturbed system, restricting the application range of the FP approach vis-à-vis the analytical technique.

Thus, although some ab initio FP calculations of NMR parameters have been reported in the literature,[29−31] analytic rather than numerical differentiation has been used in nearly all such calculations. Once the (nontrivial) programming has been carried out, these methods have important practical advantages, avoiding all the problems of numerical differentiation discussed above. For this reason, we now turn to the problem of calculating the second derivatives of the optimized energy by analytical techniques. The obvious way to proceed is to start with the standard expression for the electronic energy and take the total derivative of this expression with respect to the perturbation parameters—that is, with respect to the magnetic induction and the nuclear magnetic moments. With some notable modifications for nonvariational wave functions this is the procedure we shall follow in the subsequent sections.

B. Derivatives for Variational Wave Functions

Let us begin by considering, in general terms, the evaluation of NMR parameters for a variational wave function. Ignoring the details of the parametrization of the electronic energy, we write the electronic-energy function in the presence of the magnetic induction $\mathbf{B}$ and the nuclear magnetic dipole moments $\mathbf{M}_K$ in the form $E(\mathbf{B},\mathbf{M};\lambda)$, where λ is the set of parameters that determine and characterize the wave function. For the moment, we shall assume that the electronic energy is fully variational with respect to the electronic parameters λ. The electronic energy may then be calculated from the expression

$$E(\mathbf{B},\mathbf{M}) = E(\mathbf{B},\mathbf{M};\lambda^*) \tag{52}$$

where λ^* represents the optimal values of the electronic parameters λ and where the optimized energy function $E(\mathbf{B},\mathbf{M};\lambda^*)$ satisfies the variational conditions

$$\left.\frac{\partial E(\mathbf{B},\mathbf{M};\lambda)}{\partial \lambda}\right|_{\lambda=\lambda^*} = 0 \tag{53}$$

for *all* values of $\mathbf{B}$ and $\mathbf{M}$. To ensure that the variational conditions eq 53 are always fulfilled, the electronic parameters λ must change in a very specific manner with $\mathbf{B}$ and $\mathbf{M}$. The variational conditions eq 53 therefore implicitly determine the dependence of the optimized electronic parameters λ^* on $\mathbf{B}$ and $\mathbf{M}$.

1. First Derivatives for Variational Wave Functions

Let us now consider the gradient of the electronic energy $E(\mathbf{B},\mathbf{M})$ with respect to the nuclear magnetic moment $\mathbf{M}_K$. Using the chain rule, we obtain

$$\frac{\mathrm{d}E(\mathbf{B},\mathbf{M})}{\mathrm{d}\mathbf{M}_K} = \left.\left[\frac{\partial E(\mathbf{B},\mathbf{M};\lambda)}{\partial \mathbf{M}_K} + \frac{\partial E(\mathbf{B},\mathbf{M};\lambda)}{\partial \lambda}\frac{\partial \lambda}{\partial \mathbf{M}_K}\right]\right|_{\lambda=\lambda^*} \tag{54}$$

In the brackets on the right-hand side, the first term represents the *explicit* dependence of the electronic energy on $\mathbf{M}_K$ and arises, for example, from the dependence of the Hamiltonian on the nuclear magnetic moments; the second term represents the *implicit* dependence of the energy function on $\mathbf{M}_K$ and arises since the wave function changes as the nuclear moments vary. The derivatives of the optimized electronic parameters with respect to the magnetic moments $\partial\lambda/\partial\mathbf{M}_K$ tell us how, to first order, the wave function changes when the perturbation is applied.

Combining eqs 53 and 54, we obtain the following simple expression for gradient of the electronic energy with respect to the nuclear magnetic moments

$$\frac{\mathrm{d}E(\mathbf{B},\mathbf{M})}{\mathrm{d}\mathbf{M}_K} = \frac{\partial E(\mathbf{B},\mathbf{M};\lambda^*)}{\partial \mathbf{M}_K} \tag{55}$$

We note in passing that for zero field and zero magnetic moments, the expression eq 55 corresponds to the hyperfine coupling tensor:

$$\mathbf{A}_K = \left.\frac{\partial E(\mathbf{B},\mathbf{M};\lambda^*)}{\partial \mathbf{M}_K}\right|_{\mathbf{B}=0,\mathbf{M}=0} \tag{56}$$

Clearly, to obtain the hyperfine coupling tensors, we need not evaluate the response of the wave function $\partial\lambda/\partial\mathbf{M}_K$. This is an important result (an example of the Hellmann−Feynman theorem, see section III.A) which, as we shall shortly see, simplifies the calculation of the shielding and spin−spin coupling tensors. As already discussed, the nuclear hyperfine coupling tensor itself vanishes for closed-shell systems (see eq 44) and is of no interest to us here—it is needed only as a stepping stone to the evaluation of the nuclear shieldings and the indirect spin−spin coupling tensors.

2. Shielding Constants for Variational Wave Functions

An expression for the shielding tensors is obtained by differentiating the gradient eq 55 with respect to **B**

$$\frac{d^2E(\mathbf{B},\mathbf{M})}{d\mathbf{B}\,d\mathbf{M}_K} = \left[\left(\frac{\partial}{\partial \mathbf{B}} + \frac{\partial\lambda}{\partial\mathbf{B}}\frac{\partial}{\partial\lambda}\right)\frac{\partial E(\mathbf{M},\mathbf{B};\lambda)}{\partial \mathbf{M}_K}\right]\Bigg|_{\lambda=\lambda^*} = \left[\frac{\partial^2 E(\mathbf{B},\mathbf{M};\lambda)}{\partial\mathbf{B}\,\partial\mathbf{M}_K} + \frac{\partial^2 E(\mathbf{M},\mathbf{B};\lambda)}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{B}}\right]\Bigg|_{\lambda=\lambda^*} \quad (57)$$

For zero field and zero nuclear magnetic moments, we recover according to eq 14 the nuclear shielding tensors

$$\boldsymbol{\sigma}_K = \mathbf{1} + \left[\frac{\partial^2 E(\mathbf{B},\mathbf{M};\lambda)}{\partial\mathbf{B}\,\partial\mathbf{M}_K} + \frac{\partial^2 E(\mathbf{M},\mathbf{B},\lambda)}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{B}}\right]\Bigg|_{\mathbf{B}=0,\mathbf{M}=0,\lambda=\lambda^*} \quad (58)$$

or, more compactly,

$$\boldsymbol{\sigma}_K = \mathbf{1} + \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\mathbf{B}} + \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{B}} \quad (59)$$

In the following, we shall always assume that the derivatives are taken at zero field $\mathbf{B} = 0$, for zero magnetic moments $\mathbf{M} = 0$, and for the optimized parameters $\lambda = \lambda^*$, and, for clarity of presentation, we shall write the derivatives in the compact form eq 59.

We conclude that, for a fully variational wave function, only the first-order response of the wave function with respect to the external field $\partial\lambda/\partial\mathbf{B}$ is required to calculate the nuclear shieldings $\boldsymbol{\sigma}_K$. In other words, neither the second-order responses $\partial^2\lambda/\partial\mathbf{B}\,\partial\mathbf{M}_K$ nor the first-order responses $\partial\lambda/\partial\mathbf{M}_K$ are required for the evaluation of the nuclear shieldings. These are important results since they imply that—for any molecule of any size—we need never determine more than three responses of a variational wave function in order to calculate the full set of nuclear shieldings.

At this point, we note that we may derive an expression for the shielding tensor also by differentiation first with respect to **B** and next with respect to $\mathbf{M}_K$. We then obtain the following alternative expression for the shielding tensor:

$$\boldsymbol{\sigma}_K = \mathbf{1} + \frac{\partial^2 E}{\partial\mathbf{B}\,\partial\mathbf{M}_K} + \frac{\partial^2 E}{\partial\mathbf{B}\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{M}_K} \quad (60)$$

Although mathematically equivalent, the first expression eq 59 is to be preferred since, whereas eq 60 requires the calculation of three responses for each shielded nucleus, eq 59 requires the calculation of only three responses, irrespective of the size of the molecule.

Finally, it is possible to use a more symmetric expression for the shielding constants

$$\boldsymbol{\sigma}_K = \mathbf{1} + \frac{\partial^2 E}{\partial\mathbf{B}\,\partial\mathbf{M}_K} + \frac{\partial^2 E}{\partial\mathbf{B}\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{M}_K} + \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{B}} + \frac{\partial^2 E}{\partial\lambda^2}\frac{\partial\lambda}{\partial\mathbf{B}}\frac{\partial\lambda}{\partial\mathbf{M}_K} \quad (61)$$

An advantage of this expression over the two previous expressions eqs 59 and 60 is that the (numerical) error in the shielding constant as calculated from eq 61 is quadratic in the (numerical) error in the responses $\partial\lambda/\partial\mathbf{B}$ and $\partial\lambda/\partial\mathbf{M}_K$.[32,33] In contrast, when calculated from either eq 59 or eq 60, the shielding constant is linear in the error in the responses. For an error in the response of 10^{-3}, eq 61 therefore gives the same error in the shielding constant as does eq 59 with an error of 10^{-6} in the response. Nevertheless, unless the responses $\partial\lambda/\partial\mathbf{M}_K$ are needed for some other purposes as well (for example, for the calculation of the spin−spin coupling constants), this numerical advantage of the symmetric expression eq 61 is considerably less important than the fact that eq 59 requires the solution of only three responses (one for each component of the magnetic field), independent of the number of nuclei.

3. Indirect Spin−Spin Coupling Constants for Variational Wave Functions

To calculate the reduced indirect nuclear spin−spin coupling constants, we proceed in the same way as for the shielding constants. This time, however, we differentiate the first derivatives eq 56 with respect to the full set of nuclear magnetic moments. According to eq 15, we then obtain the following expression for the reduced indirect spin−spin coupling constants

$$\mathbf{K}_{KL} = \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L} + \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{M}_L} - \mathbf{D}_{KL} \quad (62)$$

Clearly, we can no longer avoid the calculation of the response of the wave function with respect to the full set of nuclear magnetic moments. For this reason, the evaluation of the full set of spin−spin coupling constants in a molecule is a much more expensive undertaking than the evaluation of all the shielding constants, in particular for molecules containing a large set of nuclei.

For practical reasons, it is better to write the expression for the spin−spin coupling constants in the more symmetric manner

$$\mathbf{K}_{KL} = \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L} + \frac{\partial^2 E}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{M}_L} + \frac{\partial^2 E}{\partial\mathbf{M}_L\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{M}_K} + \frac{\partial^2 E}{\partial\lambda^2}\frac{\partial\lambda}{\partial\mathbf{M}_K}\frac{\partial\lambda}{\partial\mathbf{M}_L} - \mathbf{D}_{KL} \quad (63)$$

First, like the symmetric expression for the shieldings eq 61, this expression is stable toward numerical errors in the wave function responses. Thus, the error in $\mathbf{K}_{KL}$ is quadratic in the error in $\partial\lambda/\partial\mathbf{M}_K$ when calculated from eq 63 but linear when calculated from eq 62. Second, when applied to nonvariational wave functions, the symmetric expression eq 63 leads to substantial additional savings, as we shall discuss in section IV.C.

4. Response Equations for Variational Wave Functions

Let us now consider the evaluation of the first-order responses of the wave function. We have already noted that the variational conditions eq 53 determine the dependence of the wave function on **B** and **M**. Differentiating these conditions with respect to **B** and invoking the chain rule, we obtain the conditions

$$\frac{\mathrm{d}}{\mathrm{d}\mathbf{B}}\frac{\partial E}{\partial \lambda} = \frac{\partial^2 E}{\partial \mathbf{B}\partial \lambda} + \frac{\partial^2 E}{\partial \lambda^2}\frac{\partial \lambda}{\partial \mathbf{B}} = 0 \tag{64}$$

which may be written in the form of a set of linear equations

$$\frac{\partial^2 E}{\partial \lambda^2}\frac{\partial \lambda}{\partial \mathbf{B}} = -\frac{\partial^2 E}{\partial \lambda\, \partial \mathbf{B}} \tag{65}$$

These equations are known as the response equations since they determine the first derivative (i.e., the first-order response) of the wave function with respect to the applied magnetic field (they are also called first-order perturbation equations, and correspondingly the solutions are called first-order perturbation corrections to the wave function). To determine the response of the wave function to the nuclear magnetic moments, we proceed in the same way and obtain

$$\frac{\partial^2 E}{\partial \lambda^2}\frac{\partial \lambda}{\partial \mathbf{M}_K} = -\frac{\partial^2 E}{\partial \lambda\, \partial \mathbf{M}_K} \tag{66}$$

Clearly, the response equations have the same general form for all perturbations—the only differences between the linear sets of equations eqs 65 and 66 are in their right-hand sides. It should be noted that although the two response equations eqs 65 and 66 have the same general form, the space and spin symmetries are different for the two perturbations. In practice, these symmetries are always exploited to simplify the calculations and to reduce their cost as much as possible, making practical implementations of these response equations different.

Let us introduce the following notation for the electronic gradient and the electronic Hessian of the optimized wave function

$$\mathbf{F} = \partial E/\partial \lambda \tag{67}$$

$$\mathbf{G} = \partial^2 E/\partial \lambda^2 \tag{68}$$

Naively, one would think that the response equations should be solved by first inverting the electronic Hessian and then obtaining the solutions by simple matrix−vector multiplications according to the expressions

$$\partial\lambda/\partial\mathbf{B} = -\mathbf{G}^{-1}(\partial\mathbf{F}/\partial\mathbf{B}) \tag{69}$$

$$\partial\lambda/\partial\mathbf{M}_K = -\mathbf{G}^{-1}(\partial\mathbf{F}/\partial\mathbf{M}_K) \tag{70}$$

In this approach, we may for example calculate the shieldings according to the expression

$$\boldsymbol{\sigma}_K = \mathbf{1} + \frac{\partial^2 E}{\partial \mathbf{B}\,\partial \mathbf{M}_K} - \frac{\partial \mathbf{F}^T}{\partial \mathbf{M}_K}\,\mathbf{G}^{-1}\frac{\partial \mathbf{F}}{\partial \mathbf{B}} \tag{71}$$

The attraction of such an approach is that once the Hessian has been inverted, the calculation of each independent wave function response becomes very fast. In practice, because of the large number of wave function parameters in λ (for example, 10^6 parameters may now be used), this approach is not possible except for the smallest systems—the cost of calculating the Hessian would be very high and its dimensions so large that it cannot be stored on disk. Instead, the wave function responses are solved for iteratively.

In the iterative approach, each wave function response is obtained in a process where the electronic Hessian is multiplied by a number of “trial vectors” [33] (generated in some special manner of numerical analysis) until the norm of the difference between the left- and right-hand sides of the response equations is smaller than some preset threshold. Usually, 10 to 20 iterations are required for a satisfactory solution. The great advantage of this approach is that there is no need to construct the Hessian explicitly—we need only to calculate products of the Hessian with the trial vectors, which can usually be accomplished at a cost much lower than the complete construction of the Hessian. In this way, we avoid not only the construction of the electronic Hessian, we avoid also its storage.

C. Derivatives for Nonvariational Wave Functions

In section IV.B, we presented the analytical expressions needed for the calculation of NMR parameters from variational wave functions. However, many of the approaches (and in particular some of the more accurate ones) used in the calculation of NMR parameters are not variational. We shall now see that by a suitable modification of the energy functional, all computational methods of ab initio theory can be cast in a variational form, enabling us to apply the variational perturbation theory to nonvariational methods as well.

1. The Variational Lagrangian

All the results for variational wave functions in section IV.B may be used for nonvariational wave functions as well by introducing an energy functional that gives the same energy as the wave function itself, but that in addition is variational. For this purpose, we invoke Lagrange’s method of undetermined multipliers.[17,34] The optimized parameters λ of a variational or nonvariational energy functional

$$E(\mathbf{B},\mathbf{M}) = E_{nv}(\mathbf{B},\mathbf{M};\lambda^*) \tag{72}$$

are in general determined from a set of linear or nonlinear equations

$$\mathbf{e}(\mathbf{B},\mathbf{M};\lambda^*) = 0 \tag{73}$$

which, for the special case of a variational wave function, coincide with the variational conditions eq 53. The Lagrangian for the variational optimization of the energy $E_{nv}(\mathbf{B},\mathbf{M};\lambda)$ is obtained by introducing one multiplier for each of the nonvariational constraints, eq 73

$$L(\mathbf{B},\mathbf{M};\lambda,\bar{\lambda}) = E_{nv}(\mathbf{B},\mathbf{M};\lambda) + \bar{\lambda}^T\mathbf{e}(\mathbf{B},\mathbf{M};\lambda) \tag{74}$$

Differentiating this Lagrangian with respect to the parameters $\bar{\lambda}$, we recover eq 73

$$\frac{\partial L(\mathbf{B},\mathbf{M};\lambda,\bar{\lambda})}{\partial\bar{\lambda}} = \mathbf{e}(\mathbf{B},\mathbf{M};\lambda) = 0 \tag{75}$$

whereas, when differentiating with respect to λ, we obtain a new set of linear equations

$$\frac{\partial L(\mathbf{B},\mathbf{M};\lambda,\bar{\lambda})}{\partial\lambda} = \frac{\partial E_{nv}(\mathbf{B},\mathbf{M};\lambda)}{\partial\lambda} + \bar{\lambda}^T\frac{\partial\mathbf{e}(\mathbf{B},\mathbf{M};\lambda)}{\partial\lambda} = 0 \tag{76}$$

This set of equations is solved to determine the Lagrange multipliers $\bar{\lambda}$. We note that there is only one set of equations to be solved, independently of the type and number of external perturbations considered. For the optimized energy, the Lagrangian yields the same energy at $\lambda = \lambda^*$ and $\bar{\lambda} = \bar{\lambda}^*$ as the original energy functional

$$E(\mathbf{B},\mathbf{M}) = E_{nv}(\mathbf{B},\mathbf{M};\lambda^*) = L(\mathbf{B},\mathbf{M};\lambda^*,\bar{\lambda}^*) \tag{77}$$

For the calculation of the unperturbed energy, the only advantage of the Lagrangian energy expression L over the original expression E_{nv} is that the Lagrangian is stable toward small numerical errors in the wave function, the error in the energy calculated from the Lagrangian being quadratic rather than linear in such errors. The true usefulness of the Lagrangian becomes apparent only when derivatives (properties) are calculated.

2. Shielding Constants for Nonvariational Wave Functions

To arrive at an expression for the shielding tensors for nonvariational wave functions, we first note that eq 59 now takes the form

$$\boldsymbol{\sigma}_K = \frac{\partial^2 L}{\partial\mathbf{M}_K\,\partial\mathbf{B}} + \frac{\partial^2 L}{\partial\mathbf{M}_K\,\partial\lambda}\frac{\partial\lambda}{\partial\mathbf{B}} + \frac{\partial^2 L}{\partial\mathbf{M}_K\,\partial\bar{\lambda}}\frac{\partial\bar{\lambda}}{\partial\mathbf{B}} + \mathbf{1} \tag{78}$$

We have here replaced the energy function of eq 59 by the Lagrangian (which now plays the key role in the formulation of the derivatives). Also, since there are two separate sets of variables (both of which are variational with respect to the Lagrangian), we have separated the response contribution to the derivatives into two parts, one that involves the primary variables λ and the other involving the Lagrange multiplier variables $\bar{\lambda}$. Together, λ and $\bar{\lambda}$ constitute the full set of variables. Substituting the Lagrangian eq 74 in eq 78, we may write the shieldings in the more explicit form

$$\boldsymbol{\sigma}_K = \left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\mathbf{B}} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\mathbf{B}}\right) + \left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\lambda} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\lambda}\right)\frac{\partial\lambda}{\partial\mathbf{B}} + \frac{\partial\mathbf{e}^T}{\partial\mathbf{M}_K}\frac{\partial\bar{\lambda}}{\partial\mathbf{B}} + \mathbf{1} \tag{79}$$

Thus, to calculate the nuclear shieldings for nonvariational wave functions, we must solve six sets of response equations (three for the primary parameters and three for the multipliers) rather than just three (as for variational wave functions). In addition, we must solve one set of equations to determine the undifferentiated multipliers eq 76 and set up the Lagrangian eq 74. An expression symmetric in both perturbations and independent of the first derivatives of the multipliers $\bar{\lambda}$ may be set up for the shielding constants. However, it would be less useful than eq 79, containing the first derivatives of λ with respect to $\mathbf{M}_K$ as well as $\mathbf{B}$.

3. Indirect Spin–Spin Coupling Constants for Nonvariational Wave Functions

To set up the expression for the indirect spin−spin coupling tensors for nonvariational wave functions, we proceed in the same manner as for the shieldings and obtain from eq 62

$$\mathbf{K}_{KL} = \left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L}\right) + \left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\lambda} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\lambda}\right)\frac{\partial\lambda}{\partial\mathbf{M}_L} + \frac{\partial\mathbf{e}^T}{\partial\mathbf{M}_K}\frac{\partial\bar{\lambda}}{\partial\mathbf{M}_L} - \mathbf{D}_{KL} \tag{80}$$

To calculate the spin−spin coupling constants from this expression, we need the first derivatives of the primary variables λ as well as of the multipliers $\bar{\lambda}$. It is, however, possible to reduce the number of linear response equations to be solved by basing our calculations on the symmetric expression eq 63 rather than on the nonsymmetric expression eq 62. Using eq 63, we arrive at the alternative expression

$$\begin{aligned}\mathbf{K}_{KL} = {}&\left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\mathbf{M}_L}\right) + \\ &\left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_K\,\partial\lambda} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_K\,\partial\lambda}\right)\frac{\partial\lambda}{\partial\mathbf{M}_L} + \\ &\left(\frac{\partial^2 E_{nv}}{\partial\mathbf{M}_L\,\partial\lambda} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\mathbf{M}_L\,\partial\lambda}\right)\frac{\partial\lambda}{\partial\mathbf{M}_K} + \\ &\left(\frac{\partial^2 E_{nv}}{\partial\lambda^2} + \bar{\lambda}^T\frac{\partial^2\mathbf{e}}{\partial\lambda^2}\right)\frac{\partial\lambda}{\partial\mathbf{M}_K}\frac{\partial\lambda}{\partial\mathbf{M}_L} - \mathbf{D}_{KL}\end{aligned} \tag{81}$$

where $\mathbf{M}_K$ and $\mathbf{M}_L$ occur in a symmetric fashion. Unlike eq 80, this expression contains the derivatives of only the primary variables λ. In most situations, this expression is therefore more economical than eq

80, reducing the number of first-order equations to be solved by a factor of 2.

4. Response Equations for Nonvariational Wave Functions

Finally, let us consider the solution of the response equations for nonvariational wave functions. Inserting the variational Lagrangian into the general expression eq 65 and keeping in mind that we have now two distinct classes of variables, we obtain equations of the form

$$\begin{pmatrix} \frac{\partial^2 L}{\partial \lambda^2} & \frac{\partial^2 L}{\partial \lambda\, \partial \bar{\lambda}} \\ \frac{\partial^2 L}{\partial \bar{\lambda}\, \partial \lambda} & \frac{\partial^2 L}{\partial \bar{\lambda}^2} \end{pmatrix} \begin{pmatrix} \frac{\partial \lambda}{\partial \mathbf{B}} \\ \frac{\partial \bar{\lambda}}{\partial \mathbf{B}} \end{pmatrix} = - \begin{pmatrix} \frac{\partial^2 L}{\partial \lambda\, \partial \mathbf{B}} \\ \frac{\partial^2 L}{\partial \bar{\lambda}\, \partial \mathbf{B}} \end{pmatrix} \tag{82}$$

Again, we obtain a more explicit expression by substituting eq 74 for the Lagrangian into these equations. Carrying out some simple algebra, we arrive at the following two sets of equations for the primary variables and for the multipliers

$$\frac{\partial \mathbf{e}}{\partial \lambda} \frac{\partial \lambda}{\partial \mathbf{B}} = - \frac{\partial \mathbf{e}}{\partial \mathbf{B}} \tag{83}$$

$$\left(\frac{\partial \bar{\lambda}}{\partial \mathbf{B}}\right)^T \frac{\partial \mathbf{e}}{\partial \lambda} = -\left(\frac{\partial^2 E_{nv}}{\partial \lambda\, \partial \mathbf{B}} + \bar{\lambda}^T \frac{\partial^2 \mathbf{e}}{\partial \lambda\, \partial \mathbf{B}}\right) - \left(\frac{\partial^2 E_{nv}}{\partial \lambda^2} + \bar{\lambda}^T \frac{\partial^2 \mathbf{e}}{\partial \lambda^2}\right) \frac{\partial \lambda}{\partial \mathbf{B}} \tag{84}$$

The first set of equations determines the response of the primary variables $\partial\lambda/\partial\mathbf{B}$ and the second set, the response of the multiplier variables $\partial\bar{\lambda}/\partial\mathbf{B}$. The equations must be solved in the order written. A similar set of equations may of course be set up for the response with respect to the nuclear moments $\mathbf{M}_K$.

The results obtained in the previous sections are particular cases of the $2n + 1$ rule for primary variables and the $2n + 2$ rule for the secondary variables in a variational (Lagrangian) formulation of electronic energies. Thus, according to the $2n + 1$ rule for the primary variables, we may calculate molecular properties up to order $2n + 1$ from a knowledge of the primary variables to order n. Likewise, according to the $2n + 2$ rule of the secondary (multiplier) variables, we may calculate molecular properties to order $2n + 2$ from a knowledge of the secondary variables to order n. Although the $2n + 2$ rule is stronger than the $2n + 1$ rule, it may sometimes be advantageous to calculate properties from the $2n + 1$ rule rather than the $2n + 2$ rule (as is the case for shieldings from nonvariational wave functions, see section IV.C.2). For a demonstration of both rules for variational energies and Lagrangians, see Helgaker and Jørgensen.[17]

V. The Electronic Hamiltonian for ab Initio Calculations of NMR Parameters

Having presented variational perturbation theory in the previous section, we are now ready for a more technical discussion of the evaluation of NMR parameters. For this discussion, we shall use the formalism of second quantization, in which the wave function and Hamiltonian are expressed in a uniform manner in terms of a set of elementary creation and annihilation operators, see for instance ref 35. In the present section, we discuss the Hamiltonian operator, with emphasis on the effects arising from the use of field-dependent orbitals, thus preparing for the discussion of the various wave function models in section VI.

A. The Electronic Hamiltonian in Second Quantization

In second quantization, the electronic Hamiltonian operator is expressed as a linear combination of singlet and triplet excitation operators. The singlet excitation operators are given by the expression

$$E_{pq} = a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta} \tag{85}$$

where, for example, $a^\dagger_{p\alpha}$ and $a_{p\alpha}$ are the creation and annihilation operators associated with the spin–orbital $\psi_{p\alpha}$. In Cartesian form, the triplet operators

$$\mathbf{T}_{pq} = \{T^x_{pq}, T^y_{pq}, T^z_{pq}\} \tag{86}$$

may be written as

$$T^x_{pq} = \frac{1}{2}(a^\dagger_{p\alpha} a_{q\beta} + a^\dagger_{p\beta} a_{q\alpha}) \tag{87}$$

$$T^y_{pq} = \frac{1}{2i}(a^\dagger_{p\alpha} a_{q\beta} - a^\dagger_{p\beta} a_{q\alpha}) \tag{88}$$

$$T^z_{pq} = \frac{1}{2}(a^\dagger_{p\alpha} a_{q\alpha} - a^\dagger_{p\beta} a_{q\beta}) \tag{89}$$

In the following, we assume that the ψ_p, in terms of which the excitation operators and the Hamiltonian are constructed, constitute an orthonormal set of molecular orbitals (MO's), obtained from a set of atomic orbitals (AO's) in the usual manner. Anticipating the use of the field-dependent AO's of section V.B, we shall further assume that the MO's depend on the magnetic field $\mathbf{B}$. The detailed form of this dependence is discussed in section V.C.

In terms of the singlet and triplet excitation operators, the electronic Hamiltonian eq 23 becomes

$$\hat{H}(\mathbf{B},\mathbf{M}) = \hat{H}^{(0)} + \mathbf{B}^T(\hat{\mathbf{h}}^{\mathrm{orb}}_B + \hat{\mathbf{h}}^{\mathrm{spn}}_B) + \sum_K \mathbf{M}^T_K(\hat{\mathbf{h}}^{\mathrm{pso}}_K + \hat{\mathbf{h}}^{\mathrm{fc}}_K + \hat{\mathbf{h}}^{\mathrm{sd}}_K) + \sum_K \mathbf{B}^T \hat{\mathbf{h}}^{\mathrm{dia}}_{BK} \mathbf{M}_K + \sum_{K>L} \mathbf{M}^T_K\, \hat{\mathbf{h}}^{\mathrm{dso}}_{KL} \mathbf{M}_L + \mathbf{B}^T \hat{\mathbf{h}}^{\mathrm{dia}}_{BB}\, \mathbf{B} - \mathbf{B}^T \sum_K \mathbf{M}_K + \sum_{K>L} \mathbf{M}^T_K \mathbf{D}_{KL} \mathbf{M}_L \tag{90}$$

The first term entering this Hamiltonian is the zeroth-order Hamiltonian

$$\hat{H}^{(0)} = \sum_{pq} h_{pq}(\mathbf{B}) E_{pq} + \frac{1}{2}\sum_{pqrs} g_{pqrs}(\mathbf{B})(E_{pq}E_{rs} - \delta_{rq}E_{ps}) + \sum_{K>L}\frac{Z_K Z_L}{R_{KL}} \quad (91)$$

where we have used the notation

$$h_{pq} = \left\langle \psi_p(\mathbf{B}) \left| -\frac{1}{2}\nabla^2 - \sum_K \frac{Z_K}{r_K} \right| \psi_q(\mathbf{B}) \right\rangle \quad (92)$$

$$g_{pqrs} = \left\langle \psi_p(\mathbf{r}_1,\mathbf{B})\ \psi_q(\mathbf{r}_1,\mathbf{B}) \left| \frac{1}{r_{12}} \right| \psi_r(\mathbf{r}_2,\mathbf{B})\ \psi_s(\mathbf{r}_2,\mathbf{B}) \right\rangle \quad (93)$$

The other operators in the Hamiltonian contribute to the first-order singlet corrections

$$\hat{\mathbf{h}}_B^{\mathrm{orb}} = -\frac{1}{2} i \sum_{pq} \langle \psi_p(\mathbf{B}) | \mathbf{r}_O \times \nabla | \psi_q(\mathbf{B}) \rangle E_{pq} \quad (94)$$

$$\hat{\mathbf{h}}_K^{\mathrm{pso}} = -i\alpha^2 \sum_{pq} \left\langle \psi_p(\mathbf{B}) \left| \frac{\mathbf{r}_K \times \nabla}{r_K^3} \right| \psi_q(\mathbf{B}) \right\rangle E_{pq} \quad (95)$$

the first-order triplet corrections

$$\hat{\mathbf{h}}_B^{\mathrm{spn}} = \sum_p \mathbf{T}_{pp} \quad (96)$$

$$\hat{\mathbf{h}}_K^{\mathrm{fc}} = \frac{8\pi\alpha^2}{3} \sum_{pq} \langle \psi_p(\mathbf{B}) | \delta(r_K) | \psi_q(\mathbf{B}) \rangle\ \mathbf{T}_{pq} \quad (97)$$

$$\hat{\mathbf{h}}_K^{\mathrm{sd}} = -\alpha^2 \sum_{pq} \left\langle \psi_p(\mathbf{B}) \left| \frac{r_K^2 \mathbf{1} - 3\mathbf{r}_K \mathbf{r}_K^T}{r_K^5} \right| \psi_q(\mathbf{B}) \right\rangle \mathbf{T}_{pq} \quad (98)$$

and the second-order singlet corrections

$$\hat{\mathbf{h}}_{BB}^{\mathrm{dia}} = \frac{1}{8} \sum_{pq} \langle \psi_p(\mathbf{B}) | r_O^2 \mathbf{1} - \mathbf{r}_O \mathbf{r}_O^T | \psi_q(\mathbf{B}) \rangle\ E_{pq} \quad (99)$$

$$\hat{\mathbf{h}}_{BK}^{\mathrm{dia}} = \frac{\alpha^2}{2} \sum_{pq} \left\langle \psi_p(\mathbf{B}) \left| \frac{(\mathbf{r}_O^T \mathbf{r}_K)\mathbf{1} - \mathbf{r}_O \mathbf{r}_K^T}{r_K^3} \right| \psi_q(\mathbf{B}) \right\rangle E_{pq} \quad (100)$$

$$\hat{\mathbf{h}}_{KL}^{\mathrm{dso}} = \frac{\alpha^4}{2} \sum_{pq} \left\langle \psi_p(\mathbf{B}) \left| \frac{(\mathbf{r}_K^T \mathbf{r}_L)\mathbf{1} - \mathbf{r}_K \mathbf{r}_L^T}{r_K^3\ r_L^3} \right| \psi_q(\mathbf{B}) \right\rangle E_{pq} \quad (101)$$

The first term contributes to the magnetizability only and is not needed here. In these expressions, we have indicated that the MO's depend on the external magnetic field through the use of field-dependent orbitals, as discussed shortly.

To calculate the NMR properties, we must analyze the derivatives of the Hamiltonian operator eq 90, taking into consideration the dependence of the AO's on the magnetic field **B**. Let us consider the diamagnetic contributions first. Differentiating the Hamiltonian eq 90 twice, we obtain

$$\frac{\mathrm{d}^2\hat{H}}{\mathrm{d}\mathbf{B}\ \mathrm{d}\mathbf{M}_K} = \hat{\mathbf{h}}_{BK}^{\mathrm{dia}} + \frac{\mathrm{d}\hat{\mathbf{h}}_K^{\mathrm{pso}}}{\mathrm{d}\mathbf{B}} + \frac{\mathrm{d}\hat{\mathbf{h}}_K^{\mathrm{fc}}}{\mathrm{d}\mathbf{B}} + \frac{\mathrm{d}\hat{\mathbf{h}}_K^{\mathrm{sd}}}{\mathrm{d}\mathbf{B}} - \mathbf{1} \quad (102)$$

$$\frac{\mathrm{d}^2\hat{H}}{\mathrm{d}\mathbf{M}_K\ \mathrm{d}\mathbf{M}_L} = \hat{\mathbf{h}}_{KL}^{\mathrm{dso}} + \mathbf{D}_{KL} \quad (103)$$

where the field dependence of the FC and SD contributions will vanish for closed-shell molecules because of the triplet nature of these perturbations. Turning to the paramagnetic contributions to the properties, we find that the first derivatives of the Hamiltonian eq 90 are given by

$$\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{B}} = \hat{\mathbf{h}}_B^{\mathrm{orb}} + \hat{\mathbf{h}}_B^{\mathrm{spn}} + \frac{\mathrm{d}\hat{H}^{(0)}}{\mathrm{d}\mathbf{B}} \quad (104)$$

$$\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{M}_K} = \hat{\mathbf{h}}_K^{\mathrm{pso}} + \hat{\mathbf{h}}_K^{\mathrm{fc}} + \hat{\mathbf{h}}_K^{\mathrm{sd}} \quad (105)$$

Comparing the second-quantization diamagnetic operators eqs 102 and 103 with their first-quantization counterparts eqs 45 and 46 and likewise the second-quantization paramagnetic operators eqs 104 and 105 with eqs 32 and 36, we find that the second-quantization operators contain, in addition to the terms present in their first-quantization counterparts, terms that arise from the dependence of the AO's on the magnetic field **B**. The reason for the presence of the additional terms is the necessity to maintain gauge-origin independence in the calculations by the use of magnetic field-dependent basis functions, as explained in section V.B. In Sec V.C, we consider the evaluation of these new terms using $\mathrm{d}\hat{\mathbf{h}}_K^{\mathrm{pso}}/\mathrm{d}\mathbf{B}$ as an example.

B. The Gauge-Origin Problem

As seen from eq 28, the vector potential representing the external magnetic field induction **B**

$$\mathbf{A}_O(\mathbf{r}) = {}^1\!/_2 \mathbf{B} \times (\mathbf{r} - \mathbf{O}) \quad (106)$$

and therefore also the Hamiltonian in eq 23, is not uniquely defined since we may choose the position of the gauge origin **O** freely and still satisfy the requirement eq 25

$$\mathbf{B} = \nabla \times \mathbf{A}_O(\mathbf{r}) \quad (107)$$

In contrast, all observable properties of the system—the electronic energy and the nuclear shieldings, for instance—should be independent of the choice of gauge origin. This gauge-origin independence can occur only if the wave function ψ changes in a very specific manner as we change the position of the gauge origin.

Let us consider first a general gauge transformation of the vector potential. For any scalar function $f(\mathbf{r})$, the curl of the gradient vanishes identically:

$$\nabla \times \nabla f = 0 \quad (108)$$

Accordingly, we may write a general gauge transformation of the vector potential in the following manner:

$$\mathbf{A}_{O'}(\mathbf{r}) = \mathbf{A}_O(\mathbf{r}) + \nabla f(\mathbf{r}) \qquad (109)$$

where $f(\mathbf{r})$ is some scalar function. For such a gauge transformation, the exact wave function transforms as

$$\psi'(\mathbf{r}) = \exp[-if(\mathbf{r})]\,\psi(\mathbf{r}) \qquad (110)$$

and gauge invariance of the energy and other properties is thereby maintained. For example, it is easily verified that

$$\langle\psi'|H'|\psi'\rangle = \langle\psi|H|\psi\rangle \qquad (111)$$

where H' is the gauge-transformed Hamiltonian, constructed from $\mathbf{A}_{O'}(\mathbf{r})$ rather than $\mathbf{A}_O(\mathbf{r})$. Except for a constant overall phase factor, the expression in eq 110 constitutes an exact relationship between two wave functions that have been separately and independently determined for two different choices of the vector potential $\mathbf{A}_{O'}(\mathbf{r})$ and $\mathbf{A}_O(\mathbf{r})$. The two wave functions describe the same physical state since

$$|\psi'(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2 \qquad (112)$$

but correspond to different representations of the magnetic field.

Let us now consider the particular gauge transformation associated with a shift of the gauge origin from $\mathbf{O}$ to $\mathbf{O}'$:

$$\mathbf{A}_{O'}(\mathbf{r}) = \mathbf{A}_O(\mathbf{r}) + \nabla f(\mathbf{r}) \qquad (113)$$

For such a transformation, the scalar function is given as the simple triple product

$$f(\mathbf{r}) = {}^1/_2\mathbf{B} \times (\mathbf{O} - \mathbf{O}')\cdot\mathbf{r} \qquad (114)$$

and the gauge-transformed wave function may consequently be written as

$$\psi_{O'}(\mathbf{r}) = \exp[-i\,{}^1/_2\mathbf{B} \times (\mathbf{O} - \mathbf{O}')\cdot\mathbf{r}]\psi_O(\mathbf{r}) \qquad (115)$$

where $\psi_{O'}(\mathbf{r})$ and $\psi_O(\mathbf{r})$ are the wave functions associated with the gauge origins $\mathbf{O}'$ and $\mathbf{O}$, respectively.

Having discussed gauge transformations of the exact wave function, we now turn our attention to approximate electronic wave functions. For an approximate wave function expanded in a finite-dimensional variational space, there is no guarantee that it will transform correctly upon a change of the gauge origin—for this to happen, the variational space would have to be sufficiently flexible to reproduce the gauge transformation in eq 115 exactly. Indeed, within a finite linear variational subspace, gauge-origin invariance can *never* be obtained exactly, only approximately for small displacements of the gauge origin. In such cases, therefore, the calculated energies and properties will depend on the choice of gauge origin.

The lack of gauge invariance in approximate calculations gives rise to several problems. First, for the calculation to be reproducible, we must in each case report the position of the gauge origin used. In a few cases, a *natural* choice can be made for the gauge origin (for example, at the nucleus in an atomic calculation as discussed shortly) but mostly no such choice can be made, making the results of the calculation ambiguous. Second, the quality of the calculated results may depend critically on the choice of gauge origin for the vector potential, making reliable a priori prediction of molecular magnetic properties difficult.

Let us begin by investigating the notion of a natural gauge origin more closely. Consider a one-electron atomic system in a magnetic field $\mathbf{B}$ and assume that the unperturbed system is represented by the approximate wave function χ_{lm}, which we may take to be a Slater orbital or some other approximate representation of the atomic state. The unperturbed wave function is centered on $\mathbf{N}$ (the atomic nucleus) and is assumed to be an eigenfunction of the (effective) Hamiltonian H_0 and of the operator for angular momentum along the z direction L_z^N

$$H_0\chi_{lm} = E_0\chi_{lm} \qquad (116)$$

$$L_z^N\chi_{lm} = m_l\chi_{lm} \qquad (117)$$

The superscript N in L_z^N signifies that the angular momentum is defined relative to $\mathbf{N}$. We now apply the magnetic field with the gauge origin chosen at $\mathbf{N}$:

$$\mathbf{A}_N(\mathbf{r}) = {}^1/_2\mathbf{B} \times (\mathbf{r} - \mathbf{N}) \qquad (118)$$

Constructing the perturbed Hamiltonian in the usual manner and carrying out some simple algebra, we find that the unperturbed wave function χ_{lm} is correct to first order in the magnetic field $\mathbf{B}$:

$$(H_0 + {}^1/_2BL_z^N + O(B^2))\,\chi_{lm} = (E_0 + {}^1/_2m_lB)\,\chi_{lm} + O(B^2) \qquad (119)$$

On the other hand, if we apply the field with a different gauge origin $\mathbf{M}$

$$\mathbf{A}_M(\mathbf{r}) = {}^1/_2\mathbf{B} \times (\mathbf{r} - \mathbf{M}) \qquad (120)$$

then the unperturbed wave function is correct only to zeroth order in the field (see also ref 36)

$$(H_0 + {}^1/_2BL_z^M + O(B^2))\,\chi_{lm} = E_0\chi_{lm} + O(B) \qquad (121)$$

since χ_{lm} is not an eigenfunction of L_z^M. Thus, the approximate wave function is biased toward $\mathbf{N}$ in the sense that with this choice of gauge origin, the wave function is correct to first order in the field, whereas, with any other choice of gauge origin, it is correct only to zeroth order. Clearly, for one-electron atomic systems, a natural gauge origin exists.

Once a natural gauge origin $\mathbf{N}$ has been identified, we may use it as a reference gauge origin and enforce gauge-origin independence by attaching to the wave function the phase factor associated with a shift from $\mathbf{N}$ to the true gauge origin $\mathbf{O}$. We now obtain a wave function of the form

$$\omega_{lm}(\mathbf{A}_O) = \exp[-{}^1/_2 i\mathbf{B} \times (\mathbf{N} - \mathbf{O})\cdot\mathbf{r}]\chi_{lm} \qquad (122)$$

which is correct to first order in the field **B** for *any* choice of gauge origin **O**, as may easily be verified. Moreover, it may readily be shown[37] that the expectation value of the one-electron Hamiltonian

$$E(\mathbf{B}) = \langle \omega_{lm}(\mathbf{A}_O)|H(\mathbf{A}_O)|\omega_{lm}(\mathbf{A}_O)\rangle \qquad (123)$$

is independent of the gauge origin **O**, always returning the energy that would be obtained with the gauge origin at **N**. In a sense, we have arrived at an approximate but gauge-origin-independent description of the atomic system. However, it is gauge-origin-independent by design rather than because of some inherent flexibility in the description. Nevertheless, since our choice of reference gauge origin was made because it provides a superior description of the electronic system in the field, we expect the resulting wave function eq 122 to represent well the electronic system in a magnetic field.

Since, for an atomic system, we may always place the gauge origin at the nuclear center, the introduction of the complex phase factor in the atomic orbital according to eq 122 may appear to be an academic exercise of no practical consequence. The importance of the phase factors in the orbitals becomes apparent only when several atoms are considered simultaneously. We cannot simultaneously place the gauge origin **O** at all the atomic nuclei in the system and the introduction of the complex phase factors becomes essential to ensure a uniform description of the electronic system. Indeed, without the complex phase factors attached, a description of a pair of isolated, noninteracting atoms would depend on their relative separation and such a description of the electronic system would *not* be size extensive. This lack of size extensivity in common gauge approaches manifests itself for instance in qualitatively wrong shielding surfaces.[38]

Let us now consider the evaluation of magnetic properties for molecular systems—that is, for systems of interacting atoms. Following the presentation above, we may attach the complex phase factors directly to the AO's, equipping each basis function with its own complex phase factor according to eq 122. A spherical-harmonic Gaussian-type orbital (GTO) may then be written in the form

$$\omega_\nu(\mathbf{B}) = \exp[-{}^1/_2 i\mathbf{B} \times (\mathbf{N} - \mathbf{O})\cdot\mathbf{r}]S_{lm}(\mathbf{r}) \exp(-ar^2) \qquad (124)$$

where $S_{\mathrm{lm}}(\mathbf{r})$ is a standard solid harmonic function. The resulting AO's are known as London atomic orbitals or gauge-invariant atomic orbitals (GIAO's). Although this name has been criticized as the GIAO's should be considered gauge dependent rather than gauge independent,[39] we shall keep to Ditchfield's original acronym,[40] interpreting it as indicating that the GIAO's give rise to gauge-independent molecular properties.

GIAO's were introduced by London in 1937[41] to investigate π-electron ring currents in aromatic molecules using Hückel theory. GIAO's were used by Hameka in the 1960s[42,43] and by Ditchfield in the 1970s,[44] but it is only since the presentation of an efficient implementation of the approach using modern analytical derivative techniques by Woliński, Hinton, and Pulay in 1990[45] that the use of London orbitals has become widespread.

In the London orbital approach, each AO is equipped with a phase factor. However, it is possible to attach local phase factors to the MO's rather than to the AO's, as done in the Individual Gauge for Localized Orbitals (IGLO) method developed by Kutzelnigg[46,47]—the first method that enabled the systematic study of nuclear shieldings in larger molecular systems using distributed gauge origins.[36,48] In the IGLO method, the gauge origin for the core orbitals and the lone pairs is located at the corresponding nucleus, whereas the bonding valence orbitals have their gauge origins at the center of electronic charge of the orbitals. However, to avoid the delocalized nature of valence orbitals—for which no obvious local gauge origin exists—the MO's are localized prior to the calculation of the molecular properties. The use of localized orbitals makes it possible to approximate the computationally demanding derivative two-electron integrals by use of completeness relations.[36] The IGLO method is thus computationally less expensive than the GIAO method, where no such approximations are introduced. However, these approximations should be kept in mind when choosing a proper basis set in an IGLO calculation.

A distributed gauge-origin method similar to the IGLO approach is the Localized Orbitals/Localized Origins (LORG) method of Bouman and Hansen,[39] see the discussion by Kutzelnigg.[36] This method was formulated within the random-phase approximation but has also been extended to include second-order correlation effects in the Second-order LORG (SOLO) approach.[49] In the Full LORG method, the gauge origin is chosen to be at the center of the electronic charge for the localized orbitals, as in the IGLO approach. However, whereas, in the IGLO approach, the local gauge origins are related to the localized orbitals in the magnetic-field perturbed wave function, in the Full LORG approach the local gauge origins are related to the centroids of the localized orbitals in the nuclear magnetic-moment perturbed wave function. In Full LORG, the local gauge origins may thus be located far away from the orbitals of the magnetic-field perturbed wave function, leading to the same problems as in conventional SCF due to unphysical long-range shielding contributions. This problem is avoided in the standard LORG method, where the local gauge origins are chosen to be at the nucleus for which the shielding is calculated for all orbitals attached to this nucleus, and at the center of electronic charge for the remaining ones. A comparison of the results obtained using the LORG and IGLO approaches has been presented by Facelli et al.[50]

Bader and Keith have introduced the Individual Gauges for Atoms in Molecules (IGAIM)[51] and Continuous Set of Gauge Transformations (CSGT)[52] (denoted Continuous Transformation of the Origin of the Current Density (CTOCD) by Lazzeretti, Malagoli, and Zanasi[53]) methods for use with the "atoms in molecules" approach developed by Bader.[54] The theoretical foundations of the latter choice of distributed gauge origins have been discussed by Lazzeretti et al.[53] Zanasi et al.[55] also introduced an approach in which the paramagnetic contribution to the current density is made to vanish, abbreviated by them as CTOCD-PZ[56] (with the approach of Bader and Keith called CTOCD-DZ). However, none of these methods have been implemented for correlated wave functions and a more thorough discussion of these methods is therefore beyond the scope of this review. The interested reader is referred to the recent review by Fukui.[7]

Of the above-mentioned methods for solving the gauge-origin problem, by far the most common are the GIAO and IGLO methods. In practice the basis set must be flexible enough to describe properly the nuclear magnetic moment perturbations, and only small differences in the calculated shieldings are observed between the two approaches. The use of localized MO's enables the IGLO approach to reduce the computational time. However, this localization may not always be well-defined and the IGLO method is not easily extended to correlated wave functions and to other magnetic properties, although an MCSCF extension of the method exists.[57] In contrast, by attaching the gauge origins to the AO's themselves, the GIAO approach is transparent to the correlation treatment and has therefore been implemented for most correlated wave functions.[58−63] The method is also easily generalized to other molecular magnetic properties.[28,64−67]

C. Field-Dependent Orbitals and Orbital Connections

We have seen how, to solve the gauge-dependence problem for finite basis sets, we must introduce in our calculations atomic orbitals $\omega_\mu(\mathbf{B})$ that depend explicitly on the external field **B**. For the construction of the electronic Hamiltonian, we need a basis of MO's, constructed as linear combinations of these AO's. Moreover, for this construction to be valid, we need to make sure that these MO's stay orthonormal for all values of the field strength, even though the AO's change as the field is turned on. To ensure orthonormality, we follow the approach of refs 68 and 69.

For the unperturbed molecular system, we calculate a set of orthonormal MO's in the normal way:

$$\phi_p = \sum_\mu C^{(0)}_{p\mu}\omega_\mu(\mathbf{0}) \tag{125}$$

For the perturbed system, we first set up a set of nonorthogonal unmodified MO's (UMO's) using the MO coefficients of the unperturbed system

$$\phi^{\mathrm{UMO}}_p(\mathbf{B}) = \sum_\mu C^{(0)}_{p\mu}\omega_\mu(\mathbf{B}) \tag{126}$$

The nonorthogonality of the UMO's follows since the overlap of the AO's depends on the perturbation

$$S_{pq}(\mathbf{B}) = \langle\phi^{\mathrm{UMO}}_p(\mathbf{B})|\phi^{\mathrm{UMO}}_q(\mathbf{B})\rangle = \sum_{\mu\nu} C^{(0)}_{p\mu}C^{(0)}_{q\nu}\langle\omega_\mu(\mathbf{B})|\omega_\nu(\mathbf{B})\rangle \tag{127}$$

We then arrive at the final orthonormalized MO's (OMO's) by a orthonormalization of the UMO's:

$$\psi^{\mathrm{OMO}}_p(\mathbf{B}) = \sum_n \phi^{\mathrm{UMO}}_q(\mathbf{B})\, T_{qp}(\mathbf{B}) \tag{128}$$

where $\mathbf{T}(\mathbf{B})$ is known as the orbital connection matrix,[68] satisfying the conditions

$$\mathbf{T}^T(\mathbf{B})\mathbf{S}(\mathbf{B})\mathbf{T}(\mathbf{B}) = \mathbf{1} \tag{129}$$

In principle, any choice of connection matrix will do and common choices of connection matrix include the Gram−Schmidt orthogonalization[70]

$$T^R_{pq} = 0 \quad p > q \tag{130}$$

$$T^I_{pq} = 0 \quad p \geq q \tag{131}$$

where we have written **T** as a sum of a real and an imaginary part $\mathbf{T} = \mathbf{T}^R + \mathbf{T}^I$, and the symmetric orthogonalization[69,71]

$$\mathbf{T}(\mathbf{B}) = \mathbf{S}(\mathbf{B})^{-1/2} \tag{132}$$

However, as discussed by Olsen et al.,[72] for the calculation of magnetic properties, these connections suffer from problems related to numerical instability. A stable connection is obtained by requiring the OMO's in the presence of the magnetic field to be as similar as possible to the UMO's in the absence of the field. This requirement leads us to the natural connection[72]

$$\mathbf{T}(\mathbf{B}) = \mathbf{W}^{-1}(\mathbf{B})[\mathbf{W}(\mathbf{B})\mathbf{S}(\mathbf{B})^{-1}\mathbf{W}(\mathbf{B})^T]^{1/2} \tag{133}$$

where

$$W_{pq}(\mathbf{B}) = \langle\phi^{\mathrm{UMO}}_p(\mathbf{0})|\phi^{\mathrm{UMO}}_q(\mathbf{B})\rangle = \sum_{\mu\nu} C^{(0)}_{p\mu}\, C^{(0)}_{q\nu}\langle\omega_\mu(\mathbf{0})|\omega_\nu(\mathbf{B})\rangle \tag{134}$$

The natural connection gives numerically stable results,[73] which is particularly important for larger systems and when numerical differentiation of second-order properties is used to obtain nonlinear properties such as shielding polarizabilities.[28]

To illustrate the evaluation of the integral derivatives in the OMO representation, let us consider the derivative of a PSO integral:

$$\frac{\mathrm{d}}{\mathrm{d}\mathbf{B}}\langle\psi_p(\mathbf{B})|\mathbf{h}^{\mathrm{pso}}|\psi_q(\mathbf{B})\rangle\bigg|_{\mathbf{B}=0} = \frac{\mathrm{d}}{\mathrm{d}\mathbf{B}}\langle\phi^{\mathrm{UMO}}_p(\mathbf{B})|\mathbf{h}^{\mathrm{pso}}|\phi^{\mathrm{UMO}}_q(\mathbf{B})\rangle\bigg|_{\mathbf{B}=0} \tag{135}$$

$$+ \sum_r \langle\phi_r(\mathbf{0})|\mathbf{h}^{\mathrm{pso}}|\phi_q(\mathbf{0})\rangle \frac{\mathrm{d}T^*_{rp}}{\mathrm{d}\mathbf{B}}\bigg|_{\mathbf{B}=0} \tag{136}$$

$$+ \sum_r \langle\phi_p(\mathbf{0})|\mathbf{h}^{\mathrm{pso}}|\phi_r(\mathbf{0})\rangle \frac{\mathrm{d}T_{rq}}{\mathrm{d}\mathbf{B}}\bigg|_{\mathbf{B}=0} \tag{137}$$

where the first derivative of the connection matrix is given by

$$\left.\frac{d\mathbf{T}}{d\mathbf{B}}\right|_{\mathbf{B}=0} = -\left.\frac{d\mathbf{W}}{d\mathbf{B}}\right|_{\mathbf{B}=0} \qquad (138)$$

The integrals appearing in these equations may be evaluated in the AO basis using the techniques discussed by Helgaker and Taylor.[74] Second derivatives are obtained by a generalization of this scheme, see for example refs 17, 72, and 75.

VI. The ab Initio Calculation of NMR Parameters

Having considered the second-quantization Hamiltonian operators and the dependence of the MO's on the external magnetic field through the use of perturbation-dependent AO's, we turn our attention to the calculation of the nuclear magnetic shielding and spin–spin coupling constants for the standard models of quantum chemistry: the Hartree–Fock model, the full configuration–interaction model, the multiconfigurational self-consistent field model, the coupled-cluster model, and Møller–Plesset perturbation theory. For each model, we consider first the calculation of the electronic energy and (if applicable) the electronic wave function. Next, the calculation of NMR parameters for the given model is discussed. As well as presenting the basic equations needed to calculate the energy and NMR parameters for the different models, we discuss the important computational aspects for each model and provide a review of the recent literature, with emphasis on methodological developments and computer implementations.

A. Hartree–Fock Approximation

In the Hartree–Fock approximation, the wave function is represented by a single electronic configuration, variationally optimized to provide the best possible approximation to the exact wave function. The Hartree–Fock approximation is particularly well suited to describe closed-shell ground-state wave functions at the molecular equilibrium geometry, which is just the situation encountered in NMR experiments. For nuclear shieldings, the Hartree–Fock approximation is therefore a useful one, applicable to most systems of interest in NMR experiments, providing results of reasonable quality. For nuclear spin–spin couplings, on the other hand, the Hartree–Fock approximation is not very useful, not having the flexibility for an accurate description of the perturbations responsible for setting up these couplings, in particular in the triplet space.

1. Wave Function and Energy

In restricted Hartree–Fock (RHF) theory, a closed-shell electronic state is represented by a Slater determinant of doubly occupied molecular orbitals. In second quantization, our ansatz for the wave function may be written in the form

$$|\kappa\rangle = \exp(-\hat{\kappa})\Big(\prod_i a^\dagger_{i\alpha}\, a^\dagger_{i\beta}\Big)|vac\rangle \qquad (139)$$

where the orbital–rotation operator is given by

$$\hat{\kappa} = \sum_i \kappa_i \hat{\kappa}_i \qquad (140)$$

in terms of a set of elementary orbital–rotation operators $\hat{\kappa}_i$ applied to a set of trial MO's. The form of the orbital–rotation operators will be discussed below. The dependence of the orbital–rotation operators on the external magnetic field can be neglected for time-independent magnetic properties as shown by Helgaker and Jørgensen.[37] The Hartree–Fock state $|\mathrm{HF}\rangle$ is variationally optimized with respect to the orbital–rotation parameters κ

$$E^{(0)}_{HF} = \langle HF|\hat{H}|HF\rangle = \min_{\kappa} \langle \kappa|\hat{H}|\kappa\rangle \qquad (141)$$

and the optimized Hartree–Fock state is usually expressed as

$$|HF\rangle = \Big(\prod_i a^\dagger_{i\alpha}\, a^\dagger_{i\beta}\Big)|vac\rangle \qquad (142)$$

that is, in terms of a set of orbitals where the orbital-rotation parameters κ_i are zero.

A completely general form for the orbital–rotation operator $\hat{\kappa}$ is given by

$$\hat{\kappa} = i\sum_{p>q} {}^{I}\kappa^{0}_{pq} E^{+}_{pq} + \sum_{p>q} {}^{R}\kappa^{0}_{pq} E^{-}_{pq} + i\sum_{\alpha}\sum_{p>q} {}^{I}\kappa^{\alpha}_{pq} T^{\alpha+}_{pq} + \sum_{\alpha}\sum_{p>q} {}^{R}\kappa^{\alpha}_{pq} T^{\alpha-}_{pq} \qquad (143)$$

where α runs over the three Cartesian directions and

$$E^{\pm}_{pq} = E_{pq} \pm E_{qp} \qquad (144)$$

$$T^{\alpha\pm}_{pq} = T^{\alpha}_{pq} \pm T^{\alpha}_{qp} \qquad (145)$$

The operators E^{-}_{pq} and iE^{+}_{pq} carry out real and imaginary singlet orbital rotations, respectively, whereas the operators $T^{\alpha+}_{pq}$ and $iT^{\alpha-}_{pq}$ carry out the corresponding triplet rotations of the orbitals. For the optimization of RHF wave function, only real singlet rotations are needed and a general parametrization of RHF wave function may be written in the manner

$$|\mathrm{RHF}(\kappa)\rangle = \exp\Big(-\sum_{p>q} {}^{R}\kappa^{0}_{pq}\, E^{-}_{pq}\Big)|0\rangle \qquad (146)$$

However, if the RHFs symmetry restrictions on the wave function are relaxed (as appropriate for a system perturbed by an external magnetic field and by nuclear magnetic moments), we must include in our wave function the full set of rotations present in eq 143. It should further be noted that not all orbital–rotation operators E^{-}_{pq} need to be included in eq 146. Thus, for closed-shell RHF states, only those rotation operators that mix unoccupied and occupied orbitals must be included; the remaining orbital–rotation operators are redundant and may be omitted for the purpose of optimizing the RHF state.

The Hartree–Fock wave function represents a situation where the electrons behave independently of one another, interacting only through a mean field. Indeed, the Hartree–Fock wave function may be found by solving a set of effective, one-electron Schrödinger equations for the spin orbitals. The one-electron equations are called the Fock equations and the associated effective Hamiltonian is the Fock operator

$$\hat{f} = \sum_{pq} f_{pq} E_{pq} \tag{147}$$

whose elements f_{pq} constitute the Fock matrix. In the Fock operator

$$\hat{f} = \hat{h} + \hat{V} \tag{148}$$

the one-electron part of the true Hamiltonian is retained but the two-electron part is replaced by an effective, one-electron Fock potential $\hat{V}$, which incorporates the effects of the Coulomb repulsion among the electrons in an average sense

$$\hat{V} = \sum_{pq} V_{pq} E_{pq} \tag{149}$$

$$V_{pq} = \sum_{i} (2g_{pqii} - g_{piiq}) \tag{150}$$

In these expressions, whereas the index i runs only over the occupied orbitals, the summations over p and q are over the full set of orbitals—unoccupied as well as occupied. In the canonical representation of the Hartree–Fock wave function, the spin–orbitals are eigenfunctions of the Fock operator

$$\hat{f} a^{\dagger}_{p\sigma} |vac\rangle = \epsilon_p a^{\dagger}_{p\sigma} |vac\rangle \tag{151}$$

and the eigenvalues are known as the orbital energies.

2. Hartree–Fock Second-Order Properties

Having discussed the Hartree–Fock wave function and its optimization, we may proceed to carry out a standard perturbation expansion of the energy, using the general theory presented in section IV. To second order in the perturbation, we obtain

$$E^{(0)}_{HF} = \langle \mathrm{HF} | \hat{H}^{(0)} | \mathrm{HF} \rangle \tag{152}$$

$$E^{(1)}_{HF} = \langle \mathrm{HF} | \hat{H}^{(1)} | \mathrm{HF} \rangle \tag{153}$$

$$E^{(2)}_{HF} = \langle \mathrm{HF} | \hat{H}^{(2)} | \mathrm{HF} \rangle + \langle \mathrm{HF} | [\hat{\kappa}^{(1)}, \hat{H}^{(1)}] | \mathrm{HF} \rangle \tag{154}$$

As expected from the general theory, the zeroth- and first-order energies may be calculated from the unperturbed Hartree–Fock state. For the calculation of the second-order energy, the first-order perturbed wave function, determined by $\hat{\kappa}^{(1)}$, the perturbation correction to the orbital-rotation operator, is needed as well. For closed-shell states, the first-order energy eq 153 vanishes for the magnetic perturbations considered here, as discussed in section III.C.

The Hartree–Fock conditions in the zeroth- and first-order in perturbation theory may be written in the form

$$\langle \mathrm{HF} | [\hat{\kappa}_i, \hat{H}^{(0)}] | \mathrm{HF} \rangle = 0 \tag{155}$$

$$\sum_j \langle \mathrm{HF} | [\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]] | \mathrm{HF} \rangle \, \kappa^{(1)}_j = -\langle \mathrm{HF} | [\hat{\kappa}_i, \hat{H}^{(1)}] | \mathrm{HF} \rangle \tag{156}$$

The zeroth-order conditions eq 155 (known as the Brillouin conditions) constitute a nonlinear set of conditions on the unperturbed Hartree–Fock state. The first-order conditions eq 156 represent a set of linear equations for the perturbed wave function $\hat{\kappa}^{(1)}$. Note that the right-hand side in eq 156 has the same structure as the expectation value of the Brillouin conditions but that the first-order Hamiltonian has now replaced the zeroth-order Hamiltonian.

3. Detailed Expressions for Second-Order Properties

For the special case of the Hartree–Fock wave function, we shall consider the evaluation of the second-order properties in greater detail than for the remaining models of this section, so as to illustrate some of the features of NMR derivative calculations common to all models. Although, in the following, we discuss the spin–spin coupling constants as well as shieldings, we recall that at the restricted Hartree–Fock level, only the calculation of shieldings is meaningful.

First, to obtain the diamagnetic contributions in eq 154, we need the expectation values given by

$$\left\langle \mathrm{HF} \left| \frac{\mathrm{d}^2 \hat{H}}{\mathrm{d}\mathbf{B}\, \mathrm{d}\mathbf{M}_K} \right| \mathrm{HF} \right\rangle = \left\langle \mathrm{HF} \left| \hat{\mathbf{h}}^{\mathrm{dia}}_{BK} + \frac{\mathrm{d}\hat{\mathbf{h}}^{\mathrm{pso}}_K}{\mathrm{d}\mathbf{B}} \right| \mathrm{HF} \right\rangle - \mathbf{1} \tag{157}$$

$$\left\langle \mathrm{HF} \left| \frac{\mathrm{d}^2 \hat{H}}{\mathrm{d}\mathbf{M}_K\, \mathrm{d}\mathbf{M}_L} \right| \mathrm{HF} \right\rangle = \langle \mathrm{HF} | \hat{\mathbf{h}}^{\mathrm{dso}}_{KL} | \mathrm{HF} \rangle + \mathbf{D}_{KL} \tag{158}$$

In eq 157, the contributions from the triplet operators in eq 102 vanish and there is a contribution from the dependence of $\hat{\mathbf{h}}^{\mathrm{pso}}$ on the magnetic field (because the GIAO's are field-dependent). Second, for the gradient parts in eq 156, we obtain

$$\left\langle \mathrm{HF} \left| \left[\hat{\kappa}_i, \frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{B}} \right] \right| \mathrm{HF} \right\rangle = \begin{cases} \left\langle \mathrm{HF} \left| \left[iE^{+}_{pq}, \hat{\mathbf{h}}^{\mathrm{orb}}_B + \dfrac{\mathrm{d}\hat{H}^{(0)}}{\mathrm{d}\mathbf{B}} \right] \right| \mathrm{HF} \right\rangle & \text{if } \hat{\kappa}_i = iE^{+}_{pq} \\ 0 & \text{otherwise} \end{cases} \tag{159}$$

$$\left\langle \mathrm{HF} \left| \left[\hat{\kappa}_i, \frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{M}_K} \right] \right| \mathrm{HF} \right\rangle = \begin{cases} \langle \mathrm{HF} | [iE^{+}_{pq}, \hat{\mathbf{h}}^{\mathrm{pso}}_K] | \mathrm{HF} \rangle & \text{if } \hat{\kappa}_i = iE^{+}_{pq} \\ \langle \mathrm{HF} | [T^{\alpha-}_{\mathrm{pq}}, \hat{\mathbf{h}}^{\mathrm{fc}}_K + \hat{\mathbf{h}}^{\mathrm{sd}}_K] | \mathrm{HF} \rangle & \text{if } \hat{\kappa}_i = T^{\alpha-}_{\mathrm{pq}} \\ 0 & \text{otherwise} \end{cases} \tag{160}$$

For one-electron-perturbing operators, these expressions correspond to a matrix element between a virtual and an occupied orbital.

From a consideration of spin and real–imaginary symmetries, most of the elements of the perturbed electronic gradients eqs 159 and 160 are zero. The final expressions for the Hartree–Fock shielding and indirect spin–spin coupling tensors are now easily obtained in accordance with eqs 59 and 62

$$\boldsymbol{\sigma}_K = \left\langle \mathrm{HF}\left|\hat{\mathbf{h}}_{BK}^{\mathrm{dia}} + \frac{\mathrm{d}\hat{\mathbf{h}}_K^{\mathrm{pso}}}{\mathrm{d}\mathbf{B}}\right|\mathrm{HF}\right\rangle + \sum_{p>q}\langle \mathrm{HF}|[iE_{pq}^{+},(\hat{\mathbf{h}}_K^{\mathrm{pso}})^T]|\mathrm{HF}\rangle \frac{\mathrm{d}^I\kappa_{pq}^0}{\mathrm{d}\mathbf{B}} \quad (161)$$

$$\mathbf{K}_{KL} = \langle \mathrm{HF}|\hat{\mathbf{h}}_{KL}^{\mathrm{dso}}|\mathrm{HF}\rangle + \sum_{p>q}\langle \mathrm{HF}|[iE_{pq}^{+},(\hat{\mathbf{h}}_K^{\mathrm{pso}})^T]|\mathrm{HF}\rangle \frac{\mathrm{d}^I\kappa_{pq}^0}{\mathrm{d}\mathbf{M}_L} + \sum_{\alpha}\sum_{p>q}\langle \mathrm{HF}|[T_{pq}^{\alpha-},(\hat{\mathbf{h}}_K^{\mathrm{fc}})^T + (\hat{\mathbf{h}}_K^{\mathrm{sd}})^T]|\mathrm{HF}\rangle \frac{\mathrm{d}^R\kappa_{pq}^{\alpha}}{\mathrm{d}\mathbf{M}_L} \quad (162)$$

The singlet response equations for the field perturbations eq 65 are given by

$$\sum_{r>s}\langle \mathrm{HF}|[iE_{pq}^{+}, [iE_{rs}^{+}, \hat{H}]]|\mathrm{HF}\rangle \frac{\mathrm{d}^I\kappa_{rs}^0}{\mathrm{d}\mathbf{B}} = -\left\langle \mathrm{HF}\left|\left[iE_{pq}^{+}, \hat{\mathbf{h}}_B^{\mathrm{orb}} + \frac{\mathrm{d}\hat{H}^{(0)}}{\mathrm{d}\mathbf{B}}\right]\right|\mathrm{HF}\right\rangle \quad (163)$$

whereas the singlet and triplet equations for the nuclear-moment perturbations eq 66 become

$$\sum_{r>s}\langle \mathrm{HF}|[iE_{pq}^{+}, [iE_{rs}^{+}, \hat{H}]]|\mathrm{HF}\rangle \frac{\mathrm{d}^I\kappa_{rs}^0}{\mathrm{d}\mathbf{M}_K} = -\langle \mathrm{HF}|[iE_{pq}^{+}, \hat{\mathbf{h}}_K^{\mathrm{pso}}]|\mathrm{HF}\rangle \quad (164)$$

$$\sum_{r>s}\langle \mathrm{HF}|[T_{pq}^{\alpha-}, [T_{rs}^{\alpha-}, \hat{H}]]|\mathrm{HF}\rangle \frac{\mathrm{d}^R\kappa_{rs}^{\alpha}}{\mathrm{d}\mathbf{M}_K} = -\langle \mathrm{HF}|[T_{pq}^{\alpha-}, \hat{\mathbf{h}}_K^{\mathrm{fc}} + \hat{\mathbf{h}}_K^{\mathrm{sd}}]|\mathrm{HF}\rangle \quad (165)$$

It should be noted that, in eqs 163–165, there is no coupling of perturbations of singlet and triplet spin symmetries, nor any coupling of the different components of the triplet perturbations. These results follow from standard considerations of group theory and in particular from the Wigner–Eckart theorem.

From the above expressions for the response equations, it would appear that for each NMR-active nucleus, we must solve three linear singlet equations eq 164 and nine linear triplet equations eq 165. However, the number of independent triplet equations is only six. To see this, we note that the β component of $\hat{\mathbf{h}}_K^{\mathrm{fc}} + \hat{\mathbf{h}}_K^{\mathrm{sd}}$ is an operator of the structure

$$\hat{O}^{\beta} = \sum_{\gamma}\sum_{rs} O_{rs}^{\beta\gamma}\, T_{rs}^{\gamma} \quad (166)$$

where the $O_{pq}^{\alpha\beta}$ are symmetric in the Cartesian components. Inserting this operator into the perturbed electronic gradient, we obtain

$$\begin{aligned}\langle \mathrm{HF}|[T_{pq}^{\alpha-},\hat{O}^{\beta}]|\mathrm{HF}\rangle &= \sum_{\gamma}\sum_{rs} O_{rs}^{\beta\gamma}\langle \mathrm{HF}|[T_{pq}^{\alpha-},T_{rs}^{\gamma}]|\mathrm{HF}\rangle \\ &= \sum_{rs} O_{rs}^{\beta\alpha}\, \langle \mathrm{HF}|[T_{pq}^{\alpha-},T_{rs}^{\alpha}]|\mathrm{HF}\rangle \\ &= \sum_{rs} O_{rs}^{\beta\alpha}\, \langle \mathrm{HF}|[T_{pq}^{z-},T_{rs}^{z}]|\mathrm{HF}\rangle \end{aligned} \quad (167)$$

where the last result follows from the application of the Wigner–Eckart theorem, but may easily be verified explicitly. Since the $O_{rs}^{\alpha\beta}$ are symmetric in the Cartesian indices, it follows that, in eq 165, there are only six independent right-hand sides, and hence only six independent triplet solutions.

Before we discuss the computational aspects of the Hartree–Fock approximation, we briefly describe another formulation of the response equations for the shielding. From eq 154, we may write the Hartree–Fock shieldings in the following manner

$$\boldsymbol{\sigma}_K = \mathbf{1} + \langle \mathrm{HF}|\hat{h}^{(11)}|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\hat{\kappa}^{(10)}, \hat{h}^{(01)}]|\mathrm{HF}\rangle \quad (168)$$

where we use the notation

$$\hat{h}^{(11)} = \frac{\partial^2 \hat{h}}{\partial\mathbf{B}\,\partial\mathbf{M}_K} = \sum_{pq} h_{pq}^{(11)} E_{pq} \quad (169)$$

$$\hat{h}^{(01)} = \frac{\partial \hat{h}}{\partial\mathbf{M}_K} = \sum_{pq} h_{pq}^{(01)} E_{pq} \quad (170)$$

$$\hat{\kappa}^{(10)} = \frac{\partial\hat{\kappa}}{\partial\mathbf{B}} \quad (171)$$

Expanding eq 168, we obtain

$$\boldsymbol{\sigma}_K = \mathbf{1} + \sum_{pq}\langle \mathrm{HF}|E_{pq}|\mathrm{HF}\rangle\, h_{pq}^{(11)} + \sum_{pq}\langle \mathrm{HF}|[\hat{\kappa}^{(10)}, E_{pq}]|\mathrm{HF}\rangle\, h_{pq}^{(01)} \quad (172)$$

We now introduce the one-electron density matrixes

$$D_{pq}(\kappa) = \langle \mathrm{HF}|\exp(\hat{\kappa})\, E_{pq}\, \exp(-\hat{\kappa})|\mathrm{HF}\rangle \quad (173)$$

whose lowest-order derivatives are given as

$$D_{pq}^{(00)} = \langle \mathrm{HF}|E_{pq}|\mathrm{HF}\rangle \quad (174)$$

$$D_{pq}^{(10)} = \langle \mathrm{HF}|[\hat{\kappa}^{(10)}, E_{pq}]|\mathrm{HF}\rangle \quad (175)$$

We may now write the shieldings as

$$\boldsymbol{\sigma}_K = \mathbf{1} + \sum_{pq} D_{pq}^{(00)}\, h_{pq}^{(11)} + \sum_{pq} D_{pq}^{(10)}\, h_{pq}^{(01)} \quad (176)$$

The shielding is thus seen to contain contributions from the one-electron density matrix only, although it should be noted that there are two-electron contributions in the calculation of the first derivatives of the densities.

4. The Hartree–Fock Approximation—Computational Aspects

The first important aspect of numerical implementation at the Hartree−Fock level is the handling of the two-electron integrals. In the direct Hartree−Fock method, these integrals are recomputed when needed, thus never stored on disk. In this manner, a large number of basis functions can be handled, the limiting factor being the available memory and computer time. In practice, basis sets of the order of 1500 orbitals can now be used and Hartree−Fock shielding constants have been computed for numerous large molecules such as Al_4Cp_4 ($C_{20}H_{20}Al_4$, Cp = cyclopentadienyl),[76] magnesium and zinc metalloporphyrins,[77] C_{70},[78] He@C_{180},[79] and taxol $C_{47}H_{51}NO_{14}$.[80] In many cases, it may be easier or faster to perform the calculations on a cluster of workstations than on a supercomputer, provided an efficient parallel version of the code is available. For a molecule including 60 atoms, direct Hartree−Fock calculations do not take more than 5−15 h on a small cluster of workstations (depending on the basis).[81]

All methods developed to deal with the problem of gauge dependence of magnetic properties (see section V.B) were applied first at the SCF level. The first method widely used to compute shielding constants was IGLO SCF and the first review of the results obtained at this level was published by Kutzelnigg et al. in 1990.[48] The IGLO−SCF results were sufficiently accurate to demonstrate the potential of ab initio calculations for NMR parameters.

We shall not discuss in detail shielding calculations at the SCF level. These can presently be performed routinely within a variety of programs, such as e.g., Texas/GIAO (Texas95),[81] ACES II,[82] Gaussian 94,[83] Turbomole (TurboNMR),[84,78] RPAC,[85] IGLO (and Direct IGLO, DIGLO),[86,87] and Dalton.[88] The programs differ primarily in the methods they include for the post Hartree−Fock calculations, offering specific options to compute correlation effects. They differ also in various aspects not related to shielding calculations. For example, the use of effective core potentials, optimization of the molecular geometry, or calculations of other properties, may be required and determine the choice of code.

At the Hartree−Fock level, the calculation of indirect spin−spin couplings is much less common than the calculation of shieldings. The Hartree−Fock spin−spin couplings can be useless (e.g., wrong by orders of magnitude) and although the results of a specific calculation may agree with experiment, the Hartree−Fock values are in general unreliable due to the triplet nature of perturbing operators, see section III.C. For a discussion of SCF results, we refer to the early reviews of the calculations of spin−spin coupling constants.[89,90] As a rule of thumb, only molecules without multiple bonds can be studied at the SCF level and the calculation of couplings to nuclei with lone pairs should be avoided.

B. The FCI Approximation

Having considered the SCF wave function, which represents the best one-determinant approximation to the wave function, we now describe the best approximation that is possible within the determinant representation of electronic wave functions in Fock space: the full CI (FCI) wave function.

1. The FCI Wave Function and Energy

In the FCI approximation, the wave function is written as a linear combination of the full set of Slater determinants that may be constructed from a given set of orthonormal molecular orbitals. Since the full set of determinants is used, there is no need to consider orbital rotations. The ansatz for the FCI wave function is therefore simply

$$|\mathbf{C}\rangle = \sum_{\mu} C_{\mu}|\mu\rangle \tag{177}$$

The optimized FCI wave function

$$|\mathrm{FCI}\rangle = \sum_{\mu} C_{\mu}^{(0)}|\mu\rangle \tag{178}$$

satisfies the variational condition

$$E_{\mathrm{FCI}}^{(0)} = \frac{\langle \mathrm{FCI}|\hat{H}|\mathrm{FCI}\rangle}{\langle \mathrm{FCI}|\mathrm{FCI}\rangle} = \min_{\mathbf{C}} \frac{\langle \mathbf{C}|\hat{H}|\mathbf{C}\rangle}{\langle \mathbf{C}|\mathbf{C}\rangle} \tag{179}$$

Its simplicity notwithstanding, the usefulness of the FCI approximation is severely limited by the factorial dependence of the number of Slater determinants on the number of spin−orbitals. In a given spin−orbital basis, the number of N-electron Slater determinants that may be constructed from a set of M spin−orbitals is given by

$$N_{det} = \binom{M}{N} = \frac{M!}{N!(M-N)!} \tag{180}$$

making the FCI approximation intractable for all but the smallest systems. Currently, the only systems that can be treated to high accuracy by the FCI method are systems containing two to four electrons. FCI calculations on larger systems (such as the water molecule) may still be useful, but primarily as a benchmark for other, less flexible treatments of many-electron systems in the same orbital basis.

2. FCI Second-Order Properties

The second-order expressions for the FCI properties are given as

$$E_{\mathrm{FCI}}^{(0)} = \langle \mathrm{FCI}|\hat{H}^{(0)}|\mathrm{FCI}\rangle \tag{181}$$

$$E_{\mathrm{FCI}}^{(1)} = \langle \mathrm{FCI}|\hat{H}^{(1)}|\mathrm{FCI}\rangle \tag{182}$$

$$E_{\mathrm{FCI}}^{(2)} = \langle \mathrm{FCI}|\hat{H}^{(2)}|\mathrm{FCI}\rangle + 2\langle \mathrm{FCI}|\hat{H}^{(1)}|C^{(1)}\rangle - 2E_{\mathrm{FCI}}^{(1)}\langle \mathrm{FCI}|C^{(1)}\rangle \tag{183}$$

where we have assumed that the FCI wave function is normalized

$$\langle \mathrm{FCI}|\mathrm{FCI}\rangle = 1 \tag{184}$$

As expected, whereas the zeroth- and first-order energies are expectation values of the Hamiltonian operator (as for the Hartree−Fock wave function), in the second-order energy, there are contributions from the first-order perturbed FCI wave function.

To calculate the FCI energy to second order, we must satisfy the FCI variational conditions to first order. The zeroth-order conditions are given by

$$\langle \mu|\hat{H}^{(0)}|\mathrm{FCI}\rangle = E^{(0)}_{\mathrm{FCI}} C^{(0)}_{\mu} \tag{185}$$

which are simply the usual eigenvalue conditions for the FCI coefficients. The first-order FCI conditions may be written in the form

$$\sum_{\nu} (\langle \mu|\hat{H}^{(0)}|\nu\rangle - \delta_{\mu\nu} E^{(0)}_{\mathrm{FCI}}) C^{(1)}_{\nu} = -\langle \mu|\hat{H}^{(1)}|\mathrm{FCI}\rangle + E^{(1)}_{\mathrm{FCI}} C^{(0)}_{\mu} \tag{186}$$

For a single perturbation, the solution of the FCI first-order response equations is as expensive as the optimization of the FCI wave function itself and does not involve much extra programming.

3. FCI Properties in the Diagonal Hamiltonian Representation

The expressions for the second- and higher-order FCI energies are simplified considerably in the diagonal representation of the Hamiltonian. In this representation, we do not simply require the fulfillment of the zeroth-order conditions eq 185 but in addition we require the excited states to satisfy the conditions

$$\langle K|\hat{H}^{(0)}|L\rangle = \delta_{KL} E^{(0)}_{K} \tag{187}$$

In this representation of the Hamiltonian, the zeroth-order FCI conditions eq 185 take the simpler form

$$\langle K|\hat{H}^{(0)}|\mathrm{FCI}\rangle = 0 \tag{188}$$

and the first-order conditions eq 186 may be written as

$$(E^{(0)}_{K} - E^{(0)}_{\mathrm{FCI}}) C^{(1)}_{K} = -\langle K|\hat{H}^{(1)}|\mathrm{FCI}\rangle \tag{189}$$

where $E^{(0)}_{K}$ are the energies of the excited states. We recognize that the electronic gradient and Hessian of eqs 67−68 are given by

$$\mathbf{F}_{K}(\mathbf{C}) = \frac{\partial E(\mathbf{C})}{\partial C_{K}} = 2\langle K|\hat{H}^{(1)}|\mathrm{FCI}\rangle \tag{190}$$

$$\mathbf{G}_{KL}(\mathbf{C}) = \frac{\partial^2 E(\mathbf{C})}{\partial C_{K}\, \partial C_{L}} = 2[\langle K|\hat{H}^{(0)}|L\rangle - E^{(0)}_{\mathrm{FCI}} \langle K|L\rangle] = 2(E^{(0)}_{K} - E^{(0)}_{\mathrm{FCI}})\, \delta_{KL} \tag{191}$$

Inserting the solution 189 in the expression for the second-order FCI energy eq 183, we recover the standard expression of second-order perturbation theory

$$E^{(2)}_{\mathrm{FCI}} = \langle \mathrm{FCI}|\hat{H}^{(2)}|\mathrm{FCI}\rangle - 2\sum_{K} \frac{\langle \mathrm{FCI}|\hat{H}^{(1)}|K\rangle\langle K|\hat{H}^{(1)}|\mathrm{FCI}\rangle}{E^{(0)}_{K} - E^{(0)}_{\mathrm{FCI}}} \tag{192}$$

illustrating the close relationship that exists between standard second-order perturbation theory and the variational perturbation theory discussed here. Of course, since this expression requires full diagonalization of the Hamiltonian matrix eq 187, it is not useful for practical calculations.

FCI calculations of NMR properties are scarce. For both the shielding and spin−spin coupling constant, there are FCI results for the hydrogen molecule (see below) in a basis sufficiently large to describe well the NMR properties. For larger molecules, it is impossible to perform FCI calculations with sufficiently large basis sets. We discuss a benchmark FCI calculation for BH in section VIII.C.

C. The MCSCF Approximation

Having considered the Hartree−Fock and FCI models, which represent the best single- and full-configurational models in Fock space, we now turn our attention to the MCSCF model, in which a (small) subset of the full set of determinants is included in the wave function, which is variationally optimized with respect to both MO's and the CI coefficients.

1. The MCSCF Wave Function and Energy

In multiconfigurational self-consistent (MCSCF) theory, the wave function is written as a linear combination of determinants or configuration state functions, and the molecular orbitals and the expansion coefficients of the configuration expansion are simultaneously optimized according to the variational principle. Thus, the MCSCF wave function may be written in the form

$$|\kappa, \mathbf{C}\rangle = \exp(-\hat{\kappa}) \sum_{\mu} C_{\mu}|\mu\rangle \tag{193}$$

where C_{μ} are the configuration expansion coefficients (normalized to unity) and the operator exp $(-\hat{\kappa})$ carries out unitary transformations among the spin−orbitals in the same way as for Hartree−Fock wave functions in eq 139 (the set of orbital rotations which yield nonzero contributions depends on the choice of configurations, see below). The ground-state MCSCF wave function

$$|\mathrm{MC}\rangle = \sum_{\mu} C^{(0)}_{\mu}|\mu\rangle \tag{194}$$

satisfies the condition

$$E^{(0)}_{\mathrm{MC}} = \frac{\langle \mathrm{MC}|\hat{H}|\mathrm{MC}\rangle}{\langle \mathrm{MC}|\mathrm{MC}\rangle} = \min_{\kappa,\mathbf{C}} \frac{\langle \kappa,\mathbf{C}|\hat{H}|\kappa,\mathbf{C}\rangle}{\langle \kappa,\mathbf{C}|\kappa,\mathbf{C}\rangle} \tag{195}$$

with respect to the MO and CI coefficients.

The MCSCF model allows for a highly flexible description of the electronic system, where both the one-electron functions (the orbitals) and the N-electron expansion (the CI coefficients) may adapt to the physical situation. In most situations, MCSCF theory is best regarded as a generalization of Hartree–Fock theory to systems that are not well described by a single configuration. For example, in calculations of spin–spin coupling constants in molecules with double bonds, it may be sufficient to include two configurations[91]

$$|\mathrm{MC}\rangle = C_1|\sigma^{\mathrm{core}}(\pi)^2\rangle + C_2|\sigma^{\mathrm{core}}(\pi^*)^2\rangle \quad (196)$$

where the variational principle is invoked to optimize the configuration coefficients C_1 and C_2 as well as the molecular orbitals.

The selection of MCSCF configurations is usually not carried out by inspection of the individual configurations. Instead, whole classes of configurations are simultaneously selected following some general criterion. One particularly successful approach has been to partition the orbital space into three subspaces, containing the inactive, active, and secondary (virtual) orbitals. The inactive orbitals are doubly occupied in all configurations and the virtual orbitals are always unoccupied. The active orbitals, in contrast, have variable occupancies of zero, one, or two in the individual configurations. The MCSCF expansion is then generated by distributing the active electrons among the active orbitals in all possible ways. In the final, optimized state, the active orbitals have nonintegral occupancies between zero and two, obtained by diagonalizing the one-electron density matrix. This method is known as the complete active space (CAS) SCF method.[92] The CAS wave function may be regarded as a FCI wave function in a limited but variationally optimized active orbital space.

Another MCSCF model is based on a further partitioning of the subspace of active orbitals. In the restricted active space (RAS) SCF method, the active orbitals are partitioned into three subspaces.[93] In the first subspace, usually called RAS1, the number of electron holes is restricted; in the second subspace, called RAS2, all occupations are allowed; in the third subspace, RAS3, the number of electrons is restricted. RASSCF function may provide a good approximation to the corresponding CASSCF function using a much smaller set of configurations. More frequently, it is applied to provide a coarse description of dynamical correlation effects by including an extended set of active orbitals in the RAS3 subspace.

The MCSCF wave function is particularly well suited to studies of systems involving degenerate or nearly degenerate configurations, where static correlation is important. Although there are approaches for including dynamic correlation in MCSCF calculations,[94–97] it has proved difficult to generalize MCSCF theory in such a way that dynamical correlation effects can be calculated accurately, and these methods have not yet been applied to study NMR parameters.

2. MCSCF Second-Order Properties

Formally, the MCSCF model eq 193 may be regarded as a combination of the Hartree–Fock model eq 139 and the FCI model eq 177, since it contains the orbital–rotation parameters of the Hartree–Fock model as well as the configuration–interaction parameters of the FCI model. In the expressions for the MCSCF molecular properties,[15,69] we therefore recognize many of the elements present in the expressions for the Hartree–Fock and FCI properties:

$$E^{(0)}_{\mathrm{MC}} = \langle \mathrm{MC}|\hat{H}^{(0)}|\mathrm{MC}\rangle \quad (197)$$

$$E^{(1)}_{\mathrm{MC}} = \langle \mathrm{MC}|\hat{H}^{(1)}|\mathrm{MC}\rangle \quad (198)$$

$$E^{(2)}_{\mathrm{MC}} = \langle \mathrm{MC}|\hat{H}^{(2)}|\mathrm{MC}\rangle + \langle \mathrm{MC}|[\hat{\kappa}^{(1)},\hat{H}^{(1)}]|\mathrm{MC}\rangle + 2\langle \mathrm{MC}|\hat{H}^{(1)}|C^{(1)}\rangle - 2E^{(1)}_{\mathrm{MC}}\langle \mathrm{MC}|C^{(1)}\rangle \quad (199)$$

where we have assumed that the wave function is normalized

$$\langle \mathrm{MC}|\mathrm{MC}\rangle = 1 \quad (200)$$

The MCSCF second-order properties contain contributions from the first-order responses of the orbital–rotation parameters and of the configuration–interaction coefficients.

The zeroth-order MCSCF variational conditions are given by

$$\langle \mathrm{MC}|[\hat{\kappa}_i,\hat{H}^{(0)}]|\mathrm{MC}\rangle = 0 \quad (201)$$

$$\langle \mu|\hat{H}^{(0)}|\mathrm{MC}\rangle = E^{(0)}_{\mathrm{MC}}\, C^{(0)}_{\mu} \quad (202)$$

The MCSCF variational conditions on the orbital-rotation parameters are similar to those for the Hartree–Fock wave function eq 155, and the conditions on the configuration coefficients are the same as for the FCI wave function eq 185. The simultaneous fulfillment of both requirements makes the MCSCF wave function optimal with respect to the orbitals as well as the CI coefficients. In eq 201, we need to include only those orbital–rotation operators that mix orbitals belonging to different orbital spaces—for example, for CASSCF wave functions, the inactive–active, inactive–secondary, and active–secondary rotation operators.[35]

Turning to the first-order MCSCF conditions, we find that these may be written in the form of a linear set of equations:

$$\sum_j \langle \mathrm{MC}|[\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]]|\mathrm{MC}\rangle\, \kappa^{(1)}_j - 2\sum_\nu \langle \mathrm{MC}|[\hat{\kappa}_i, \hat{H}^{(0)}]|\nu\rangle\, C^{(1)}_\nu = -\langle \mathrm{MC}|[\hat{\kappa}_i, \hat{H}^{(1)}]|\mathrm{MC}\rangle \quad (203)$$

$$-2\sum_j \langle \mu|[\hat{\kappa}_j, \hat{H}^{(0)}]|\mathrm{MC}\rangle\, \kappa^{(1)}_j + 2\sum_\nu (\langle \mu|\hat{H}^{(0)}|\nu\rangle - \delta_{\mu\nu}E^{(0)}_{\mathrm{MC}})\, C^{(1)}_\nu = -2\langle \mu|\hat{H}^{(1)}|\mathrm{MC}\rangle + 2E^{(1)}_{\mathrm{MC}}\, C^{(0)}_\mu \quad (204)$$

In the (hypothetical) absence of couplings between the orbital–rotation parameters and the CI parameters, these equations reduce to the Hartree–Fock conditions eq 156 for the orbital rotations and the

FCI conditions eq 186 for the CI coefficients. In contrast to Hartree–Fock theory, the set of parameters in MCSCF theory is usually large—for example, as many as 10^6 determinants may be included. As discussed in section IV.B.4, we cannot invert the Hessian matrix explicitly, and we must instead apply other numerical techniques to solve the MCSCF response equations.

The two approaches developed for the calculation of shielding constants at the MCSCF level are based on the GIAO[98] and IGLO[99] approximations. When the reference MCSCF function is identical, the results obtained in the MCSCF GIAO and IGLO approaches are similar, just as for the GIAO and IGLO Hartree–Fock wave functions. There are also many MCSCF results for spin–spin coupling constants, some of which are discussed in section IX.

D. The Coupled-Cluster Approximation

None of the approximations considered so far (SCF, MCSCF, and FCI) are suitable for accurate calculations on medium and large molecular systems. For such systems, models are needed that take into account the effects of dynamical correlation and that at the same time may be extended to systems containing hundreds of electrons. We discuss here the coupled-cluster approximation and in the next section Møller–Plesset theory, concentrating again on the aspects that are related to the study of NMR properties.

1. The Coupled-Cluster Wave Function and Energy

In coupled-cluster theory, the wave function is written in the form

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle \tag{205}$$

where the cluster operator is given by

$$\hat{T} = \sum_{\mu} t_\mu \hat{\tau}_\mu \tag{206}$$

The $\hat{\tau}_\mu$ constitute a set of commuting excitation operators

$$[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0 \tag{207}$$

which, when working on the Hartree–Fock reference state, generate excited electronic states

$$\hat{\tau}_\mu|\mathrm{HF}\rangle = |\mu\rangle \tag{208}$$

In practice, the cluster operator is partitioned as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + ... \tag{209}$$

where $\hat{T}_1$ produces single excitations, $\hat{T}_2$ double excitations, and so on. The coupled-cluster singles and doubles (CCSD) model, for example, is obtained by truncating the expansion after the doubles excitations

$$|\mathrm{CCSD}\rangle = \exp(\hat{T}_1 + \hat{T}_2)|\mathrm{HF}\rangle \tag{210}$$

For closed-shell systems, we may write the CCSD cluster operators in the form

$$\hat{T}_1 = \sum_{ai} t_i^a E_{ai} \tag{211}$$

$$\hat{T}_2 = {}^1/_2 \sum_{abij} t_{ij}^{ab} E_{ai} E_{bj} \tag{212}$$

where E_{ai} are the excitation operators of eq 85, with a and b denoting unoccupied orbitals, and i and j occupied orbitals. In a similar fashion we may truncate the cluster operator after the triples excitations, giving the coupled-cluster singles, doubles, and triples (CCSDT) model and so on.

The coupled-cluster wave function is not optimized variationally. Rather, the electronic state is optimized by rewriting the Schrödinger equation in the form

$$\exp(-\hat{T})\,\hat{H}\,\exp(\hat{T})|\mathrm{HF}\rangle = E_{\mathrm{CC}}|\mathrm{HF}\rangle \tag{213}$$

which is then projected from the left by the manifold

$$\langle\mu| = \langle\mathrm{HF}|\hat{\tau}_\mu^\dagger \tag{214}$$

to yield the nonlinear coupled-cluster equations

$$\langle\mu|\exp(-\hat{T})\,\hat{H}\,\exp(\hat{T})|\mathrm{HF}\rangle = 0 \tag{215}$$

Projecting against the Hartree–Fock state, we obtain the coupled-cluster energy

$$E_{\mathrm{CC}} = \langle\mathrm{HF}|\exp(-\hat{T})\,\hat{H}\,\exp(\hat{T})|\mathrm{HF}\rangle \tag{216}$$

For systems dominated by the Hartree–Fock configuration, the coupled-cluster hierarchy of energies (CCSD, CCSDT, and so on) converges quite rapidly to the true electronic energy. However, the high cost of the calculations makes the coupled-cluster hierarchy applicable only at low levels. For instance, the optimization of the CCSD energy scales as n^6 and the CCSDT energy as n^8, where n is the number of orbitals.

Since, for many applications, the CCSD level is not sufficiently accurate for quantitative investigations and the CCSDT level is too expensive, levels intermediate between CCSD and CCSDT in cost and accuracy have been developed. Among these levels, the CCSD(T) model, in which the effects of the triples are taken into account in a perturbative manner and added to the CCSD energy, has been particularly successful (see for instance ref 100).

The coupled-cluster model, as currently developed, is not sufficiently flexible to describe electronic structures characterized by large static correlation effects. Typically, therefore, the CC wave function cannot describe bond breakings and molecular dissociations, where the Hartree–Fock wave function no longer provides a useful zeroth-order approximation. For the calculation of NMR parameters, this restriction is not too severe since most ground-state equilibrium systems are dominated by a single electronic configuration.

2. Coupled-Cluster Lagrangian

To evaluate molecular properties from coupled-cluster wave functions, we apply the general theory of section IV and begin by preparing a variational

Lagrangian for the coupled-cluster energy.[17,101,102] In coupled-cluster theory, the energy is calculated from eq 216 subject to the constraints eq 215 as well as to the Brillouin conditions eq 155, where only the operators $\hat{\kappa}_i$ mixing the occupied and unoccupied orbitals have to be considered. Introducing one Lagrangian multiplier for each constraint, we obtain

$$L_{\mathrm{CC}} = (\mathrm{HF}(t)|\hat{H}_\kappa|\mathrm{HF}(t)) + \sum_\mu \bar{t}_\mu (\mu(t)|\hat{H}_\kappa|\mathrm{HF}(t)) + \sum_i \bar{\kappa}_i \langle \mathrm{HF}|[\hat{\kappa}_i, \hat{H}_\kappa]|\mathrm{HF}\rangle \quad (217)$$

For a compact and transparent representation of the Lagrangian, we have here introduced the orbital-rotated Hamiltonian operator

$$\hat{H}_\kappa = \exp(\hat{\kappa})\, \hat{H} \exp(-\hat{\kappa}) \quad (218)$$

to allow for rotations among the orbitals and the short-hand notation

$$|A(t)) = \exp(\hat{T})\, |A\rangle \quad (219)$$

$$(A(t)| = \langle A| \exp(-\hat{T}) \quad (220)$$

for electronic states operated on by the exponential cluster operator $\exp(\hat{T})$. A still more compact representation is obtained by introducing the notation

$$\bar{\hat{\kappa}} = \sum_i \bar{\kappa}_i \hat{\kappa}_i \quad (221)$$

and the state

$$(\Lambda(t, \bar{t})| = (\mathrm{HF}(t)| + \sum_\mu \bar{t}_\mu (\mu(t)| \quad (222)$$

We may now write the Lagrangian in the form

$$L_{\mathrm{CC}}(t_\mu, \bar{t}_\mu, \kappa_i, \bar{\kappa}_i) = (\Lambda(t, \bar{t})|\hat{H}_\kappa|\mathrm{HF}(t)) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}, \hat{H}]|\mathrm{HF}\rangle \quad (223)$$

where we have indicated the dependence of the Lagrangian on the cluster amplitudes t_μ, the cluster multipliers $\bar{t}_\mu$, the orbital–rotation parameters κ_i, and the orbital–rotation multipliers $\bar{\kappa}_i$. To determine the coupled-cluster variational Lagrangian, we follow the standard procedure of section IV, making the Lagrangian stable with respect to variations in the full set of variables t_μ, $\bar{t}_\mu$, κ_i, and $\bar{\kappa}_i$. The corresponding conditions are given in the next section.

In the Lagrangian eq 223, we have made a rather general ansatz, making the energy dependent on the orbitals as well as on the cluster amplitudes. For many purposes, however, we may neglect the orbital rotations, describing the perturbation entirely in terms of the cluster amplitudes. Thus, for spin–spin coupling constants, we may keep the orbitals fixed and equal to those obtained by optimizing the Hartree–Fock wave function in the absence of the perturbations. In this case, the CC Lagrangian is written simply as

$$L_{\mathrm{CC}}(t_\mu, \bar{t}_\mu) = (\Lambda(t, \bar{t})|\hat{H}|\mathrm{HF}(t)) \quad (224)$$

In the absence of the orbital–rotation parameters, the orbital relaxation effects are approximately described in terms of the single-excitation amplitudes t_i^a. We also note that to describe the modification of the wave function in the presence of spin perturbations, excitation operators more general than those present in eqs 211 and 212 are needed, containing triplet excitation operators as well.

3. Coupled-Cluster Second-Order Properties

Having set up the Lagrangian for the coupled-cluster energy, we may proceed to calculate the properties as for any other variational energy function. We shall use for the unperturbed states the notation

$$|A) = |A(t^{(0)})) = \exp(\hat{T}^{(0)})|A\rangle \quad (225)$$

$$(A| = (A(t^{(0)})| = \langle A| \exp(-\hat{T}^{(0)}) \quad (226)$$

To second order in the perturbation, we obtain

$$L_{\mathrm{CC}}^{(0)} = (\Lambda|\hat{H}^{(0)}|\mathrm{HF}) = (\mathrm{HF}|\hat{H}^{(0)}|\mathrm{HF}) \quad (227)$$

$$L_{\mathrm{CC}}^{(1)} = (\Lambda|\hat{H}^{(1)}|\mathrm{HF}) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, \hat{H}^{(1)}]|\mathrm{HF}\rangle \quad (228)$$

$$L_{\mathrm{CC}}^{(2)} = (\Lambda|\hat{J}^{(2)}|\mathrm{HF}) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, \hat{J}^{(2)}]|\mathrm{HF}\rangle + 2\,(\Lambda|[\hat{H}^{(1)}, \hat{T}^{(1)}]|\mathrm{HF}) + (\Lambda|[[\hat{H}^{(0)}, \hat{T}^{(1)}], \hat{T}^{(1)}]|\mathrm{HF}) \quad (229)$$

where the derivatives of the Hamiltonian are given by

$$\hat{H}_\kappa^{(0)} = \hat{H}^{(0)} \quad (230)$$

$$\hat{H}_\kappa^{(1)} = \hat{H}^{(1)} + [\hat{\kappa}^{(1)}, \hat{H}^{(0)}] \quad (231)$$

$$\hat{H}_\kappa^{(2)} = \hat{H}^{(2)} + [\hat{\kappa}^{(2)}, \hat{H}^{(0)}] + 2\,[\hat{\kappa}^{(1)}, \hat{H}^{(1)}] + [\hat{\kappa}^{(1)}, [\hat{\kappa}^{(1)}, \hat{H}^{(0)}]] = \hat{J}^{(2)} + [\hat{\kappa}^{(2)}, \hat{H}^{(0)}] \quad (232)$$

In the absence of orbital-rotation parameters, the terms involving the zeroth-order orbital–rotation multipliers $\bar{\kappa}_i^{(0)}$ and the perturbed orbital–rotation parameters $\kappa_i^{(1)}$ and $\kappa_i^{(2)}$ vanish, making the properties particularly simple:

$$L_{\mathrm{CC}}^{(0)} = (\Lambda|\hat{H}^{(0)}|\mathrm{HF}) \quad (233)$$

$$L_{\mathrm{CC}}^{(1)} = (\Lambda|\hat{H}^{(1)}|\mathrm{HF}) \quad (234)$$

$$L_{\mathrm{CC}}^{(2)} = (\Lambda|\hat{H}^{(2)}|\mathrm{HF}) + 2\,(\Lambda|[\hat{H}^{(1)}, \hat{T}^{(1)}]|\mathrm{HF}) + (\Lambda|[[\hat{H}^{(0)}, \hat{T}^{(1)}], \hat{T}^{(1)}]|\mathrm{HF}) \quad (235)$$

These expressions for $L_{\mathrm{CC}}^{(n)}$ and $L_{\mathrm{CC}}^{(n)}$ agree with the $2n + 1$ rule for the primary variables and with the $2n + 2$ rule for the multipliers. For example, for the calculation of the second-order energy $L_{\mathrm{CC}}^{(2)}$, we need only calculate $\bar{T}$ to first order in the perturbation and the corresponding multipliers $\bar{t}_\mu$ to zero order. Note that, in the expression for $L_{\mathrm{CC}}^{(2)}$, the operator $\hat{\mathcal{J}}^{(2)}$ rather than $\hat{H}_{\kappa}^{(2)}$ appears, the only difference between these operators being that the term containing $\hat{\kappa}^{(2)}$ is absent from $\hat{\mathcal{J}}^{(2)}$, in agreement with the $2n + 1$ rule.

The expressions given for the coupled-cluster second derivatives above are quadratic in the perturbed wave function and correspond to for example eq 81 for the spin−spin coupling constants. As such, they are not suitable for the calculation of shielding constants, since they would require the solution of response equations for the nuclear magnetic moments as well as for the external magnetic field. We therefore here give also the expression that is linear in the perturbed wave function and which corresponds to the general expressions eq 79 for the shieldings and eq 80 for the spin−spin couplings

$$L_{\mathrm{CC}}^{(2)} = (\Lambda|\hat{H}^{(2)}|\mathrm{HF}) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, \hat{H}^{(2)}]|\mathrm{HF}\rangle + (\Lambda|[\hat{H}^{(1)}, \hat{T}^{(1)}]|\mathrm{HF}) + (\Lambda|[\hat{\kappa}^{(1)}, \hat{H}^{(1)}]|\mathrm{HF}) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, [\hat{\kappa}^{(1)}, \hat{H}^{(1)}]]|\mathrm{HF}\rangle + (\Lambda^{(1)}|\hat{H}^{(1)}|\mathrm{HF}) + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(1)}, \hat{H}^{(1)}]|\mathrm{HF}\rangle \quad (236)$$

$$L_{\mathrm{CC}}^{(2)} = (\Lambda|\hat{H}^{(2)}|\mathrm{HF}) + (\Lambda|[\hat{H}^{(1)}, \hat{T}^{(1)}]|\mathrm{HF}) + (\Lambda^{(1)}|\hat{H}^{(1)}|\mathrm{HF}) \quad (237)$$

In these expressions, we have used the short-hand notation

$$(\Lambda^{(1)}| = \sum_{\mu} \bar{t}^{(1)}\, (\mu| \quad (238)$$

for the first-order multiplier state. By using these expressions, which obey the $2n + 1$ rather than $2n + 2$ rule for the multipliers, the coupled-cluster shielding constants may be calculated by solving a total of six equations for the amplitudes and their multipliers and, if required, a total of six equations for the orbital−rotation parameters and their multipliers. Since the perturbed parameters occur only linearly, there is no need to calculate the wave function perturbed with respect to the nuclear magnetic moments.

Having considered the coupled-cluster energy to second order, let us now consider the response equations required for their construction. The zeroth-order equations are given by

$$\langle \mathrm{HF}|[\hat{\kappa}_i^{(0)}, \hat{H}^{(0)}]|\mathrm{HF}\rangle = 0 \quad (239)$$

$$(\mu|\hat{H}^{(0)}|\mathrm{HF}) = 0 \quad (240)$$

$$\sum_{\nu} \bar{t}_{\nu}^{(0)}\, (\nu|[\hat{H}^{(0)}, \hat{\tau}_{\mu}]|\mathrm{HF}) = -\,(\mathrm{HF}|[\hat{H}^{(0)}, \hat{\tau}_{\mu}]|\mathrm{HF}) \quad (241)$$

$$\sum_{j} \langle \mathrm{HF}|[\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]]|\mathrm{HF}\rangle\, \bar{\kappa}_j^{(0)} = -\,(\Lambda|[\hat{\kappa}_i, \hat{H}^{(0)}]|\mathrm{HF}) \quad (242)$$

The zeroth-order equations eq 239 are just the Hartree−Fock Brillouin conditions eq 155; likewise, the conditions eq 240 are just the usual coupled-cluster amplitudes equations eq 215. To satisfy these conditions, we must solve sets of nonlinear equations that scale as n^4 for the orbitals and n^6 for the amplitudes in the CCSD approximation. To determine the Lagrange multipliers from eqs 241 and 242, we need to solve two sets of linear equations, each scaling as the corresponding nonlinear equations. Except for the different right-hand sides, the zeroth-order equations for the orbital−rotation multipliers have the same structure as the first-order equations for the perturbed Hartree−Fock equations eq 156. Note that the zeroth-order equations eqs 239−242 must be solved in the order written: (1) for the orbitals, (2) for the amplitudes, (3) for the amplitude multipliers, (4) for the orbital multipliers. The last equations are omitted if the Lagrangian L_{CC} rather than L_{CC} is used.

Having solved the zeroth-order equations, we must determine the first-order responses of the amplitudes and the orbitals (if included in the energy functional) in order to calculate the energy to second order. For the primary variables, the first-order equations are given as

$$\sum_{j} \langle \mathrm{HF}|[\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]]|\mathrm{HF}\rangle\, \kappa_j^{(1)} = -\,\langle \mathrm{HF}|[\hat{\kappa}_i, \hat{H}^{(1)}]|\mathrm{HF}\rangle \quad (243)$$

$$\sum_{\nu} (\mu|[\hat{H}^{(0)}, \hat{\tau}_{\nu}]|\mathrm{HF}) t_{\nu}^{(1)} = -\,(\mu|\hat{H}_{\kappa}^{(1)}|\mathrm{HF}) \quad (244)$$

and for their multipliers the equations are

$$\sum_{\nu} \bar{t}_{\nu}^{(1)}\, (\nu|[\hat{\tau}_{\mu}, \hat{H}^{(0)}]|\mathrm{HF}) = (\Lambda|[\hat{H}_{\kappa}^{(1)}, \hat{\tau}_{\mu}]|\mathrm{HF}) + (\Lambda|[[\hat{\tau}_{\mu}, \hat{H}^{(0)}], \hat{T}^{(1)}]|\mathrm{HF}) \quad (245)$$

$$\sum_{j} \bar{\kappa}_j^{(1)}\, \langle \mathrm{HF}|[\hat{\kappa}_j, [\hat{\kappa}_i, \hat{H}^{(0)}]]|\mathrm{HF}\rangle = -\,(\Lambda|[\hat{\kappa}_i, \hat{H}^{(1)}]|\mathrm{HF}) - (\Lambda|[\hat{\kappa}_i, \hat{\kappa}^{(1)}, \hat{H}^{(0)}]|\mathrm{HF}) - (\Lambda|[[\hat{\kappa}_i, \hat{H}^{(0)}], \hat{T}^{(1)}]|\mathrm{HF}) - \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, [\hat{\kappa}_i, \hat{H}^{(1)}]]|\mathrm{HF}\rangle - \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, [\hat{\kappa}_i, \hat{\kappa}^{(1)}, \hat{H}^{(0)}]]|\mathrm{HF}\rangle \quad (246)$$

In eq 246, we have introduced the symmetrized double commutator

$$[\hat{A}, \hat{B}, \hat{H}] = {}^{1}/_{2}[\hat{A}, [\hat{B}, \hat{H}]] + {}^{1}/_{2}[\hat{B}, [\hat{A}, \hat{H}]] \quad (247)$$

The orbital equations eq 243 are simply the perturbed Hartree−Fock equations eq 156, whereas the first-order amplitude equations eq 244 are similar to the zeroth-order amplitude multiplier equations eq 241. Note that the matrix appearing in eqs 241, 244, and 245

$$J_{\mu\nu} = (\mu|[\hat{H}^{(0)}, \hat{\tau}_{\nu}]|\mathrm{HF}) \quad (248)$$

(known as the coupled-cluster Jacobian) is nonsymmetric, unlike the symmetric Hartree−Fock Hessian appearing in the linear equations for the orbital−rotation parameters and their multipliers eqs 242, 243, and 246.

4. The Coupled-Cluster Approximation—Computational Aspects

The expressions given in the previous section correspond to a strict implementation within the standard hierarchy of coupled-cluster approximations. In studies of NMR parameters, there are several approximations and models in use that are best considered variations on the basic coupled-cluster model described above. Moreover, different formulations are used for the shielding and spin–spin coupling constants. For instance, in the studies of the shielding constants, the density matrix formulation is often used, thus the shielding is finally given by an expression corresponding to eq 176, but involving correlated density matrixes.

The CCSD(T) model, which scales as n^7, has been very successful, in particular for the calculation of geometrical properties (structure and force constants). This approximation is also the most accurate in a series of methods considered by Gauss and Stanton for nuclear shielding calculations. The series includes second[59,103] and higher-order many-body perturbation schemes—MP3 and SDQ-MP4[60] (see below)—as well as the CCSD[61,104] and the CCSD(T) approximations.[62] A related CC2 approximation has also been applied to calculate shielding constants.[63] All these methods have been incorporated into the ACES II program,[82] which also permits CCD and QCISD calculations (which both are simplified versions of CCSD). The ACES II program has some advantages that are particularly important for accurate shielding calculations for large molecules. First, GIAO's have been implemented for all the methods—from MP2 to CCSD(T)—used to calculate nuclear shieldings. Second, as described by Gauss and Stanton,[104] an asymmetric form is used for the calculation of the nuclear shieldings (see also eqs 236 and 237 and the following discussion), avoiding the calculation of derivatives with respect to the nuclear magnetic moments.

A series including MP2, MP3, and the linearized coupled-cluster double excitation (L-CCD) model has been applied by Cybulski and Bishop (see refs 105 and 106 and references therein) to calculate the shielding constants for small molecules. These calculations do not involve any scheme to solve the gauge-dependence problem, but, for the small molecules considered, the use of large atomic basis sets ensures accurate results. The L-CCD results are in good agreement with the CCSD(T) isotropic and anisotropic shieldings of ref 62.

The application of coupled-cluster functions to compute nuclear spin–spin coupling constants also requires an extension of the standard approach, as triplet excitation operators are involved. An analytic formulation of perturbation equations for spin–spin couplings is used in a set of models called equations-of-motion CC (EOM-CC) which has been developed by Bartlett et al.[107–109] and successfully applied in a series of calculations. For the studies of time-independent properties (such as the NMR parameters), there are two types of EOM-CC models in use: the CI-like EOM-CC model and the quadratic EOM-CC model. In both models the orbital relaxation effects are neglected.[107,108] The quadratic EOM-CC model is identical to the standard CC model with fixed orbitals as described by eq 235 (this approach has been discussed earlier in other contexts[102] not related to the study of spin–spin couplings). The CI-like EOM-CC model differs from the standard CC model in the terms quadratic in the perturbed amplitudes in eq 235, which are calculated in a different manner.

The initial equations are—as for all the nonvariational methods—asymmetric for the EOM-CC approach, and the similarity to other EOM or CI-like methods follows from a reinterpretation of the final expressions. The final equations for spin–spin couplings are, in contrast to the shielding, symmetric in both perturbations, thus, in agreement with the general $2n + 2$ rule, the perturbation corrections to the Lagrangian multiplier variables are not required, the response equations have to be solved only for the perturbed primary variables—that is, the coupled-cluster amplitudes (compare eqs 80 and 81). Different approximations to the CI-like EOM-CCSD approach have been considered in recent works.[108,109] They can speed up the calculation by more than an order of magnitude;[109] however, the Fermi contact contribution for some of the studied constants was affected by the approximations introduced.

Nuclear spin–spin coupling constants have also been studied, applying the finite perturbation scheme and the quadratic (QCI) CI theory. The applied QCI singles and doubles (QCISD) model differs from the CCSD model in that certain contributions involving the singles amplitudes are absent, both from the energy expression eq 215 as well as from the projected CC equations eq 216. In general, the QCISD model performs much the same as the CCSD model when static correlation effects are unimportant.

E. Møller–Plesset Theory

In those cases where the Hartree–Fock approximation constitutes a reasonable zeroth-order approximation to the exact wave function, one can try to improve it by perturbation theory. The most popular such scheme is Møller–Plesset perturbation theory.

1. The Møller–Plesset Expansion

In Møller–Plesset perturbation theory, the Hamiltonian is partitioned as

$$\hat{H} = \hat{f} + \hat{\Phi} + h_{\mathrm{nuc}} \tag{249}$$

where $\hat{f}$ is the Fock operator eq 147, h_{nuc} is the multiplicative nuclear–nuclear term, and $\hat{\Phi}$ the fluctuation potential, given by

$$\hat{\Phi} = {}^{1}/_{2} \sum_{pqrs} g_{pqrs} \left(E_{pq}E_{rs} - \delta_{qr}E_{ps}\right) - \hat{V} \tag{250}$$

where $\hat{V}$ is the Fock potential defined in eqs 148–150. The Hartree–Fock wave function is the zeroth-order eigenfunction

$$\hat{f}|\mathrm{HF}\rangle = \sum_i \epsilon_i |\mathrm{HF}\rangle \qquad (251)$$

(assuming the canonical representation) with the Hartree–Fock energy as the first-order energy

$$E_{\mathrm{HF}} = \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle = \sum_i \epsilon_i + \langle \mathrm{HF}|\hat{\Phi}|\mathrm{HF}\rangle + h_{\mathrm{nuc}} \qquad (252)$$

Applying standard perturbation theory, we obtain the following expression for the energy to second-order in the fluctuation potential, known as the second-order Møller–Plesset (MP2) energy

$$E_{\mathrm{MP2}} = E_{\mathrm{HF}} - \sum_{aibj} \frac{(2g_{aibj} - g_{ajbi})g_{aibj}}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \qquad (253)$$

The MP2 correction usually constitutes a large fraction of the total correlation energy and provides a useful correction to the Hartree–Fock energy, at a cost significantly smaller than that of the CCSD wave function (n^5 rather than n^6). Therefore, MP2 theory represents a highly successful approach to the calculation of the correlation energy providing, for many purposes, surprisingly accurate, size-extensive corrections. Higher-order corrections, such as MP3 and MP4, may also be derived but are considerably more expensive and do not always provide a smooth convergence toward the FCI energy, and may even diverge.[110] For the study of shieldings, an increasing number of MP2 calculations has appeared in the literature. However, the method has gained little interest in the study of nuclear spin–spin coupling constants as the triplet instability problems of the Hartree–Fock model carry over to the Møller–Plesset model. The Hartree–Fock basis of the Møller–Plesset model makes this approach, even to a greater extent than CCSD theory, restricted to systems dominated by a single electronic configuration, making the theory ill-suited for the study of near-degeneracy problems.

2. Møller–Plesset Lagrangian

For the evaluation of the MP2 energy and its derivatives, it is convenient to reformulate the theory somewhat. Thus, we write the second-order energy in the form

$$E_{\mathrm{MP2}} = \langle \mathrm{HF}|[\hat{\Phi}, \hat{T}]|\mathrm{HF}\rangle \qquad (254)$$

where $\hat{T}$ is a linear combination of excitation operators

$$\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu \qquad (255)$$

whose amplitudes satisfy the equations

$$\sum_\nu \langle \mu|[\hat{f}, \hat{\tau}_\nu]|\mathrm{HF}\rangle\, t_\nu = -\langle \mu|\hat{\Phi}|\mathrm{HF}\rangle \qquad (256)$$

where the Fock operator may be written in the form

$$\hat{f} = \frac{1}{2}\sum_{pq,\sigma} \langle \mathrm{HF}|[a^\dagger_{q\sigma}, [a_{p\sigma}, \hat{H}]]_+|\mathrm{HF}\rangle\, E_{pq} \qquad (257)$$

To arrive at the expression for the second-order energy eq 253, we may use the following biorthonormal representation of the excited states

$$\left|\begin{matrix} a & b \\ i & j \end{matrix}\right\rangle = \frac{1}{3}(1 + \delta_{ab}\delta_{ij})^{-1}\,(2E_{ai}E_{bj} + E_{aj}E_{bi})|\mathrm{HF}\rangle \qquad (258)$$

$$\left\langle\begin{matrix} a & b \\ i & j \end{matrix}\right| = \frac{1}{2}\langle \mathrm{HF}|\, E_{ia}E_{jb} \qquad (259)$$

to simplify the algebra relative to an orthonormal basis of excited states.

3. Møller–Plesset Second-Order Properties

For the perturbed system, we do not insist on the canonical representation since degeneracies among the occupied or virtual orbitals may lead to instabilities in the derivatives.[111] Instead, we require the perturbed orbitals to fulfill the Brillouin condition

$$\langle \mathrm{HF}|[\hat{\kappa}_i, \hat{H}_\kappa]|\mathrm{HF}\rangle = 0 \qquad (260)$$

We may now construct the Møller–Plesset Lagrangian, taking eq 254 as the energy and eqs 256 and 260 as the constraints on the amplitudes and the orbitals. We obtain

$$L_{\mathrm{MP2}} = \langle \mathrm{HF}|[\hat{\Phi}_\kappa, \hat{T}]|\mathrm{HF}\rangle + \langle \bar{t}|\hat{\Phi}_\kappa|\mathrm{HF}\rangle + \langle \bar{t}|[\hat{f}[\hat{H}_\kappa], \hat{T}]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\bar{\hat{\kappa}}, \hat{H}_\kappa]|\mathrm{HF}\rangle \qquad (261)$$

where we have introduced the notation

$$\hat{A}_\kappa = \exp(\hat{\kappa})\, \hat{A}\, \exp(-\hat{\kappa}) \qquad (262)$$

$$\hat{f}[\hat{A}] = \frac{1}{2}\sum_{pq,\sigma} \langle \mathrm{HF}|[a^\dagger_{q\sigma}, [a_{p\sigma}, \hat{A}]]_+|\mathrm{HF}\rangle\, E_{pq} \qquad (263)$$

$$\langle \bar{t}| = \sum_\mu \bar{t}_\mu \langle \mu| \qquad (264)$$

From the variational Lagrangian eq 261, we may obtain the Møller–Plesset properties in the usual manner. Thus, to second order in the perturbation, we obtain

$$L^{(0)}_{\mathrm{MP2}} = \langle \mathrm{HF}|[\hat{\Phi}^{(0)}, \hat{T}^{(0)}]|\mathrm{HF}\rangle \qquad (265)$$

$$L^{(1)}_{\mathrm{MP2}} = \langle \mathrm{HF}|[\hat{\Phi}^{(1)}_\kappa, \hat{T}^{(0)}]|\mathrm{HF}\rangle + \langle \bar{t}^{(0)}|\hat{\Phi}^{(1)}_\kappa|\mathrm{HF}\rangle + \langle \bar{t}^{(0)}|[\hat{f}[\hat{H}^{(1)}], \hat{T}^{(0)}]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, \hat{H}^{(1)}]|\mathrm{HF}\rangle \qquad (266)$$

$$L^{(2)}_{\mathrm{MP2}} = \langle \mathrm{HF}|[\hat{\Phi}^{(2)}_\kappa, \hat{T}^{(0)}]|\mathrm{HF}\rangle + \langle \bar{t}^{(0)}|\hat{\Phi}^{(2)}_\kappa|\mathrm{HF}\rangle + \langle \bar{t}^{(0)}|[\hat{f}[\hat{H}^{(2)}], \hat{T}^{(0)}]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\bar{\hat{\kappa}}^{(0)}, \hat{H}^{(2)}]|\mathrm{HF}\rangle + \langle \mathrm{HF}|[\hat{\Phi}^{(1)}_\kappa, \hat{T}^{(1)}]|\mathrm{HF}\rangle + \langle \bar{t}^{(0)}|[\hat{f}[\hat{H}^{(1)}], \hat{T}^{(1)}]|\mathrm{HF}\rangle \qquad (267)$$

The zeroth-order variational conditions are

$$\sum_{\nu} \langle \mu | [\hat{f}, \hat{\tau}_{\nu}] | \mathrm{HF} \rangle t_{\nu}^{(0)} = - \langle \mu | \hat{\Phi}^{(0)} | \mathrm{HF} \rangle \tag{268}$$

$$\sum_{\nu} \bar{t}_{\nu}^{(0)} \langle \nu | [\hat{f}, \hat{\tau}_{\mu}] | \mathrm{HF} \rangle = - \langle \mathrm{HF} | [\hat{\Phi}^{(0)}, \hat{\tau}_{\mu}] | \mathrm{HF} \rangle \tag{269}$$

$$\sum_{j} \langle \mathrm{HF} | [\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]] | \mathrm{HF} \rangle \, \bar{\kappa}_j^{(0)} = - \langle \mathrm{HF} | [[\hat{\kappa}_i, \hat{\Phi}^{(0)}], \hat{T}^{(0)}] | \mathrm{HF} \rangle - \langle \bar{t}^{(0)} | [\hat{\kappa}_i, \hat{\Phi}^{(0)}] | \mathrm{HF} \rangle - \langle \bar{t}^{(0)} | [\hat{f}[[\hat{\kappa}_i, \hat{H}^{(0)}]], \hat{T}^{(0)}] | \mathrm{HF} \rangle \tag{270}$$

and the first-order equations

$$\sum_{j} \langle \mathrm{HF} | [\hat{\kappa}_i, [\hat{\kappa}_j, \hat{H}^{(0)}]] | \mathrm{HF} \rangle \, \kappa_j^{(1)} = - \langle \mathrm{HF} | [\hat{\kappa}_i, \hat{H}^{(1)}] | \mathrm{HF} \rangle \tag{271}$$

$$\sum_{\nu} \langle \mu | [\hat{f}, \hat{\tau}_{\nu}] | \mathrm{HF} \rangle t_{\nu}^{(1)} = - \langle \mu | \hat{\Phi}_{\kappa}^{(1)} | \mathrm{HF} \rangle - \langle \mu | [\hat{f}[\hat{H}^{(1)}], \hat{T}^{(0)}] | \mathrm{HF} \rangle \tag{272}$$

The number of studies of the chemical shifts applying the MP2 approximation is large and rapidly increasing. As for Hartree–Fock, these studies are presently devoted to the analysis of specific NMR problems rather than to theoretical or computational aspects of the method. Most of the calculations are GIAO-MP2 (using ACES II[82]), and they have been performed for systems smaller than those studied at the Hartree–Fock level because of the basis-set limitations. Very recently, an integral-direct GIAO-MP2 code has been developed,[112,113] enabling calculations for large molecules—for example, 288 basis functions have been used in studies of the anthracenium cation. This code appears to represent the most promising ab initio approach to the study of shieldings in large molecules, MP2 being the only method currently available that combines GIAO's with electron correlation in an integral direct approach.

F. Polarization Propagator Formalism

A variety of linear response approximations can be formulated starting with the equations of motion. In polarization propagator methods, the focus is not on the reference wave function, but on the perturbation itself, which is described in terms of excitation and deexcitation operators. In the polarization propagator formalism one can derive the response equations obtained in other approaches—for example those previously discussed for SCF or MCSCF wave functions. In this section we shall concentrate on those approximations that cannot be derived otherwise and have been applied to study NMR parameters.

Consider a set of variational parameters λ_i and their complex conjugates, and let $\hat{\lambda}_i$ represent the corresponding excitation operators. Assuming the molecule to be in the reference state $|0\rangle$, the excited states corresponding to the "free oscillations" (see e.g., ref 18) can be obtained from the generalized eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_n - \omega_n \begin{pmatrix} \mathbf{S} & \mathbf{\Delta} \\ -\mathbf{\Delta}^* & -\mathbf{S}^* \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_n = 0 \tag{273}$$

where ω_n is the eigenvalue and $\left(\begin{smallmatrix} \mathbf{Z} \\ \mathbf{Y} \end{smallmatrix}\right)_n$ the eigenvector of the nth excited state. In terms of the double commutator eq 247, we have

$$A_{ij} = \langle 0 | [\hat{\lambda}_i, \hat{H}, \hat{\lambda}_j^{\dagger}] | 0 \rangle \tag{274}$$

$$B_{ij} = \langle 0 | [\hat{\lambda}_i, \hat{H}, \hat{\lambda}_j] | 0 \rangle \tag{275}$$

which are elements of the generalized Hessian matrix (compare with eq 156) and

$$S_{ij} = \langle 0 | [\hat{\lambda}_i, \hat{\lambda}_j^{\dagger}] | 0 \rangle \tag{276}$$

$$\Delta_{ij} = \langle 0 | [\hat{\lambda}_i, \hat{\lambda}_j] | 0 \rangle \tag{277}$$

which are metric-type matrix elements. In the SCF approximation for instance, when λ_i are the orbital–rotation operators, S_{ij} corresponds to the overlap matrix and $\Delta_{ij} = 0$.

The response expressions are derived considering the application of a perturbation x oscillating with a frequency ω. We obtain

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{S} & \mathbf{\Delta} \\ -\mathbf{\Delta}^* & -\mathbf{S}^* \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix} = - \begin{pmatrix} \mathbf{M} \\ \mathbf{M}^* \end{pmatrix} \tag{278}$$

where

$$M_i = \left\langle 0 \left| \left[\hat{\lambda}_i, \frac{\partial \hat{H}}{\partial x} \right] \right| 0 \right\rangle \tag{279}$$

The vector $\left(\begin{smallmatrix} \mathbf{Z} \\ \mathbf{Y} \end{smallmatrix}\right)$ describes the response to the perturbation ("forced oscillations") and the corresponding second-order property is given by

$$E_{\mathrm{PPA}}^{(2)}(\omega) = (\mathbf{Z} \quad \mathbf{Y})^{\dagger} \begin{pmatrix} \mathbf{M} \\ \mathbf{M}^* \end{pmatrix} = (\mathbf{M} \quad \mathbf{M}^*)^{\dagger} \mathbf{\Pi}(\omega) \begin{pmatrix} \mathbf{M} \\ \mathbf{M}^* \end{pmatrix} \tag{280}$$

where $\mathbf{\Pi}(\omega)$ may be expressed in terms of the eigenvectors and eigenvalues of eq 273 as

$$\mathbf{\Pi}(\omega) = \sum_{\omega_n > 0} \left[\frac{1}{\omega - \omega_n} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_n (\mathbf{Z}^{\dagger} \quad \mathbf{Y}^{\dagger})_n - \frac{1}{\omega + \omega_n} \begin{pmatrix} \mathbf{Y}^* \\ \mathbf{Z}^* \end{pmatrix}_n (\mathbf{Y}^{*\dagger} \quad \mathbf{Z}^{*\dagger})_n \right] \tag{281}$$

where we have invoked the symmetry of the eigenvectors associated with ω_n and $-\omega_n$. For a static perturbation, $E_{\mathrm{PPA}}^{(2)}(0)$ is proportional to $\mathrm{d}^2E/\mathrm{d}x^2$ and $\mathbf{\Pi}(\omega{=}0)$ is the analogue of $\mathbf{G}^{-1}$, the inverse of the electronic Hessian eq 71. For a time-independent real or pure imaginary perturbing operator, the dimension of the problem is reduced by a factor of 2 by adding or subtracting the two sets of equations for M and M^* in eqs 278.

The equations derived in the polarization propagator approach depend on the choice of parameters λ_i

and on the approximation chosen for the reference state. In the simplest case, when $|0\rangle$ is the SCF wave function and we consider only orbital rotations, we obtain for $\omega \neq 0$ the time-dependent Hartree–Fock (TDHF) equations, also known as the random-phase approximation (RPA). For $\omega = 0$, we recover the linear response equations eq 156, often called the coupled-perturbed HF (CPHF) equations or simply the coupled HF (CHF) equations.

An early extension of RPA is the method developed by Galasso[114] and called the equations-of-motion (EOM). In this approach, the reference function is defined as

$$|0\rangle = N\,(1 + {}^1/_2 \sum_{kl} C_{kl} X_k^\dagger X_l^\dagger)|\mathrm{HF}\rangle \qquad (282)$$

where N is a normalization constant, $X_k^\dagger$ are (spin-adapted) particle–hole (1p–1h) operators and the coefficients C_{kl} are determined by perturbation theory. The response equations are then formulated including in the set λ_i the 1p–1h operators and, in another approximation, additional selected 2p–2h operators (1p–1h operators are equivalent, in our notation, to E_{pq} or T_{pq}, depending on the perturbation, the spin-adapted 2p–2h operators can be expressed as linear combinations of products of these operators). This method has been successfully applied to, for instance, the study of nuclear spin–spin coupling constants in large molecules, see section IX.D.

A more systematic way to treat correlation effects is obtained by using an expansion of all the matrix elements in the response equations eq 278 with the fluctuation potential $\hat{\Phi}$ eq 250 as the ordering parameter. In this way, one determines both the operators λ_i to be included and the coefficients C_{kl} in a systematic manner. In constructing for instance the matrix element A_{ij} in eq 274, we expand the wave function in terms of $\hat{\Phi}$ (denoting by $P^{[n]}$ the quantities accurate to order n in this perturbation)

$$|0\rangle = |\mathrm{HF}\rangle + |0\rangle^{[1]} + |0\rangle^{[2]} + \ldots \qquad (283)$$

and use the corresponding partitioning of the Hamiltonian eq 249. In this context, the RPA method is the analogue of the SCF approach—it describes the polarization propagator and linear response properties accurately to first order in the fluctuation potential.

The next approximation, called the second-order polarization propagator approach (SOPPA), includes all terms to second-order—that is $A^{[0]}$, $A^{[1]}$, $A^{[2]}$, $B^{[0]}$, and so on. For a detailed description of the equations, we refer to the reviews by Oddershede et al.[115,116] In the CCSDPPA[117] and SOPPA(CCSD)[118] approximations, the coefficients C_{kl} are replaced by coupled-cluster amplitudes. In this manner, some of the terms are summed to infinite order in the fluctuation potential. However, since other third- and higher-order terms are not included, the method is accurate only to second-order. SOPPA and related approximations have been applied in numerous studies of shielding and spin–spin coupling constants, some of which are discussed below. A method that combines the SOPPA approach with the use of localized orbitals to obtain gauge-origin independent results has been developed and is known as SOLO.[49] In another approach that yields gauge-invariant results, the diamagnetic contribution to the shielding is also evaluated as a response property, using the same approximations as for the paramagnetic contributions.[119]

G. Explicitly Correlated Wave Functions

Correlated wave functions which depend explicitly on the interelectronic separation r_{ij}, are nowadays used for large molecular systems.[120] However, H_2 is the only molecule for which the NMR shielding constant has been studied using explicitly correlated methods. The perturbation scheme used in that study is equivalent to a sum–over–states approach (the results are discussed in section VIII). Although such wave functions are potentially very accurate because of the elaborate description of the electron correlation effects, they suffer from the same gauge-origin problems as do the standard methods, unless some measures are taken to avoid this as discussed in section V.B. So far, for explicitly correlated wave functions, no analogous approach has been developed.

H. DFT

Density functional theory (DFT) provides new opportunities for computational applications of quantum chemistry. DFT methods enable accurate calculations on systems that cannot easily be treated by standard methods beyond Hartree–Fock, such as large organic molecules or molecules with transition metal atoms. Following the development of various DFT approximations, corresponding perturbation theoretical schemes have been applied to the study of nuclear shielding and spin–spin coupling constants.[9]

DFT calculations are relatively inexpensive, and numerical evidence indicates that when the SCF and DFT results differ significantly (for example, when the correlation effects are large), the DFT values are usually more reliable. However, we should keep in mind that "although DFT has a rigorous base, in application it is semi-empirical" and that there is "no way to systematically converge to the exact result".[121] This contrasts with conventional ab initio approaches, for which we can estimate a priori the quality of a calculation and improve the calculation systematically by extending the basis set and by improving the correlation treatment.

We shall discuss here only some aspects of DFT methods that are related to the calculation of NMR properties (see recent reviews[9,122]). In the presence of a magnetic field, the Hohenberg–Kohn theorem is no longer valid. Instead, the expressions determining the energy and the magnetic properties are obtained by introducing an exchange-correlation density functional that depends on the density ρ and on the paramagnetic current density

$$\mathbf{j}_p(\mathbf{r}) = -i\sum_k (\phi_k^*(\mathbf{r})\nabla\phi_k(\mathbf{r}) - \phi_k(\mathbf{r})\nabla\phi_k^*(\mathbf{r})) \qquad (284)$$

(see eqs 293 and 294). Together with some assumptions for the dependence of the energy functional on

$\mathbf{j}_p(\mathbf{r})$, these densities form the basis for the current-density functional theory (CDFT).[123,124]

The explicit form of the current density functionals has received little attention in the literature. The work of Lee et al.[124] indicates that the functionals of Vignale, Rasolt, and Geldart[122] are unable to give a correct representation of the magnetic perturbation. Another approach to the study of magnetic perturbations using DFT has recently been proposed by Holas and March,[125] but has not yet been applied to the study of NMR properties. Salsbury and Harris have recently discussed simple methods that enable calculations of shielding constants[126,127] or Fermi contact terms in spin–spin coupling constants[128] within the DFT approach.

Numerous standard approximations for the exchange-correlation potential used in many DFT approximations, including or excluding in addition the dependence on paramagnetic current density in the calculation of NMR parameters, have been applied. As for ab initio methods, the calculations are performed using a finite basis and the gauge dependence of the shielding constants thus has to be considered. The techniques used in other methods (GIAO, IGLO, CSGT) have been combined with the DFT approach. No single approximation appears to be superior to the others. For a comparison of the results, we refer to the original papers.[80,124,129–131]

By scaling the excitation energies, Malkin et al.[9] have improved the results obtained in sum-over-states density-functional calculations. Although their results are generally in good agreement with experiment, and some theoretical justification for this procedure may be given, such a scaling appears from a theoretical point of view to be somewhat unsatisfactory.

Using various DFT approximations, Cheeseman et al.[80] have carried out a study of chemical shifts for a series of molecules. For shieldings with large correlation effects (nitrogen and oxygen shieldings, in particular), the DFT results show some improvement on the SCF values for nuclear shieldings. However, the improvements are not systematic and better results are obtained at the MP2 level. For carbon shieldings, the SCF and DFT results are of comparable accuracy. The authors speculate that the inclusion of a magnetic-field-dependent term in the exchange-correlation functional will improve the DFT results. Results of similar quality have been obtained for the shielding constants in other DFT calculations—see for example refs 124 and 129. Although DFT may perform better than MP2 for some molecules,[132] much work remains to be done to improve the density functionals before definitive predictions can be made.[124]

Despite all current problems, we will undoubtedly see more DFT calculations in the future. Numerical experience indicates that the results are sufficiently accurate for many purposes, in particular when some experimental data are available for comparison.

VII. Basis Sets

The choice of the atomic basis set is a crucial decision in any ab initio calculation. The basis set needs to be large enough to describe the effects of the applied perturbations as well as to model the molecular charge distribution and (if appropriate) the electron correlation effects. At the same time, the basis set should be small enough so that it can be used for the molecule of interest. The choice of the basis set thus depends both on the accuracy aimed at in the investigation and on the size of the molecule. In the following, we shall concentrate on those particular aspects of basis-set construction that are related to the calculation of magnetic properties. For a more general discussion of basis sets, we refer to the review by Helgaker and Taylor.[74]

In the discussion of basis sets, it is important to distinguish between the requirements for different levels of approximation. For treatments where an explicit and accurate representation of the Coulomb hole[18] is not attempted (i.e., at the SCF and MCSCF levels) or not required (i.e., at the DFT level), the basis-set requirements are more modest, although the special requirements for magnetic perturbations make the selection of basis set nontrivial. For calculations that aim also at an accurate description of dynamical correlation effects, the basis-set requirements are much more stringent since large basis sets are needed for an accurate representation of the Coulomb hole. For this purpose, special families or hierarchies of basis sets have been developed that allow us to approach the basis-set limit in a systematic manner. The most common of such hierarchies are the atomic natural orbitals (ANOs)[133–136] and the correlation-consistent basis sets,[137–141] both of which give systematic improvements in energies with increasing size.

A. Basis Sets for Nuclear Shieldings

For nuclear shieldings, the choice of basis set depends on the particular method used for solving the gauge-origin problem. In the idealized limit of a complete basis set, all methods for solving the gauge-origin problem give the same results since, in this limit, they all give the same perturbed and unperturbed wave functions. Concerning large but finite basis sets, basis sets that are saturated with respect to the PSO perturbation are usually fairly well converged also with respect to the magnetic-field perturbation—irrespective of what kind of distributed gauge origins are used. For the smaller sets (for which the basis set may also be unsaturated for the PSO perturbation), significant differences exist among the various methods, as has been discussed at length in the literature. We here draw attention to the SCF comparisons of IGLO, LORG, and GIAO's in C_3Cl_4[142–145] and the comparisons of CTOCD, GIAO, and LORG for fluoromethane by Enevoldsen and Oddershede.[146] Furthermore, Cheeseman et al. compared the convergence of GIAO's with the CSGT method in a study of the relative performance of SCF and DFT.[80] As GIAO's show the best basis-set convergence and are moreover employed by most quantum-chemistry programs capable of computing nuclear shieldings, we shall in the following discussion restrict ourselves to results obtained using GIAO's. Most of the conclusions and recommendations are valid for the other methods as well, although the smaller basis sets may not be adequate for all methods.

Table 1. Families of Basis Sets Used in the Investigation of the Convergence of Nuclear Shielding Constants at the SCF Level

Pople/McLean−Chandler basis sets	the basis sets developed by Pople and co-workers[148−153] now most commonly known from the Gaussian program system[83]
Karlsruhe basis sets	the basis sets developed in Karlsruhe by Ahlrichs and co-workers[154]
IGLO basis sets	the basis sets developed by Schindler and Kutzelnigg,[46,47] based on a compilation by Huzinaga[155] and extended with diffuse and polarizing functions; the basis sets are of valence triple-ζ quality or better
ANO(Lund)	the Atomic Natural Orbital (ANO) basis sets of Widmark and co-workers[133−135] in various different contraction schemes
correlation-consistent basis sets	the correlation-consistent basis sets of Dunning and co-workers,[137,138,156] tailored to give systematic convergence of correlation energies and molecular electric properties

Table 2. Absolute Minimum, Maximum, and Mean Deviation from the Estimated Hartree−Fock Limit of the Heavy-Atom Shieldings for the Basis Sets Investigated (In Addition the Signs of the Deviations Are Indicated)

basis	no. of basis functions[a]	min.	max.	mean	sign
6-31G	9	0.5	33.2	12.2	+/−
6-31G**	14	0.6	43.4	13.6	+
6-311G	13	1.4	13.5	4.7	+/−
6-311G**	18	0.8	9.8	3.7	+/−
6-311++G**	22	0.1	7.9	1.7	+/−
6-311++G(2d,2p)	27	0.0	7.6	1.9	+/−
Karlsruhe-SVP	14	3.6	35.5	12.6	+
Karlsruhe-DZP	15	1.8	36.9	12.1	+/−
Karlsruhe-TZP	20	1.0	4.6	1.8	+/−
Karlsruhe-QZP	23	0.4	3.2	1.5	+/−
IGLO II	22	0.6	7.9	2.7	+/−
IGLO III	35	0.1	1.6	0.5	+/−
IGLO IV	51	0.0	2.8	0.8	+/−
ANO(Lund) (3s1p/3s2p1d)	14	1.2	14.9	6.7	+
ANO(Lund) (3s2p1d/4s3p2d1f)	30	0.7	14.6	6.4	+/−
ANO(Lund) (4s3p2d/5s4p3d2f)	46	0.0	5.4	1.4	+/−
ANO(Lund) (4s3p2d/6s5p3d2f)	50	0.3	2.1	0.9	−
ANO(Lund) (4s3p3d/6s5p4d3f)	62	0.1	3.6	1.1	−
cc-pVDZ	14	3.9	39.3	13.0	+
aug-cc-pVDZ	23	2.8	30.6	11.3	+
cc-pVTZ	30	0.0	8.6	2.5	+
aug-cc-pVTZ	46	0.2	8.4	2.4	+
cc-pVQZ	55	0.1	4.7	1.1	+
aug-cc-pVQZ	80	0.0	0.1	0.1	+

[a] The number of basis functions for a heavy atom, assuming a spherical Gaussian basis set.

In the literature, no systematic studies of the basis-set convergence of nuclear shieldings have been carried out in which different families of basis sets are compared. Rather, all investigations have been restricted to studies of the convergence properties within a given family of basis sets—see, for instance, refs 45, 47, and 103. Using GIAO's, Dahle et al. have undertaken a systematic investigation of the basis-set convergence of nuclear shieldings at the SCF level,[147] comparing the convergence of the five families of basis sets described in Table 1. In this study, the calculated shieldings are compared with the estimated Hartree−Fock limits for nine molecules (CH_4, NH_3, H_2O, SiH_4, PH_3, H_2S, CO_2, C_2H_4, and C_2H_2), chosen to include elements from the first three rows of the periodic table and to include systems with double and triple bonds.

In Table 2, we have listed, for the second- and third-row atoms, the percentage deviation of the shielding from the estimated Hartree−Fock limit. In most cases, the Hartree−Fock limit is taken as the shielding obtained with the largest correlation-consistent and ANO−Lund basis sets. In the few cases where these basis sets have not converged to a common value, the average of the shieldings obtained for the two basis sets is used. The hydrogen shieldings follow the same pattern as the shieldings in Table 2, but with smaller deviations.

As seen from Table 2, rather large basis sets must be used to approach the Hartree−Fock limit closely. If we aim for errors less than 5%, none of the Pople/McLean−Chandler basis sets are useful since, for these basis sets, the deviation always exceeds 5% for at least one of the molecules investigated. Still, with polarization and diffuse functions added, the average error is small for the 6-311G basis. Excellent results are obtained with the two largest sets of Schindler and Kutzelnigg, which, for all nine molecules, give results with an error less than 3%. However, these basis sets are fairly large and not useful for larger molecules. Also, the larger ANO basis sets perform well and have the advantage of being constructed for calculations that include the effects of dynamical correlation. For larger molecules, the TZP and QZP sets of Ahlrichs and co-workers have the best overall characteristics—although fairly small, these sets give results with small deviations from the Hartree−Fock limit. Regarding the correlation-consistent sets, only the cc-pVQZ set gives results with errors less than 5% for all the molecules investigated.

To summarize, for an accurate calculation of nuclear shieldings, a basis set of at least valence triple-ζ quality and with at least one set of polarization functions is needed. This finding is in accordance with the observation of Carmichael[29] that for reliable calculations of shieldings, there is a need for flexibility in the outer-core inner-valence regions. Basis sets with tightly contracted core orbitals, such as the correlation-consistent basis sets and the small ANO sets, have little flexibility in the core region and perform poorly in calculations of nuclear shieldings. The recently developed core−valence correlation-consistent sets cc-pCVXZ[140] might well improve on the performance of the correlation-consistent sets (at the expense of using even larger basis sets).

For nuclei for which no standard basis sets have been developed for the accurate calculation of shieldings, some attempts at extending the standard (usually small) basis sets have been made. Examples include selenium,[157] gallium, chlorine, and bromine.[158] However, for such heavier atoms, the lack of large basis sets makes it difficult to establish the

Hartree–Fock limit and thus to investigate the performance of the smaller sets. Moreover, comparison with experiment is complicated by the large relativistic effects on heavy-atom shieldings, see section XI.A.

Instead of choosing small atomic basis sets (and lowering the accuracy of the results), one can reduce the size of the molecular basis set by the use of *locally dense* basis sets.[159] In this approach, the nuclei of interest (and sometimes also the neighboring atoms) are described by a large basis set, whereas the remaining atoms (or the surrounding molecules in supermolecule calculations) are described by a smaller basis set. Although this approach leads to smaller basis sets, it appears somewhat unsatisfactory, in particular with the advent of efficient direct and parallel codes for the calculation of shieldings.[78,81] Nevertheless, the results presented by Chestnut et al. are good[159] and the method has been successfully used for studying large molecular systems.[160–162]

We close the discussion of basis-set requirements for nuclear shieldings by commenting on an approach for extending standard basis sets so that they become approximately gauge-origin independent. The first-order basis functions (FOBs) of Sugimoto and Nakatsuji can give fairly accurate results using CPHF programs without the introduction of field-dependent orbitals.[163] The FOBs are based on the idea of Epstein that the original, unperturbed basis set should span as much of the perturbed space as possible.[164] Following this principle, any standard basis set may be extended toward an accurate description of magnetic properties by adding functions with the same exponents but higher angular momentum. The principle is here the same as that behind the polarized basis of Sadlej.[165,166] Although this approach simplifies the calculation of the shieldings in the sense that no programming is required beyond what is needed for field-independent orbitals, it does lead to larger basis sets, thereby increasing the cost of the calculations (also for the optimization of the wave function). In contrast, in the GIAO and IGLO approaches, the same effect is achieved by extending the basis set only in that part of the orbital space where the higher angular-momentum functions are needed—namely, for the representation of the perturbed wave function. The only drawback of these two methods is that they require a significant programming effort on the part of the developer.

B. Basis Sets for Spin–Spin Couplings

If systematic studies of basis-set convergence of nuclear shieldings are scarce, they are almost nonexistent for spin–spin couplings, mainly because of the lack of black-box methods for the calculation of such couplings. The usual dominance of the Fermi-contact contribution (which requires an accurate description of the nuclear region) to the total coupling constant makes standard basis sets inadequate. Furthermore, the usual imposition of singlet spin symmetry on the wave function (e.g., in restricted Hartree–Fock theory with doubly occupied molecular orbitals) means that the wave function may not be stable toward triplet perturbation operators and that the triplet space may be poorly represented. For the calculation of spin–spin coupling constants, therefore, one should use more advanced methods, which makes basis-set studies much more expensive.

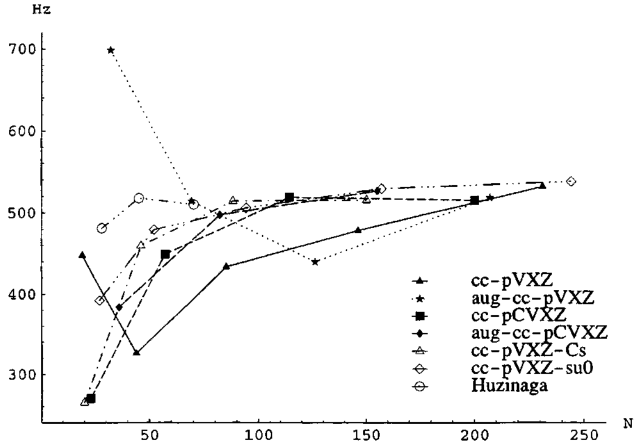

Figure 1. Basis set dependence of spin–spin coupling constant in HF. Based on Figure 1 of Helgaker, T.; Jaszuński, M.; Ruud, K.; Górska, A. *Theor. Chem. Acc.* **1998,** *99*, 175. Reprinted with permission of Springer-Verlag Gmbh & Co. KG. Copyright 1998.

Oddershede and co-workers have investigated the basis-set requirements for accurate spin–spin couplings, in particular with respect to the Fermi-contact term.[167–169] For basis-set saturation, orbital exponents as large as 150 000 were shown to be necessary, even for the hydrogen molecule. For basis sets of more moderate size, Barszczewicz et al. have shown that good results may be obtained with the two IGLO sets H III and H IV, although some lack of basis-set saturation is still observed.[170,171]

A systematic study of the basis-set requirements was recently presented by Helgaker et al.,[172] who studied the convergence of MCSCF spin–spin coupling constants using different correlation-consistent basis sets[137–141] as well as the IGLO sets. As previously found for the spin densities,[173] it was demonstrated that the valence augmented correlation-consistent basis sets do not converge smoothly for the spin–spin coupling constants and that for smooth convergence, the much larger core–valence correlation-consistent sets must be used instead. For a (6331) CASSCF wave function, the performance of the various basis sets is shown for the HF molecule in Figure 1. The calculated coupling constants are seen to depend strongly on the quality of the basis set. Helgaker et al. proposed a smaller family of basis sets, where the *s* orbitals of the correlation-consistent basis set are fully decontracted and one or more tight *s* functions are added in a geometric series. These sets, denoted cc-pVXZ-*sun* (where *su* indicates the use of uncontracted *s* functions and *n* is the number of tight *s* functions added to the original cc-pVXZ basis), converge smoothly toward the basis set limit with increasing *n*.

VIII. Shielding Constants

For our discussion of calculations of shielding constants, we begin with the most accurate calculations on the smallest molecules and then proceed to

Table 3. The Nuclear Shielding Constants of Second-Row Hydrides

		nuclear shielding constants, ppm							
		CH_4		NH_3		H_2O		HF	
method	ref(s)	σ(C)	σ(H)	σ(N)	σ(H)	σ(O)	σ(H)	σ(F)	σ(H)
SCF/GIAO	60	194.8	31.7	262.3	31.7	328.1	30.7	413.6	28.4
MP2/GIAO	60	201.0	31.4	276.5	31.4	346.1	30.7	424.2	28.9
MP2/common origin[a]	179,106	200.8	31.50	275.0	31.56	344.9	30.97	424.4	29.15
MP3/GIAO	60	198.8	31.5	270.1	31.6	336.7	30.9	417.8	29.1
MP3/common origin	106	198.8	31.54	269.1	31.69	336.0	31.17	418.0	29.29
MP4/GIAO	60	198.6	31.5	269.9	31.6	337.5	30.9	418.7	29.1
L-CCD/common origin	106	198.6	31.54	268.8	31.72	335.9	31.25	417.6	29.45
CC2/GIAO	63	201.1	31.4	276.0	31.4	345.6	30.7	424.2	28.9
CCSD/GIAO	104	198.7	31.5	269.7	31.6	336.9	30.9	418.1	29.1
CCSD(T)/GIAO	62	198.9	31.6	270.7	31.6	337.9	30.9	418.6	29.2
SOPPA[b]	180	196.0	31.20	266.0	31.21	330.6	30.61	411.5	29.08
CASSCF(3210)/IGLO	57,181	193.39	31.13	257.8	30.95	323.04	30.47	402.67	29.26
CASSCF(6331)/GIAO[c]	58	200.4	31.19	269.6	31.02	335.3	30.21	419.6	28.49
experiment[d]		198.7	30.61	264.54	31.2	344.0	30.052	410	28.5
					± 1.0	± 17.2	± 0.015	± 6	± 0.2

[a] Note that the shieldings reported in ref 179 for water have been corrected in ref 106. [b] Geertsen's method[119] was applied to maintain gauge invariance of the results (see section VI.F). [c] The results presented for CH_4 and NH_3 have been calculated for this review. [d] The experimental results have been taken from refs 182 (C in CH_4), 183 (H in CH_4, H_2O, and HF), 184 (N and H in NH_3), 185 (O in H_2O), and 186 (F in HF).

more approximate studies of larger systems. The calculations discussed were selected to illustrate the state-of-the-art accuracy and for a comparison of different correlated methods. We do not here discuss specific spectroscopic or chemical problems nor do we attempt to present a complete list of ab initio results for the properties. Older, less accurate studies are mentioned primarily to illustrate the progress made in recent years.

A. The Hydrogen Molecule

Very accurate methods have been applied to compute the shielding constants in H_2. For this two-electron system, wave functions depending explicitly on the internuclear separation r_{12}[174,175] as well as FCI calculations in large basis sets[176,177] have been used. A comparison of the calculated shielding and a careful analysis of the experimental data give not only an estimate of the accuracy of theory and experiment, but also a means to establish the absolute shielding scale for the H atom.[177]

Komasa, Rychlewski, and co-workers have used two different explicitly correlated functions to compute σ(H).[174,175] In the first approach, correlation factors r_{12} multiply some terms in the (Hylleraas) CI expansion; in the second approach geminals of the form exp $(-\gamma_n r_{12}^2)$ are used. Using 300 geminals for the zeroth-order wave function and 100 basis functions for the first-order wave function, they obtained $\sigma(\mathrm{H}) = 26.8139$ ppm at a bond distance of 1.4 a_0.

The other recent calculations, carried out by Sundholm and co-workers,[176,177] use standard one-electron orbitals and the GIAO approach. High accuracy of the results is achieved by applying a large basis set (8s4p3d2f) and the full CI scheme to treat the correlation effects. The shielding obtained at a nuclear separation of 1.4 a_0 is 26.680 ppm.

For comparison with experiment, one must carry out rovibrational averaging of the shielding (leading to a value of about 26.34 ppm for the lowest rovibrational state) and include a small contribution from the temperature shift. The final calculated value $\sigma_{T=300K} = 26.298(20)$ ppm[177] may be compared with that deduced from the experimental spin−rotation constant, 26.288(2) ppm, and with an older experimental result of 26.363(4) ppm. For a detailed discussion of the comparison with experiment, we refer to Jameson's review.[12]

The nuclear shielding constant of the excited-state $B^1\Sigma_u^+$ has also recently been analyzed in the FCI approach.[178] This state is paramagnetic, which is reflected in the exceptional deshielding. In the lowest rovibrational state, the average value of the shielding constant was found to be −5.45 ppm.

B. Second-Row Hydrides

The second-row, 10-electron hydrides constitute an important test bed for theoretical methods, not only because of their moderate size, but also because of their fundamental chemical importance. In Table 3, we have collected the results of various ab initio calculations of the shieldings in these molecules. Because of the large number of such calculations that have been done, we have, for each method, restricted ourselves to report the numbers obtained with the "best" basis set. We have not taken into account rovibrational effects, although these may be important for an accurate comparison with experiment. We would also like to stress that there may be small differences in the geometries used in the different investigations.

From the table, we see that these hydrides display only modest correlation effects, which are quite easily recovered with most correlated methods. Molecules with only single bonds and no near-degenerate electronic states can thus be modeled quite accurately using correlation methods of rather low computational cost. Nevertheless, differences among the various correlated approaches are apparent also in these simple molecules. Although MP2 and CC2 provide similar correlation corrections, both overestimate the correction—in section VIII.D, we discuss an empirical scheme for scaling MP2 results. An oscillatory be-

Table 4. Nuclear Shielding Constants in N_2 and CO

		nuclear shielding constants, ppm		
		N_2	CO	
method	ref(s)	σ(N)	σ(C)	σ(O)
SCF/GIAO	60	−112.4	−25.5	−87.7
MP2/GIAO	60	−41.6	10.6	−46.5
MP2/common origin	179	−39.4	11.4	−44.7
MP3/GIAO	60	−72.2	−4.2	−68.3
MP3/common origin	106	−70.4	−3.4	−66.6
MP4/GIAO	60	−60.1	4.1	−52.0
L-CCD/common origin	106	−55.7	3.9	−57.4
CC2/GIAO	63	−40.6	14.2	−38.2
CCSD/GIAO	104	−63.9	0.8	−56.0
CCSD(T)/GIAO	62	−58.1	5.6	−52.9
SOPPA[a]	191	−80.2	−15.2	−83.9
CCSDPPA[a]	191	−84.1	−14.1	−19.5
CASSCF(4220)/IGLO	57,192	−40.8	13.4	−36.7
CASSCF(8331)/GIAO	58	−53.0	8.2	−38.9
experiment[b]		−61.6 ± 0.2	3.0 ± 0.9	−42.3 ± 17.2

[a] Geertsen's method[119] was applied to maintain gauge invariance of the results (see section VI.F). [b] The experimental results have been taken from refs 193 (nitrogen), 182 (carbon), and 185 (oxygen).

havior of the Møller−Plesset series is apparent in Table 3; this behavior of the perturbation series is known for other properties as well.[187] The main cause for the difference between the MCSCF/IGLO and MCSCF/GIAO results is the difference in active space, as the full-valence space of the MCSCF/IGLO calculations is unbalanced.[58,188] The MCSCF/GIAO values obtained with the larger active space are in better agreement with the other accurate results.

C. Diatomic Molecules

A systematic way to analyze any orbital-based approach for describing correlation effects is to compare the results with FCI values in the same basis set. In this context, we mention an application that set a precedence for future highly accurate studies of larger molecules—an analysis of the shielding constants in BH.[189] The results obtained for σ(B), σ(H), and the anisotropies $\Delta\sigma$(B) and $\Delta\sigma$(H) using a basis set of moderate size and approximate methods (various MPPT levels and CCSD) were compared with FCI. It was established that in this case, only the CCSD method gives reliable results and estimates of the differences between FCI and CCSD results were obtained. This estimate and CCSD values computed using a large basis were next used to extrapolate to large-basis FCI values, with corrections of 5 ppm for σ(B) and $\Delta\sigma$(B) and 0.2 ppm for σ(H) and $\Delta\sigma$(H). The accuracy of such a procedure was later confirmed by large-basis CCSD(T) results,[62] which almost coincide with the extrapolated large-basis FCI values.

To demonstrate the importance of an accurate treatment of electron correlation for other first-row diatomics, we have in Table 4 collected some results for the nuclear shieldings of the isoelectronic molecules N_2 and CO, both of which display large correlation effects. The observations made for the first-row hydrides reappear for these two molecules but in a more pronounced form: the Møller−Plesset series oscillates with MP2 significantly overshooting the CCSD(T) shieldings. In fact, all correlated methods except SOPPA and CCSD overshoot the CCSD(T) results, indicating that the correlated pole structure of SOPPA and CCSD provides a more balanced treatment of the correlation problem than do the Hartree−Fock poles of the Møller−Plesset series. The influence of the pole structure on nuclear shieldings has been discussed by Fagerström and Oddershede.[190]

None of the theoretical results presented in Table 4 have taken into account rovibrational corrections. The inclusion of these effects is important for an accurate comparison with experiment, in particular with the accuracy obtainable with the CCSD(T) method.[177] We return to a more detailed discussion of these effects in section XII.B, where the most accurate results presently obtained for diatomic molecules are compared with experimental data.

D. Larger Molecules

Owing to the increasing availability of ab initio programs for the calculation of nuclear shieldings, the ab initio literature on shieldings of larger systems is increasing rapidly. Most of these calculations have been restricted to the Hartree−Fock level and will not be discussed further here. Some examples of the truly large molecular systems that may now be investigated with Hartree−Fock and DFT methods were given in section VI.A.4, other examples can be found in, for instance, ref 194. We also refer to sections XII and XIII for a brief discussion of some SCF calculations of rovibrational effects and intermolecular forces in studies of NMR parameters. From such SCF calculations, valuable insight may be gained about specific chemical and structural problems, effects of conformational changes, local molecular environment, and so on. For example, in a recent study of carbon-shielding tensors in the carbonyl group,[195] it was argued that correlation effects are approximately geometry independent. However, these topics are largely outside the scope of the present review. For a discussion of such applications, we refer to the recent review by de Dios.[5]

Table 5. Isotropic Shieldings in Diazomethane (H_2CNN)

method	ref	isotropic shieldings, ppm			
		σ(C)	σ($N_{central}$)	σ($N_{terminal}$)	σ(H)
SCF	104	164.3	−13.3	−302.6	28.5
MBPT(2)	104	178.3	−96.7	55.6	28.4
CC2	63	178.0	−46.6	−42.9	28.3
CCSD	104	170.9	−26.7	−161.4	28.5
CCSD(T)	62	171.9	−31.6	−142.4	28.4
RAS−I[a]	199		−19.1	−121.4	
experiment[b]		164.5	−43.4	−149	

[a] The RASSCF wave function contains all occupied valence orbitals and the two unoccupied π orbitals in the RAS2 subspace. The remaining valence orbitals are included in the RAS3 subspace, with a maximum of two electrons. [b] The results for carbon are taken from ref 200, and the results for nitrogen, from ref 201.

The approximations made in the Hartree−Fock method make it suitable mainly for qualitative predictions related to particular experimental measurements. However, when a set of reference data is available, the SCF shielding constants can be systematically scaled. The scaling can be performed using empirical data, as for instance for carbon[196] and nitrogen shieldings;[197] for a series of molecules, it has also been shown that the scaling does indeed reproduce the dominant correlation corrections.[198] The scaled values are usually much better than the SCF ones and this approach provides a computationally inexpensive method to obtain fairly accurate estimates of shielding constants.

Restricting ourselves to correlated calculations, we find that the literature is still large. Rather than giving a complete review of all correlated calculations, we shall here select a few systems that have been studied at different correlated levels and focus on the relative performance of the various methods and the importance of electron correlation.

A difficult system that has been investigated at several correlated levels is diazomethane—see the results in Table 5, which have all been obtained using large GIAO basis sets. The effect of correlation on the shieldings of this fairly small molecule is quite dramatic but nevertheless fairly representative for molecules containing oxygen or nitrogen in double or triple bonds. This molecule therefore serves as a useful starting point for a general discussion of the applicability of the various correlated methods for larger molecules.

In diazomethane, the hydrogen shieldings are quite unaffected by electron correlation, as observed for many other molecules as well.[202] We note the fortuitous agreement of the SCF carbon shielding with experiment. The nitrogen shieldings are sensitive to electron correlation; not even CCSD(T), the most sophisticated method applicable to such systems, is able to get within 10 ppm of experiment, although this difference may be due to solvent effects rather than to an incomplete treatment of electron correlation. The importance of the solvent effects can be reduced by considering the relative chemical shifts (for N atoms), an approach that eliminates also the ambiguities arising from the conversion of experimental chemical shifts to an absolute shielding scale.

From Table 5, we note that the popular MP2 method overestimates the effect of correlation. This is often observed and it has been suggested that a better estimate of the correlated nuclear shieldings can be obtained by scaling the MP2 correction as[203]

$$\sigma^{\mathrm{corr}} = \sigma^{\mathrm{HF}} + {}^{2}/_{3}(\sigma^{\mathrm{MP2}} - \sigma^{\mathrm{HF}}) \tag{285}$$

In a series of molecules considered by Chesnut[203] the root-mean-square errors for σ^{corr} are much smaller than for σ^{MP2}. However, as with any purely empirical correction, this approximation appears to be rather unsatisfactory within the framework of ab initio theory. We note, for example, that it does not give good results for the nitrogen shieldings in diazomethane.

For highly correlated systems such as diazomethane, MP2 fails and more sophisticated methods must be applied. We note that CCSD represents a significant improvement on MP2 (for weakly correlated systems, however, MP2 and CCSD give approximately the same accuracy, with MP2 being computationally cheaper). The higher-order perturbation methods such as MP3 and SDQ-MP4[104] do not provide significant improvements upon MP2, in particular in view of the improvements observed at the CCSD level. The MCSCF wave function yields a good result for the relative chemical shifts of the nitrogen atoms, but the shieldings differ considerably from the experimental values. As shown in Table 5, near quantitative accuracy for the nuclear shieldings and for the relative shift is obtained in the CCSD(T) method. Some differences between theory and experiment persist even at this level but are not larger than expected, considering the neglect of solvation (as mentioned above) and the neglect of rovibrational corrections.

Jaszuński et al.[199] have calculated the shieldings (and later also the spin−spin couplings[170]) of the nitrogen atoms of four isomers of CH_2N_2 (including diazomethane) and of HN_3. For these electron-rich molecules with lone pairs, electron correlation effects were shown to be important for the shieldings. Reasonable agreement with experimental data was obtained with moderate active spaces in the MCSCF wave function.

Another system that for a long time has been a challenge to ab initio calculations because of large correlation effects is the 1-cyclopropylcyclopropylidenemethyl cation,[204] where the spectrum based on SCF shieldings has hardly any resemblance to the experimental spectrum. The spectra obtained using a variety of correlated approaches are collected in Figure 2 along with the experimental spectrum. Whereas MP2 does not give a spectrum that is easier to compare with experiment than is the Hartree−Fock spectrum, this problem is solved at the CCSD level. Only CCSD(T) provides approximately quantitative agreement.

A large number of MP2 and CCSD studies have been undertaken on organic ions.[205,206] The carbon shieldings of these ions may serve to probe their existence in organic mixtures, supporting their proposed role as reactive intermediates[206] and providing

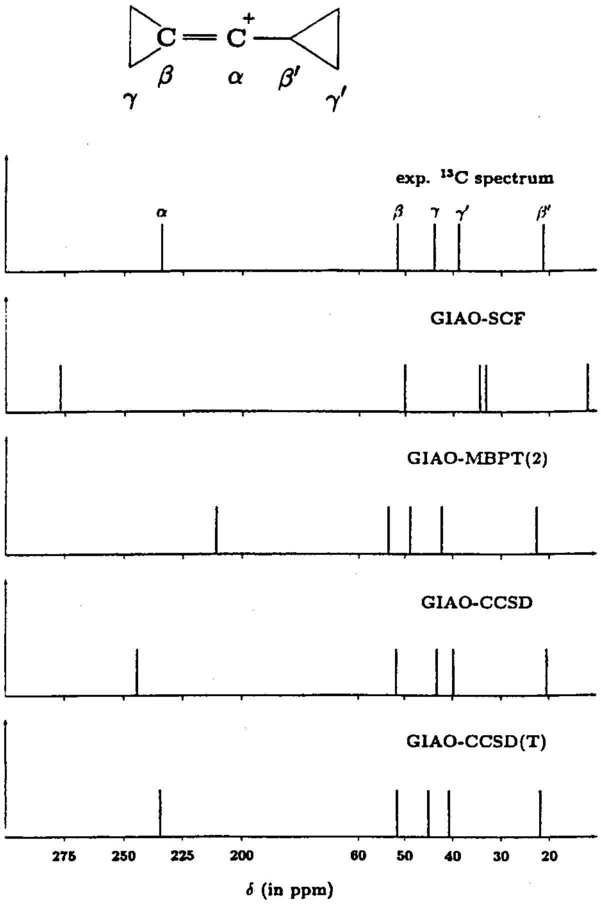

Figure 2. CCSD(T) calculation of NMR chemical shifts: consistency of calculated and measured ^{13}C chemical shifts in the 1-cyclopropylcyclopropylidenemethyl cation. Based on Figures 1 and 2 of Stanton, J. F.; Gauss, J.; Siehl, H. U. *Chem. Phys. Lett.* **1996**, *262*, 183. Reprinted with permission of Elsevier Science, The Netherlands. Copyright 1996.

useful structural information about these cations. Highly accurate CCSD(T) calculations, in close agreement with experiment, were recently presented by Gauss and Stanton for $C_2H_4^+$, $C_3H_5^+$, $C_4H_5^+$, $C_5H_7^+$, and $C_7H_9^+$.[205] By using the recent direct implementation of MP2, the studies of cations were extended to protonated aromatic molecules such as benzenonium, naphthalenium, and anthracenium.[112] Sieber, Schleyer, and Gauss used MP2 results to verify proposed structures for the phenonium and benzenonium ions, by comparing with experimental NMR data.[206]

Using SCF, MP2, and DFT methods in the GIAO approach, Orendt et al.[132] interpreted the observed NMR spectrum of matrix-isolated *o*-benzyne-1,2-$^{13}C_2$. Since this molecule has a biradicaloid nature, SCF and MP2 do not perform well. In contrast, the DFT results are in good agreement with experiment, and the analysis of the calculated tensor components provided valuable insight into the nature of the triple bond of this molecule. Because of a possibly large, undetermined indirect spin−spin coupling, the experimental spectrum could not be fully resolved. A detailed study of the electronic structure, and to some extent the NMR parameters, of *o*-benzyne using a number of different ab initio methods was recently presented by Jiao et al.[207]

Schleyer and co-workers have investigated the shieldings of carboranes[208,209] and found that the inclusion of electron correlation at the MP2 level was needed to reproduce the experimental NMR spectrum for three of the nine structures investigated.[209] However, the calculated boron shieldings in $C_2B_3H_7$ turned out to be in sharp disagreement with experiment, even though no correlation corrections were predicted by the MP2 method. Bühl et al.[209] suggested that these shieldings should be reexamined and a subsequent experimental reinvestigation[210] confirmed the theoretical predictions.

Molecules including third-row atoms have also been investigated. The selenium shielding has been studied extensively and shown to have large correlation effects.[211] In a recent CCSD investigation by Bühl, Gauss, and Stanton,[212] good agreement with experiment was obtained for H_2Se and SeCO, whereas a 40 ppm difference remains for CSe_2. For selenium shieldings, comparison with experiment is difficult since the solvent effects may be as large as 75 ppm (measured for CSe_2[213]) but also as small as 1 ppm (measured for SeF_6[214]). The anisotropies of the selenium shieldings were found to be in reasonable agreement with experiment. Using the MCSCF continuum model, Åstrand et al. have estimated the dielectric medium effects on the shieldings in H_2Se to be about 40 ppm for selenium and −0.5 ppm for hydrogen.[215]

Sundholm has presented an interesting application of ab initio methods to evaluate the structure of the thiocyanate products generated in the peroxide-catalyzed oxidation of SCN^-.[216] Comparing MP2 and CCSD nuclear shieldings and excitation energies with experimental observations, the molecular structure of the species produced in the reaction was determined.

In high-level calculations, the physical mechanisms underlying the behavior of nuclear shieldings is often lost. A nice illustration of how simple arguments, based on the electronic structure, may explain observed shieldings has been presented by van Wüllen and Kutzelnigg,[99] who studied the nuclear shieldings of carbenes. Let us assume that the prototype carbene CH_2 is located in the *xz* plane with the *z* axis along the main axis. By a simple analysis of the electronic structure, it can be predicted that the *xx* component of the carbon shielding should be strongly deshielded, whereas the *yy* component should not be significantly deshielded. These expectations were indeed confirmed by calculations.[99] Owing to the low $n-p_y$ energy gap in the carbenes, these molecules are likely to exhibit large static correlation effects. The correlation corrections predicted by Arduengo et al.[217] in DFT calculations are substantial, but in the opposite direction of what is expected and indeed found in the MCSCF/IGLO calculations of van Wüllen and Kutzelnigg. It appears that DFT does not handle well the static correlation effects in the CH_2 carbene.

Let us next discuss an example of a small molecule that still poses a challenge to modern electronic structure theory: ozone. This molecule is often considered to exhibit large static correlation effects, but significant dynamical correlation effects are also

Table 6. Isotropic Shieldings in Ozone (O_3) (in ppm)

		isotropic shieldings, ppm	
method	ref	$\sigma(O_{\mathrm{terminal}})$	$\sigma(O_{\mathrm{center}})$
SCF/IGLO	192	−2814	−2929
SCF/GIAO	62	−2785	−2716
MCSCF/IGLO[a]	192	−1153	−658
MCSCF/GIAO[b]	218	−1126	−703
MP2/GIAO	62	1007	2606
CCSD/GIAO	62	−1408	−986
CCSD(T)/GIAO	62	−1208	−755
experiment[c]		−1290, 1289(170)	−724, −625(240)

[a] Using a full-valence CASSCF wave function. [b] Using an extended RASSCF wave function. [c] The experimental data have been taken from Solomon et al.[219] and Cohen, Hillig, and Pickett,[220] respectively. The results of Solomon et al. have been converted to absolute shielding using 307.9 ppm for oxygen shielding in liquid water as a reference.[185]

present, making it difficult to find a method that can recover the full correlation effects. In Table 6, we have collected the results obtained for ozone using various MCSCF, Møller−Plesset, and coupled-cluster wave functions. In comparing the results in the table, it should be kept in mind that slightly different geometries have been used and that, because of a significant basis-set dependence, none of the calculations may be considered to be fully converged with respect to the basis set.

Whereas MP2 fails completely for this system, a significant improvement is observed at the CCSD level. At the more advanced CCSD(T) level, the agreement with experiment is reasonable but not yet satisfactory. In addition, the MCSCF wave function gives results in reasonable agreement with CCSD(T) and with experiment. The shieldings in ozone show a strong geometry dependence and rovibrational effects may be significant.[181,227] It is therefore difficult to judge more precisely the quality of these calculations.

We have seen that for nuclear shieldings, most correlated methods are capable of accounting for the major effects of electron correlation. The method of choice depends on the system under investigation and on the accuracy needed. In many cases, the relatively inexpensive MP2 method may be the method of choice although it tends to overestimate the correlation effects as indicated by the empirical scaling scheme eq 285. For molecules with large static correlation effects—for example, molecules with oxygen or nitrogen atoms in double or triple bonds—CCSD and MCSCF may be more suited. For such molecules or for molecules where certain mechanisms can be expected to dominate an observed shielding (e.g., the carbenes), small MCSCF wave functions may give reasonable results. The MCSCF wave function has the advantage that its optimization does not scale too steeply with the number of basis functions, provided a reasonably small active space can do a good job. However, unlike the Møller−Plesset or coupled-cluster approximation, MCSCF is not a "black-box" method since it requires the selection of an adequate active space.

The calculations of heavy-element shieldings are fewer than for atoms in the three first rows, the reasons being mainly the lack of adequate studies of basis set requirements, the extra computational cost due to the large number of electrons, potentially large electron correlation effects, and in particular the increasing importance of relativistic effects as one goes down in the periodic table. We shall return to the last point in section XI.

Nakatsuji and co-workers have presented several studies of the metal chemical shifts using FOBs and finite-perturbation theory[158,222] and have made important contributions to the understanding of the electronic mechanisms that determine the metal NMR chemical shift. Although good agreement with experiment has been demonstrated in many of these studies, this might be fortuitous, due to the neglect of correlation and solvent effects, as well as the use of somewhat inferior basis sets for these many-electron atoms.

In recent years, a number of DFT calculations of metal chemical shifts have been presented. However, it is beyond the scope of this review to discuss all these calculations and we refer instead to reviews devoted to DFT calculations of NMR parameters.[9,10] We note that even though "pure" DFT (with the Hartree−Fock exchange not included in the functional) in many cases performs well for transition-metal shieldings,[223] Bühl et al. have shown that proper Hartree−Fock exchange in some cases is mandatory for reproducing experimental shielding trends for some transition metal shieldings.[224,225] The reasons why the Hartree−Fock exchange must be included in the functional for these metal shieldings are still not fully understood.[194]

E. Shielding—Interpretation of the Results

In general, there is no unique way to describe or interpret the calculated shielding tensors. Although the methods described below do not necessarily provide an easy interpretation of the effects of an applied external magnetic field, they offer a model of the response of the molecule to this perturbation which may be used to rationalize the behavior of the nuclear shielding in different electronic environments.

Information relating the shielding constants to the molecular structure may be extracted from an analysis of the calculation itself. In the LORG and IGLO approaches, the use of localized orbitals enables a comparison of the individual bond contributions to the observed shielding constant. In a recent work, the natural-bond orbital (NBO) approach—where naturally localized MO's are defined to optimally describe the electron density between two centers (Lewis bonding orbital) or on a single center (lone pair)—has been combined with the use of GIAO's, providing a similar means of analysis in calculations using GIAO's.[226]

1. The Nuclear Shielding as a Tensor Property

The nuclear shielding is a tensor of rank 2. In an ab initio calculation, all the elements of this tensor are obtained, with the same approach (and, in principle, the same accuracy) for all components. In many cases it is sufficient to analyze the trace of the tensor for a comparison with experiment, but important information provided by the calculations may then be lost.

We can write the full rank-2 tensor as a sum of three tensors of rank 0, 1 and 2, respectively

$$\boldsymbol{\sigma} = \sigma_{\text{iso}}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} + \begin{bmatrix}0 & \sigma^{A}_{xy} & \sigma^{A}_{xz}\\ \sigma^{A}_{yx} & 0 & \sigma^{A}_{yz}\\ \sigma^{A}_{zx} & \sigma^{A}_{zy} & 0\end{bmatrix} + \begin{bmatrix}d_{xx} & d_{xy} & d_{xz}\\ d_{yx} & d_{yy} & d_{yz}\\ d_{zx} & d_{zy} & d_{zz}\end{bmatrix} \qquad (286)$$

where we have introduced the isotropic shielding σ of eq 4

$$\sigma_{\text{iso}} = {}^{1}/_{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \qquad (287)$$

the antisymmetry parameters

$$\sigma^{A}_{\mu\nu} = {}^{1}/_{2}(\sigma_{\mu\nu} - \sigma_{\nu\mu}) \qquad (288)$$

and finally the parameters

$$d_{\mu\nu} = {}^{1}/_{2}(\sigma_{\mu\nu} + \sigma_{\nu\mu} - 2\sigma_{\text{iso}}) \qquad (289)$$

We note that the rank-1 tensor is antisymmetric, and thus only contains three distinct elements, whereas the rank-2 tensor is symmetric and, with zero trace, has five independent elements. These definitions are discussed in more length in ref 227. Recently, a new standardized definition that relates the individual tensor components to the experimentally measured quantities has been proposed,[228] although it does not appear to have become popular in the literature.

In experiment it is very difficult to determine all the tensor elements. In the standard NMR experiments, only the symmetric part of the shielding tensor affects the spectrum (the rank-0 and rank-2 tensors in eq 286) and very few measurements of the antisymmetric part exist. We note, however, that an experimental study of the antisymmetry of the olefinic carbon atom in tetrachlorocyclopropene, C_3Cl_4[229] prompted a series of calculations.[142,144,145]

In most cases, the shielding tensors are expressed in the principal axis system, which is the coordinate system for which the rank-2 tensor is diagonal. In this case, the rank-1 tensor is disregarded and eq 286 reduces to

$$\boldsymbol{\sigma}^{\text{PAS}} = \sigma_{\text{iso}}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} + \begin{bmatrix}d^{\text{PAS}}_{xx} & 0 & 0\\ 0 & d^{\text{PAS}}_{yy} & 0\\ 0 & 0 & d^{\text{PAS}}_{zz}\end{bmatrix} \qquad (290)$$

The usual definitions of the anisotropy and asymmetry of the shielding are

$$\Delta\sigma = \sigma^{\text{PAS}}_{33} - {}^{1}/_{2}(\sigma^{\text{PAS}}_{11} + \sigma^{\text{PAS}}_{22}) \qquad (291)$$

and

$$\eta = \frac{(\sigma^{\text{PAS}}_{22} - \sigma^{\text{PAS}}_{11})}{(\sigma^{\text{PAS}}_{33} - \sigma_{\text{iso}})} \qquad (292)$$

where it is assumed that $\sigma^{\text{PAS}}_{33} \geq \sigma^{\text{PAS}}_{22} \geq \sigma^{\text{PAS}}_{11}$.

As demonstrated in a series of works by Facelli, Grant, Michl, and co-workers (see for example ref 230 and the review by Facelli in ref 11, and references therein) the calculated principal values and orientation of the principal axes provide useful information not available from experimental data. Such information gives a better understanding of the relations between the shielding tensor and the molecular structure than does the isotropic shielding on its own.

The anisotropy and asymmetry of the shielding tensor are difficult to measure and ab initio calculations may play a useful role in analyzing experimental data.[231] An example of a joint theoretical and experimental analysis of all the NMR properties—including tensor properties of the shielding, spin–spin coupling, and nuclear quadrupole coupling constants—is the recent study of formamide.[232] In another study, SCF calculations of the proton shielding tensors in the methyl group of methyl formate were used to compare the anisotropy and asymmetry with experimental data for a larger molecule.[233]

Pictorial representations of the shielding tensor were recently discussed in ref 234. In particular, the ellipsoidal representations of the symmetric part of the shielding tensor were compared with those representing the full tensor. The difference between two tensors (e.g., the change in the shielding tensor upon solvation) can be depicted in the same way.

2. The Current Density and the Nuclear Shielding

Other methods of interpreting magnetic-field effects concentrate on the field-induced changes in the electronic structure. A convenient way to illustrate these effects is to depict the field-induced current densities. Within perturbation theory, the current density $\mathbf{j}^{(1)}(\mathbf{r})$ for a nondegenerate reference state $\Psi^{(0)}$ is given by

$$\mathbf{j}^{(1)}(\mathbf{r}) = -i(\Psi^{(0)*}(\mathbf{r})\nabla\Psi^{(1)}(\mathbf{r}) - \Psi^{(1)*}(\mathbf{r})\nabla\Psi^{(0)}(\mathbf{r})) - \alpha\mathbf{A}(\mathbf{r})\Psi^{(0)*}(\mathbf{r})\Psi^{(0)}(\mathbf{r}) \qquad (293)$$

where the first term represents the paramagnetic and the second the diamagnetic part of the vector current density. We here note that only the total current density is gauge-independent—its partitioning may depend on the gauge. The induced current densities do not depend on the magnetic properties of individual nuclei, the perturbation considered is the external field only. The shielding of nucleus K can be related to the current density through the equation

$$\boldsymbol{\sigma}_K\mathbf{B} = -\alpha\int\frac{(\mathbf{r} - \mathbf{r}_K)\times\mathbf{j}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_K|^3}\,d\mathbf{r} \qquad (294)$$

The integrand in this equation has by Jameson and Buckingham been called the nuclear magnetic shielding density,[235,236] and they have suggested how to depict this density.

Examples of an analysis of induced currents and, in particular, their dependence on molecular symmetry, have been given by Lazzeretti et al.[237] More recently, induced current densities were discussed using the description of atoms in molecules[238] and again the topological aspects of these currents were analyzed.[239] It would be interesting to repeat such an analysis using more accurate methods that include correlation effects.

The calculation of ring currents has been particularly popular for aromatic molecules. These currents can now be computed, and for example the role of σ and π orbitals has been analyzed (see refs 240 and 241 for recent examples). We note, however, that Bilde and Hansen have suggested that the special magnetic properties of aromatic molecules do not arise from diamagnetic ring currents but rather from the absence of paramagnetic components in the π-electron contribution, which is a topological feature rather than a characteristic of aromatic molecules.[242]

The shielding can in principle be defined and calculated for any point in space. This feature has recently been used to analyze the effect of a magnetic field by Woliński[243] and by Schleyer et al.,[244] who studied the shielding at the center of a ring, and furthermore proposed this as a measure of aromaticity.

IX. Spin–Spin Coupling Constants

A. The Hydrogen Molecule

Not surprisingly, the most accurate calculations of nuclear spin−spin coupling constants have been carried out for H_2. For ease of comparison with experimental data, the spin−spin coupling constant of this molecule is usually reported for the HD isotopomer. For a fixed bond distance, the couplings for the other isotopomers are obtained from the magnetogyric ratios.

It has for a long time been known that electron correlation effects must be included to obtain a reasonable value of J(HD).[245] As examples of more recent work, we mention the CCSDPPA calculations of Oddershede, Geertsen, and Scuseria[167] and the MCSCF calculations of Vahtras et al.[246] In both papers, all four contributions to the coupling constant were analyzed. In the former, a study of the basis-set dependence of the Fermi-contact contribution demonstrated that convergence is slow, making it difficult to establish the basis-set limit. For example, whereas a (11s,5p,2d) GTO basis with the largest s orbital exponent equal to 5000 yields $J^{FC} = 39.24$ Hz, further addition of a single s-type function with an exponent of 15000 gives 39.69 Hz. For convergence, exponents up to 150 000 must be included.

In the work of Vahtras et al.,[246] various MCSCF wave functions were used. For a small basis, the MCSCF results were compared with FCI values. The final value of J^{FC} given by Vahtras et al. is 40.243 Hz. The differences among the various results in this work and those in ref 167 are 0.1−0.3 Hz.

For an accurate comparison of the calculated coupling constants with experiment, rotation, vibration, and temperature effects must be taken into account. The analysis of ref 246 shows that for the lowest rovibrational level, there are significant corrections to the $R = 1.4\ a_0$ value of $J = 41.21$ Hz, the $J(v{=}N{=}0)$ value being 43.17 Hz. The temperature dependence is, however, rather weak and at $T = 40$ K the coupling is 43.18 Hz. The rovibrational corrections in ref 167 are very similar.

There are two experimental values for the HD molecule: 42.94 ± 0.04[247] and 43.11 ± 0.02 Hz.[248] Although the ab initio results are closer to the latter number, more elaborate calculations would be required to refute one of the two experimental numbers.

B. Diatomic Molecules

Many aspects of the calculation of spin−spin coupling constants have been analyzed in numerous studies of the spin−spin coupling in HF. Thus, the choice of basis set was discussed in section XII.B and the rovibrational dependence of this constant is considered in section XII.C. Some results for HF are given also in the next section, where we compare various calculations on the second-row, 10-electron hydrides.

Different methods have been applied to study the indirect nuclear spin−spin coupling constants of N_2 and CO. For these isoelectronic systems, the indirect spin−spin coupling is (at the equilibrium geometry) dominated by the PSO contribution. The SOPPA,[169] MCSCF,[249] and EOM-CCSD[107] calculations all give similar values for the total coupling constants of these systems. For example, the results for $J(^{13}C^{17}O)$ are 18.23, 16.10, and 15.5 Hz, respectively, which should be compared with the experimental value of 16.4 ± 0.1 Hz. For N_2, the coupling constant is rather small and the accuracy of the experimental number for $J(^{14}N^{15}N)$ is not very high. For both molecules, there is a strong dependence of the coupling on the interatomic distance.

The nuclear spin−spin coupling constant has been computed also for other diatomics such as BH and AlH.[250]

C. Second-Row Hydrides

Most methods developed for the calculation of spin−spin coupling constants have been applied to these small molecules. A comparison of the results for the second-row hydrides (HF, H_2O, NH_3, and CH_4) illustrates some aspects of the practical application of these methods. For easy comparison with experiment, we here give the constants in hertz, but it should be kept in mind that the relative accuracy of the calculations is best judged by comparing the reduced coupling constants of eq 6, which, for all the one-bond couplings of these molecules, are of the same order of magnitude.

As shown in Table 7, the improvement of the ab initio results is primarily related to improved treatments of correlation effects. There are, however, difficulties in obtaining saturated basis sets for the spin−spin coupling constants, as reflected by the significant variations observed already at the (unreliable) SCF level. An example is $^1J^{FC}$(CH), for which

Table 7. Total Spin−Spin Coupling Constants in HF, H_2O, NH_3, and CH_4 and the Fermi Contact Contributions, FC (in Hz)[a]

HF

	SCF[107]	FPT-MP2[251]	CCSDPPA[252]	EOM-CCSD[b,107]	CASSCF[c,172]	DFT[d,31]	exp
^{1}J(FH)	654.1	570.01	524.3	513.4	542.60	396.24	500 ± 20
FC	467.5	390.71	329.4	338.2	359.84	198.0	

H_2O

	SCF[107]	FPT-MP2[251]	SOPPA-(CCSD)[253]	EOM-CCSD[b,107]	CASSCF[253]	DFT[31]	exp
^{1}J(OH)	−95.44	−74.73	−81.555	−74.90	−83.934		−80.6 ± 0.1
FC	−84.74	−64.61	−69.092	−65.45	−72.083	−56.2	
^{2}J(HH)	−22.44	−18.33	−8.581	−10.81	−9.602		−7.11 ± 0.03
FC	−23.23	−19.69	−11.866	−11.12	−12.702		

NH_3

	SCF[107]	FPT-MP2[251]		EOM-CCSD[b,107]	CASSCF[e]	DFT[31]	exp
^{1}J(NH)	52.78	42.81		41.81	42.25		43.6
FC	50.99	41.02		40.19	40.10	36.9	
^{2}J(HH)	−23.55	−19.90		−12.09	−9.77		−10.0
FC	−23.60	−20.05		−11.72	−11.21		

CH_4

	SCF[246]	FPT-MP2[251]	CCSDPPA[254]	EOM[f,255]	CASSCF[e]	DFT[30]	exp
^{1}J(CH)	157.31	130.63	123.865	115.36	116.65	131.39	120.78 ±.05
FC	155.90	129.27	122.124	113.84	114.82	129.44	
^{2}J(HH)	−27.16	−21.04	−14.308	−15.80	−13.22	−13.08	−12.564 ± 0.04
FC	−27.69	−20.53	−14.701	−15.51	−13.80	−13.31	

[a] The constants are given for ^{1}H, ^{19}F, ^{17}O, ^{14}N, and ^{13}C for assumed equilibrium geometries. Experimental data quoted after refs: 256 (HF), 107 (NH_3), 257 (H_2O), 246 (CH_4). [b] For a description of this approximation, see ref 107 and section VI.D.4. [c] All the tabulated CASSCF results were obtained with CAS 6331 wavefunctions. [d] In the DFT calculations for HF and CH_4, the SD contribution was omitted. [e] Unpublished CAS results obtained for this review (CAS 6331, HIV basis set). [f] The EOM calculations of Fronzoni and Galasso, see ref 255 for the results for some other molecules.

138.82 Hz was reported in ref 255, whereas large basis sets yield values closer to those given in Table 7—for example in ref 254, 155.57 Hz. Basis set effects of a few Hz are observed also at the CASSCF level, comparing for instance the results for $^{1}J^{FC}$(OH) and $^{2}J^{FC}$(HH) in ref 172 and 253. In Table 7, we have given the more recent values, which are likely to be close to the SCF limit (at the given geometry). Unfortunately, the basis-set error in these calculations makes a precise comparison of the correlated methods difficult.

For all the constants in Table 7, the correlated results are significantly closer to experiment than are the SCF values. For the DFT approach, the improvement is not very systematic; for the other methods, the agreement with experiment is more regular. Thus, the recent EOM-CCSD, SOPPA(CCSD), and CASSCF calculations yield better results than do the older, more approximate schemes. The differences between the calculated numbers reflect mainly the difference in the Fermi-contact term. However, although the noncontact contributions are often small, their inclusion in accurate calculations brings each calculated coupling constant into closer agreement with experiment.

The agreement of the EOM-CCSD, SOPPA(CCSD), and CASSCF results suggests that these calculations are rather accurate. For a more critical comparison, however, it is better to compare the individual contributions rather than the total coupling constants as a cancellation of errors may otherwise lead to false conclusions. For the HF molecule, for example, the total EOM-CCSD[107] and CAS 6331, HIV basis set constants are similar—513.4 and 510.21 Hz—but the corresponding PSO values are 176.2 and 181.5 Hz. The agreement for the total coupling constant must therefore be considered accidental.

In summary, for the first-row hydrides and for similar small molecules, the accuracy of the calculated coupling constants is approximately 5−10%, whereas, for HD, an accuracy of about 1% has been reached. Even when the coupling constants appear to be accurate, it is difficult to demonstrate that further improvements in the wave function will not affect the calculated spin−spin coupling constants. For these reasons, we consider 10% a fair estimate of the accuracy of state-of-the-art calculations of spin−spin couplings for such systems.

Finally, we emphasize that, for a comparison with experiment, rovibrational effects must be included as well, being of similar magnitude as the differences between the best tabulated ab initio results and experiment. Moreover, even though the solvent effects for the spin−spin couplings are often smaller than for the shieldings, it is difficult to say how well the calculated values for isolated molecules compare with liquid-phase experimental data.

D. Larger Molecules

In contrast to the calculation of the shielding constants, the number of response equations to be solved for the spin−spin coupling constants increases with the number of magnetically active nuclei in the molecule. For each nucleus considered, there are 10 independent response equations to be solved (6 SD,

Table 8. Spin−Spin Coupling Constants in C_2H_4 (in Hz)

	FV CAS[a]	RAS-I[a]	RAS-II[a]	FPT-MCSCF[b]	EOM-CCSD[c]	exp[d]
^{1}J(CC)	75.7	73.3	69.5	71.9	70.1	67.457
^{1}J(CH)	155.7	154.4	154.0	146.6	153.23	156.302
^{2}J(CH)	−5.8	−5.5	−3.0	−3.0	−2.95	−2.403
^{2}J(HH)	−2.4	−0.4	1.3	−2.7	0.44	2.394
^{3}J(HH-cis)	12.4	12.2	11.6	10.9	11.57	11.657
^{3}J(HH-trans)	18.4	18.8	18.5	18.1	17.80	19.015

[a] Unpublished results obtained for this review: Basis sets, FV CAS and RAS−I, qz + 2d1f from ACES II,[82] 158 CGTOs; in RAS−II—one tight s_C and s_H orbitals added; active spaces, the core orbitals are inactive, FV CAS is full valence CASSCF; in terms of D_{2h} orbitals of symmetry a_g, b_{3u}, b_{2u}, b_{1g}, b_{1u}, b_{2g}, b_{3g}, a_u and in the notation (RAS1/RAS2/RAS3) RAS-I = (00000000/21101100/54325321), maximum 2 electrons in RAS3; and RAS-II = (21101100/11002110/43212211), maximum 4 holes in RAS1, 2 electrons in RAS3. [b] Reference 91. [c] References 259 and 108. [d] Reference 260.

3 PSO, and 1 FC). Clearly, for large polyatomic molecules, the evaluation of the full set of spin−spin coupling constants becomes time-consuming if all the constants are required. Fortunately, in experimental work, one is rarely interested in all the coupling constants of a large molecular system and one may of course in such cases compute only those parameters that are of interest.

The most consistent approach is to evaluate all the contributions (DSO, PSO, SD, and FC) to each coupling of interest using the same wave function—that is, with the same basis set and the same correlation treatment. However, it may sometimes be useful to apply different wave functions to the different contributions. For example, in many cases, the largest contributions to the coupling constants are those from the FC operator, and these may be obtained from the solution of a single set of response equations for each nucleus. In contrast, the SD operator usually makes only a very small contribution to the total coupling constant, but requires the solution of as many as six response equations for each nucleus. It would be a waste of computer resources to compute the expensive, but small, SD contributions using the same wave function as for the (relatively) inexpensive but large FC contributions. For larger systems, therefore, it makes good sense to adopt a flexible approach, where basis-set and perhaps correlation treatments are different for the different contributions to the coupling constants. Obviously, for this approach to work, preliminary calculations must be carried out at an inexpensive level in order to estimate the magnitude of the various contributions.

A circumstance that compounds the difficulties associated with the evaluation of spin−spin coupling constants for large molecules is the inadequacy of the Hartree−Fock method for the calculation of these couplings. The inadequacy of the Hartree−Fock treatment is most prominent for the contributions that are mediated by the triplet perturbations (i.e., the SD and FC contributions) and arises since the restricted Hartree−Fock model cannot properly describe triplet perturbations of the wave function. Significant correlation effects may occur for the (usually small) noncontact contributions as well. Such effects have been observed in molecules such as diazirine[170] and N_2F_2.[258] For electron-rich molecules, it is undoubtedly better to consider at least the main correlation effects also for the PSO and SD contributions.

Table 9. Spin−Spin Coupling Constants in CH_3CN (in Hz)[a]

	SCF	CASSCF[b]	RASSCF[b]	EOM-CCSD	exp
^{1}J(CC)	128.10	91.96	71.79	*c*	58.0
^{1}J(CN)	−99.50	−30.94	−21.55	−17.20	−17.8
^{1}J(CH)	168.25	156.94	142.43	125.69	135.73
^{2}J(CN)	15.90	2.41	2.82	3.08	2.9
^{2}J(CH)	−59.13	−21.26	−15.46	−10.44	−9.94
^{3}J(NH)	−16.76	−2.64	−2.03	−1.33	−1.63
^{2}J(HH)	−38.67	−27.82	−22.91	−16.63	−16.9

[a] For a discussion of SCF, CASSCF, and RASSCF calculations and of the experimental data see ref 171; EOM-CCSD results are from ref 108. [b] In the RASSCF more active orbitals are included than in the CASSCF. [c] Not given.

In Table 8, we have listed the full set of spin−spin coupling constants in ethylene, calculated using three MCSCF wave functions, as well as relatively old (1983) finite-perturbation results[91] (with a simple MCSCF wave function), and the EOM-CCSD values.[108,259] The MCSCF results demonstrate that it is not sufficient to include the valence orbitals in the active space. The results labeled RAS-II, obtained using an enlarged active space for the most important FC contribution, appear to be the most accurate—in particular when the coupling to hydrogen atoms is considered. Even though the differences between the various methods are relatively small, all six coupling constants of the RAS-II and five in EOM-CC calculations are in better agreement with experiment than are the 1983 results. On the other hand, the differences between RAS-II, EOM-CC, and experiment are too small for any definite conclusions to be drawn. For this purpose, one would need to analyze the basis-set and geometry differences more carefully and also to estimate the rovibrational corrections to the coupling constants.

The spin−spin coupling constants in CH_3CN have been analyzed using both MCSCF wave functions[171] and the EOM-CCSD approximation.[108] As shown in Table 9, the SCF results[171] are completely wrong. The first MCSCF calculation, incorporating in the CAS space only two additional valence orbitals, gives reasonable results for most of the constants. A systematic improvement is observed in the RASSCF calculation, which gives a better estimate of the valence-shell correlation effects. Further extrapolation would bring all seven constants closer to experiment and the correlation corrections are apparently underestimated in both calculations. The EOM-CCSD calculation[108] takes into account a larger fraction of the dynamical correlation effects than does

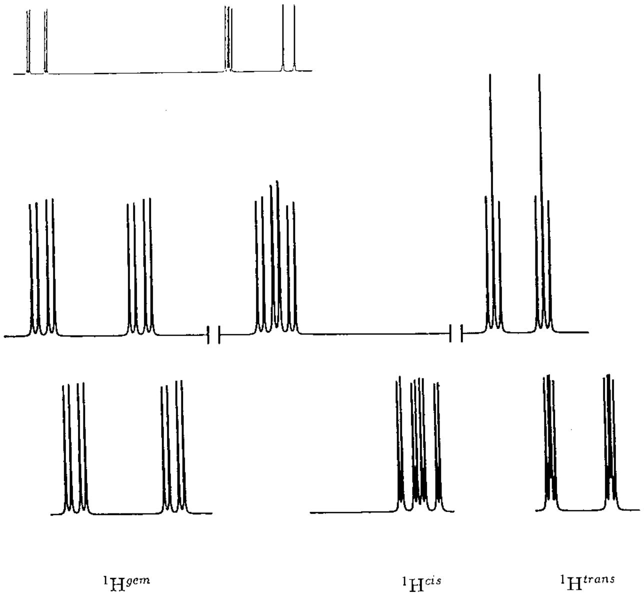

Figure 3. Simulated 500 MHz proton NMR spectra of C_2H_3F: (top) ab initio values of shielding and spin−spin coupling constants and (bottom) experimental values of shielding and spin−spin coupling constants. The relevant parts of the spectrum are enlarged, the insert shows the full spectrum for the experimental constants.

the RASSCF wave function and the results are also in better agreement with the experimental values.

For C_2H_3F, all the NMR parameters have been computed in the MCSCF approximation.[261] For all 15 spin−spin coupling constants, the agreement with known or estimated experimental values is satisfactory. The convergence of the results with the increase of the MCSCF active space and with the improvement of the basis set is slow. Obviously, the best results are obtained for those constants for which these two modifications have opposite effects on the coupling. For the other couplings, convergence is slow. Simulated proton spectra derived from the experimental and calculated NMR parameters are shown in Figure 3.

Other polyatomic molecules studied using MCSCF wave functions are vinyllithium,[262] cyclopropene,[263] a group of isoelectronic molecules including four isomers of CH_2N_2, HN_3,[170] CH_3CN and CH_3NC[171] and ethane, ethene, and ethyne.[260] In general, the results are in good agreement with experimental data, enabling a confident prediction of the sign of the larger spin−spin coupling constants. Ab initio results may be particularly useful when the experimental data are difficult to obtain—for example, when tensor properties of the spin−spin couplings are analyzed.[171,260] For N_2F_2, it has been shown that calculations can be easily applied to interpret the spectrum of an $[AX]_2$ spin system.[258] In an MCSCF study of benzene,[264] it was observed that too large values are usually obtained both for the averages of the couplings and for the anisotropies. Although the calculated couplings decrease with extension of the basis set and of the active space, it was not possible to converge the results. The calculated signs of the anisotropies $\Delta^n J(CC)$ are correct, but the magnitudes are thus overestimated.

As early as in 1987, ab initio (IGLO SCF) values of the shielding constants were used to analyze the structure of carbocations.[265] More recently, the EOM-CCSD results obtained for the spin−spin coupling constants in the $C_2H_5^+$ [266] and 2-norbornyl cations[267] were used in a similar study. The results obtained for the bridged, nonclassical structure of the cations are in good agreement with the experimental data. For such many-electron systems, which are well described by a single-determinant wave function, EOM-CCSD appears at present to be the most accurate approach.

Galasso has applied his EOM method (see section VI.F) to compute spin−spin coupling constants in a large number of polyatomic molecules—see ref 268. Most of the recent results are for the $^1J(CC)$ constants across unusual bonds in hydrocarbons, like the bridgehead bond in propellanes[269] or the ultrashort bond in bitetrahedrane.[270] The $^1J(CC)$ values are very sensitive to the geometry variations and confirm the unusual nature of the bonds in these molecules.

Finite-perturbation theory (FPT) can be applied, in principle, with any correlated wave function. Although all the contributions may be included (see ref 271), most often only the Fermi contact term has been considered, enabling calculations using correlated methods such as QCISD(T) for fairly large molecules. The results for hydrocarbons[29,272] and carbohydrates indicate that this may be a reasonable approach.

The DFT approach has been applied also to study spin−spin coupling constants, although it has not attracted the same attention as the calculation of nuclear shieldings. A summary of the present status and problems of spin−spin coupling calculations using the FPT/DFT approach was recently given by Malkina, Salahub, and Malkin.[30]

Little is known about the tensor properties of spin−spin coupling constants (see ref 273 for a general discussion of the symmetry rules). The anisotropy of the spin−spin coupling constant is difficult to measure experimentally and ab initio calculations can therefore be helpful (see refs 171 and 264 for some applications). We note that in the calculations of the anisotropy, the mixed SD-FC term (which vanishes for the isotropic couplings) often makes the dominant contribution.

X. NMR-Related Properties

In NMR, we observe the interaction of nuclear magnetic moments with an externally applied magnetic field. The nuclear magnetic moments may interact also with the magnetic field induced by the molecular rotation, giving rise to the spin−rotation corrections to molecular rotational energy levels

$$\Delta E_K = -\mathbf{I}_K^T M_K \mathbf{J} \tag{295}$$

where M_K is the spin−rotation constant of nucleus K and $\mathbf{J}$ is the total rotational angular momentum. The spin−rotation constant can thus be calculated as the energy derivative

$$M_K = -\frac{\partial^2 E}{\partial \mathbf{I}_K\, \partial \mathbf{J}} = -\gamma_K \frac{\partial^2 E}{\partial \mathbf{M}_K\, \partial \mathbf{J}} \qquad (296)$$

The overall rotation of the molecule induces an electronic magnetic moment which can be written

$$\left.\frac{\mathrm{d}H}{\mathrm{d}\mathbf{J}}\right|_{\mathbf{J}=0} = -\frac{1}{I}\sum_i \mathbf{l}_{iK} = -\frac{2}{I}\left.\frac{\partial H(\mathbf{O}{=}\mathbf{R}_K)}{\partial \mathbf{B}}\right|_{\mathbf{B}=0} \qquad (297)$$

where I is the moment of inertia tensor, and where we have indicated that the nucleus of interest is used as gauge origin. Since there is no term that is bilinear in molecular rotation and nuclear magnetic moments in the electronic Hamiltonian, we may write

$$M_K^{\mathrm{el}} = \frac{2\gamma_K}{I}\sigma_K^{\mathrm{para}}(\mathbf{O}{=}\mathbf{R}_K) = \frac{2\gamma_K}{I}[\sigma_K - \sigma_K^{\mathrm{dia}}(\mathbf{O}{=}\mathbf{R}_K)] \qquad (298)$$

using eq 47. The contribution from the nuclear framework is[274]

$$M_K^{\mathrm{nuc}} = \alpha^2\frac{\gamma_K}{I}\sum_{L\neq K}\frac{Z_L}{R_{LK}^3}[R_{LK}^2\mathbf{1} - \mathbf{R}_{LK}\mathbf{R}_{LK}^T] \qquad (299)$$

If the assumptions made in the Born–Oppenheimer approximation were satisfied exactly—that is, if the electrons adjusted themselves instantaneously to changes in the nuclear positions—the electronic and nuclear contributions would cancel each other identically. The spin–rotation constants are thus nonadiabatic effects, appearing due to the breakdown of the Born–Oppenheimer approximation.

Equation 298 is valid irrespective of the method used to solve the gauge origin dependence and was used by Ditchfield to calculate the spin–rotation constant of HF and LiH using GIAO's[44] and Sundholm et al. for H_2.[176] Gauss, Ruud, and Helgaker have derived eq 298 using rotational London atomic orbitals.[275]

For light nuclei, the small Thomas precession must be taken into account for nonequilibrium geometries.[276,277] For a diatomic molecule this correction may be written as

$$M_K^{\mathrm{Thomas}} = \frac{\alpha^2}{4\pi {m_K}^2 R}\frac{\mathrm{d}E}{\mathrm{d}R} \qquad (300)$$

where m_K is the nuclear mass and $\mathrm{d}E/\mathrm{d}R$ the force acting on nucleus K. The Thomas precession is a relativistic effect.[274,278] Because of the ${m_K}^{-2}$ dependence, this effect is more important for light than heavy nuclei.

Spin–rotation constants may be accurately determined from microwave experiments—a technique pioneered by Flygare and co-workers[274,279]—and in molecular beam experiments.[186,280] Combined with theoretically calculated diamagnetic shieldings, this approach represents the most accurate way to obtain absolute shielding scales[274] (see also section XII.B).

Spin–rotation constants are also available from measurements of NMR relaxation times. The spin–lattice relaxation rate due to spin–rotation interactions $R_{SR}(K)$ is proportional to the square of the spin–rotation constant and linearly dependent on the temperature and can in the extreme narrowing condition (i.e., ignoring the width of the observed peak) be written as[14]

$$R_{SR}(K) = {}^4/_3 IkTM_K^{\,2}\tau_{SR} \qquad (301)$$

Here k is the Boltzmann constant, T the temperature, and τ_{SR} the correlation time for the spin–rotation relaxation. The spin–rotation relaxation can be estimated from relaxation-time measurements at different temperatures.

For quadrupolar nuclei—that is, nuclei with $I_K > {}^1/_2$—the dominating relaxation mechanism is governed by the nuclear quadrupole moment, and the relaxation rate $R_Q(K)$ is, in the extreme narrowing condition, given by[14]

$$R_Q(K) = \frac{3\pi^2}{2}\frac{2I_K + 3}{I_K^2(2I_K - 1)}(q_K\langle V_K\rangle)^2\tau_C \qquad (302)$$

where the Nuclear Quadrupole Coupling Constant (NQCC) is equal to $-q_K\langle V_K\rangle$ and τ_C is the correlation time for the quadrupole coupling relaxation. We denoted as q_K the electric quadrupole moment of the nucleus, and $\langle V_K\rangle$ is the electric field gradient at the nucleus K, which is evaluated as an expectation value of the Hamiltonian

$$V_K = -\sum_i \frac{3r_{iK}^2\mathbf{1} - \mathbf{r}_{iK}^T\mathbf{r}_{iK}}{r_{iK}^5} + \frac{1}{2}\sum_{L\neq K}\frac{3R_{KL}^2\mathbf{1} - \mathbf{R}_{KL}^T\mathbf{R}_{KL}}{R_{KL}^5} \qquad (303)$$

We also note that the line width of the NMR signal for quadrupolar nuclei is dominated by the quadrupole moment through a relation similar to that for the relaxation time

$$\Delta\nu_{1/2} = \frac{3}{10}\pi\frac{2I_K + 3}{I_K^2(2I_K - 1)}(q_K\langle V_K\rangle)^2\tau_C \qquad (304)$$

where $\Delta\nu_{1/2}$ is the width of the peak at half the maximum intensity. The electric field gradient at a nucleus is more easily obtainable from ab initio calculations than are the nuclear shielding and spin–spin coupling constants since it is an expectation value of the unperturbed wave function only. Because of the ${r_K}^{-3}$ dependence, the accurate determination of nuclear quadrupole coupling constants requires, however, an accurate description of the region close to the nuclei.[281]

The nuclear shielding and spin–spin coupling constant depend on external or internal perturbations $\mathbf{x}$, and we may express this dependence by a Taylor series

$$\sigma_K = \sigma_K^{(0)} + \left.\frac{\partial \sigma_K}{\partial \mathbf{x}}\right|_{\mathbf{x}=0} \mathbf{x} + \frac{1}{2}\left.\frac{\partial^2 \sigma_K}{\partial \mathbf{x}^2}\right|_{\mathbf{x}=0} \mathbf{x}^2 + ... \quad (305)$$

$$J_{KL} = J_{KL}^{(0)} + \left.\frac{\partial J_{KL}}{\partial \mathbf{x}}\right|_{\mathbf{x}=0} \mathbf{x} + \frac{1}{2}\left.\frac{\partial^2 J_{KL}}{\partial \mathbf{x}^2}\right|_{\mathbf{x}=0} \mathbf{x}^2 + ... \quad (306)$$

By computing the various shielding and spin–spin coupling derivatives in eqs 305 and 306, information about the effects of additional perturbations on shieldings and spin–spin couplings may be obtained.

If the nuclear shieldings and spin–spin couplings are expanded with respect to nuclear distortions, we obtain the parameters that determine shielding and spin–spin coupling surfaces, important for investigating the effects of molecular rotation and vibration. We shall return to a more thorough discussion of property surfaces in section XII.

The derivatives of the nuclear shieldings with respect to an electric field, called shielding polarizabilities, may be used to investigate the effects of intra- and intermolecular interactions as well as give some indication of the effects of a surrounding solvent.[282] We return to shielding polarizabilities in section XIII.B.

The effects of applied magnetic fields on nuclear shieldings and spin–spin couplings have also been estimated. Ramsey was the first to point out the possible magnetic-field dependence of the nuclear shieldings,[283] and an estimate as well as an experimental determination were presented by Bendall and co-workers.[284,285] Raynes and Stevens estimated a change of 0.001 Hz in the spin–spin coupling in fields with a strength of 14 T, which they believe may be observable in experiments.[286] The only ab initio calculation has been done for the nuclear shielding of H^-.[287]

XI. Relativistic Effects

A. Relativistic Effects on NMR Parameters

The operators that determine the nuclear magnetic shielding and spin–spin coupling constants sample the regions close to the nuclei. For this reason, changes in the electronic structure due to relativistic effects are important for these properties. As an example, we note that the relativistic correction to the hydrogen shielding in hydrogen iodide is about 12 ppm,[288] an effect that exceeds the normal shielding range of protons. For the shielding of heavy elements, the neglect of scalar relativistic effects leads to an underestimation of the tungsten shielding by almost a factor of 3.[289] Thus, in calculations of the shieldings of molecules containing heavy elements, relativistic effects must be taken into account to obtain even qualitative agreement with experimentally observed trends.[290]

Relativistic effects on molecular properties are often classified as *direct* or *indirect*. The direct effects arise directly from relativistic corrections to the electronic structure, at a fixed molecular geometry. The indirect effects, on the other hand, arise from the changes in molecular geometry caused by the changes in the electronic structure when the effects of relativity are taken into account.

In the Breit–Pauli approximation, the dominant relativistic effects on nuclear shielding and spin–spin coupling constants arise from three Hamiltonian corrections; the mass-velocity operator

$$h^{\mathrm{mv}} = -\frac{\alpha^2}{8}\sum_i \pi_i^4 \quad (307)$$

where $\boldsymbol{\pi}_i$ is the kinetic momentum of eq 24, the Darwin operator

$$h^{\mathrm{Dar}} = \frac{\pi\alpha^2}{2}\sum_{iN}\delta(\mathbf{r}_{iN}) \quad (308)$$

and finally the spin–orbit operator

$$\mathbf{h}^{\mathrm{so}} = \frac{\alpha^2}{2}\left(\sum_{iA} Z_A \frac{\mathbf{l}_{iA}\cdot\mathbf{s}_i}{r_{iA}^3} + \sum_{ij}\frac{\mathbf{l}_{ij}(\mathbf{s}_i + 2\mathbf{s}_j)}{r_{ij}^3}\right) \quad (309)$$

where we have introduced the two-electron angular momentum operator

$$\mathbf{l}_{ij} = \mathbf{r}_{ij} \times \boldsymbol{\pi}_i \quad (310)$$

All of these operators yield contributions of second-order in α to the energy. The different terms have well-established interpretations, with the mass–velocity and Darwin corrections being the main relativistic corrections to the kinetic energy and to the nuclear-attraction energy, respectively. The spin–orbit correction describes the coupling between the electron spin and the orbital angular momentum of the electrons. The field-dependence of the spin–orbit operator has been studied by Fukui, Baba, and Inomata[291] and shown to be important for the shieldings of heavy elements.

It is common to refer to effects arising from the mass–velocity and Darwin operators as scalar relativistic effects, as these do not involve the electronic spin. In the vicinity of the nucleus, these scalar relativistic effects dominate. Still, it is difficult to know a priori whether the scalar relativistic corrections or the spin–orbit correction will dominate the relativistic effects on shielding and spin–spin coupling constants.

To investigate the main relativistic corrections to the nuclear shielding and spin–spin coupling constants starting from a nonrelativistic framework, we may consider the wave function correct to first-order in the mass–velocity, Darwin, and spin–orbit operators

$$|\Psi\rangle = |0\rangle - \sum_{n_S \neq 0}\frac{\langle n_S|h^{\mathrm{mv}} + h^{\mathrm{Dar}}|0\rangle}{E_{n_S} - E_0}|n_S\rangle - \sum_{n_T}\frac{\langle n_T|\mathbf{h}^{\mathrm{so}}|0\rangle}{E_{n_T} - E_0}|n_T\rangle \quad (311)$$

Inserting this wave function into the Ramsey equations for the nuclear shielding eq 49, we obtain the following equation for the relativistically corrected nuclear shieldings

$$\begin{aligned}\boldsymbol{\sigma}_K = \langle 0|\mathbf{h}^{\mathrm{dia}}_{BK}|0\rangle - 2\sum_{n_S\neq 0}\frac{\langle 0|\mathbf{h}^{\mathrm{orb}}_{B}|n_S\rangle\langle n_S|(\mathbf{h}^{\mathrm{pso}}_{K})^T|0\rangle}{E_{n_S}-E_0} - \\ \sum_{n_S\neq 0}\frac{\langle 0|\mathbf{h}^{\mathrm{dia}}_{BK}|n_S\rangle\langle n_S|h^{\mathrm{mv}}+h^{\mathrm{Dar}}|0\rangle}{E_{n_S}-E_0} + \\ 2\sum_{\substack{n_S,\\ m_S\neq 0}}\frac{\langle 0|\mathbf{h}^{\mathrm{orb}}_{B}|m_S\rangle\langle m_S|(\mathbf{h}^{\mathrm{pso}}_{K})^T|n_S\rangle\langle n_S|h^{\mathrm{mv}}+h^{\mathrm{Dar}}|0\rangle}{(E_{n_S}-E_0)(E_{m_S}-E_0)} + \\ 2\sum_{\substack{n_S\neq 0,\\ m_T}}\frac{\langle 0|\mathbf{h}^{\mathrm{orb}}_{B}|n_S\rangle\langle n_S|(\mathbf{h}^{\mathrm{fc}}_{K})^T+(\mathbf{h}^{\mathrm{sd}}_{K})^T|m_T\rangle\langle m_T|\mathbf{h}^{\mathrm{so}}|0\rangle}{(E_{n_S}-E_0)(E_{m_T}-E_0)}\end{aligned} \tag{312}$$

where, in the spin–orbit contribution, a sum over the spin components should be performed. In this expression, we have included all contributions bilinear in the external magnetic field induction and the nuclear magnetic moments, and we have taken the spin symmetry of the different operators into account when determining the nonvanishing contributions. Similar expressions can be derived for the indirect spin–spin coupling constants, but due to the larger number of contributions to the nonrelativistic coupling we do not write these explicitly here. The contributions to the spin–orbit corrected spin–spin coupling constant have been discussed and calculated by Kirpekar, Jensen, and Oddershede.[292]

As the mass–velocity and Darwin operators can perturb the electronic wave function significantly if heavy elements are present in the molecule, perturbation theory may not be adequate for the study of scalar relativistic effects. In the literature, this potential instability of the perturbation approach has been circumvented in three different ways: (1) using quasi-relativistic effective core potentials (RECP),[293] (2) using the frozen-core approximation,[294] and (3) using the spin-free relativistic Hamiltonian obtained from the no-pair approximation.[295,296]

In the quasi-relativistic effective core potentials, the scalar relativistic effects are included in the effective core potential. However, because NMR parameters depend critically on the electron density in the nuclear region—which may not be accurately modeled by the RECP—this approach cannot be expected to perform well for the shielding of the heavy atom itself. For this reason, RECPs have been used in molecular calculations to study only the chemical shifts of the ligands.[297]

In the frozen-core approximation, the core density is determined from four-component atomic Dirac–Fock calculations. It is then assumed that the electron density of the core orbitals remains unchanged when the atom is embedded in a molecule, the bonds formed being determined only by the valence electrons. It has been shown that the use of the frozen core approximation performs well for the calculation of nuclear shieldings,[294] and in particular that a relativistic atomic density may be used to investigate scalar relativistic effects of the shieldings of the heavy atoms.[289]

Regarding the case of heavy-atom effects on the nuclear shielding of lighter elements, several investigations have shown that these effects are often governed by spin–orbit interactions.[290,298] The expressions for the spin–spin couplings in a fully relativistic four-component framework have been derived by Aucar and Oddershede.[299]

B. Calculations of Relativistic Effects

One of the most extensively studied problems for which relativistic effects have been investigated are the hydrogen shieldings in the hydrogen halides. Calculations have been presented at various levels of theory, and the studies differ also in the contributions considered. Nakatsuji, Takashima, and Hada[300] have calculated the one-electron spin–orbit contributions from Fermi contact and spin–dipole interactions at the UHF level, whereas Malkin, Malkina, and Salahub have calculated only the one-electron Fermi contact contribution using IGLO-DFT.[301] Both these studies have employed FP approach using the spin–orbit operator and the Fermi-contact operator as perturbations, respectively. The most accurate and complete study of the hydrogen shielding in the hydrogen halides has been presented by Vaara et al.,[288] who calculated all four contributions to the spin–orbit corrected shieldings. The scalar relativistic effects to the hydrogen shieldings have been studied in the frozen-core approximation using DFT and in the relativistic no-pair approximation.[295,296]

We have collected the most accurate results from these studies in Table 10. We have not reported the findings of Ballard et al.,[295] as the scalar relativistic effects are small and the results in agreement with those of Schreckenbach and Ziegler.[294] Different contributions arising from the coupling of the spin–orbit operator with the Fermi contact and the spin–dipole operator, respectively, are denoted by $\sigma^{\mathrm{FC(1)}}$, $\sigma^{\mathrm{FC(2)}}$, $\sigma^{\mathrm{SD(1)}}$, and $\sigma^{\mathrm{SD(2)}}$, where we have furthermore indicated the coupling with the one-electron (1) or two-electron (2) part of the spin–orbit operator by a superscript.

From Table 10, we clearly see the increasing importance of the spin–orbit effects as we progress downward through the periodic table. In particular, we note that the spin–orbit correction to the hydrogen shielding in hydrogen iodide is of the same order of magnitude as the entire normal hydrogen shielding range. We also note that scalar relativistic effects appear to be negligible for the hydrogen shieldings. The UHF method can be considered only moderately successful in predicting the spin–orbit correction, although this is in part due to the neglect of the two-electron Fermi-contact contribution. The spin–orbit correction calculated by DFT is in good agreement with the MCSCF results.

The spin–orbit interaction changes not only the magnitude of the nuclear shieldings, but also the variation of the shieldings as the molecular geometry is altered. The lowest triplet-state surface may often

Table 10. Comparison of Theoretical and Experimental ^1H Shielding Constants in the HX (X = F, Cl, Br, I) Series (in ppm)

X	method	σ^{nr}	$\sigma^{FC(1)}$	$\sigma^{FC(2)}$	$\sigma^{SD(1)}$	$\sigma^{SD(2)}$	σ^{SO}	σ^{scal}	σ^{tot}
F	UHF[a]	27.33	0.17		0.02		0.18		27.52
	DFT[b]	30.04	0.17				0.17		30.21
	MCSCF[c]	28.84	0.142	−0.045	0.012	−0.004	0.11		28.94
	DFT(scalar)[d]	30.3						0.0	30.3
	exp[e]								28.5 ± 0.2
Cl	UHF[a]	29.76	0.88		0.04		0.92		30.69
	DFT[b]	31.72	0.89				0.89		32.61
	MCSCF[c]	30.82	0.799	−0.147	0.043	−0.008	0.69		31.51
	DFT(scalar)[d]	31.7						0.1	31.8
	exp[f]								31.06
Br	UHF[a]	29.91	5.15		0.18		5.33		35.24
	DFT[b]	31.27	4.76				4.76		36.03
	MCSCF[c]	31.03	4.212	−0.416	0.177	−0.018	3.96		34.98
	DFT(scalar)[d]	32.0						0.1	32.1
	exp[f]								34.96
I	UHF[a]	30.44	15.61		0.40		16.01		46.45
	DFT[b]	31.65	13.00				13.00		44.65
	MCSCF[c]	31.58	12.510	−0.837	0.396	−0.028	12.04		43.62
	DFT(scalar)[d]	32.4						0.2	32.6
	exp[f]								43.86

[a] Reference 300. [b] Reference 301. [c] Reference 288. [d] Reference 294. [e] Reference 183. [f] Reference 302. Gas-phase chemical shifts with respect to CH_4, here converted to absolute shieldings using $\sigma(H)$ in CH_4 = 30.61 ppm.[183]

become almost degenerate with the ground-state singlet surface as bonds are stretched, leading to a marked distance dependence of the spin−orbit interaction very different from that of the nuclear shieldings. For hydrogen iodide, the vibrational corrections to the nuclear shielding are negative at the nonrelativistic level, whereas they become positive when the spin−orbit corrections are taken into account.[303]

An extensive study of spin−orbit effects on the shieldings has been presented by Nakatsuji and coworkers (see for instance refs 300 and 304−306) at the UHF level, although the spin−orbit corrections calculated in these studies are probably overestimated in view of the results presented in Table 10.

Scalar relativistic effects are more important in metal carbonyls, both for the metal shielding itself—as demonstrated by Schreckenbach and Ziegler using the frozen-core approximation within DFT[294]—and for the shieldings of the ligand atoms as has been studied by Kaupp and co-workers using RECP for describing the heavy-atom and the SOS/IGLO/DFT approach.[297]

The investigation of relativistic corrections to spin−spin coupling constants is still a rather unexplored field. Apart from the early semiempirical studies by Pyykkö and Wiesenfeld,[307] we are only aware of the ab initio study of the spin−orbit effects on spin−spin couplings by Kirpekar, Jensen, and Oddershede.[292] They investigated the spin−orbit corrections to spin−spin couplings in group 14 tetrahydrides at the SCF level, showing that these corrections are in general small, somewhat contradicting the conclusions reached by Pyykkö and Wiesenfeld. However, one might expect that these particular couplings may have larger scalar relativistic effects and that correlation may prove important.

XII. Geometry Dependence and Rovibrational Effects

In a number of successful applications of ab initio methods, molecular structures have been determined by comparing calculated NMR parameters with experimental data. Typically, calculations were performed for various hypothetical molecular structures and it was found that the computed NMR parameters agree well with experiment for only one of the proposed structures, for example a bridged or a classical cation—see refs 265 and 308. In these studies, one usually considers structures with very different geometries and no special theory is needed to interpret the results. As another example, comparison of measured and calculated (RPA) shielding constants has been helpful in studies of the structure of amorphous glasses.[309] We shall not consider further such applications here but instead concentrate on variations in the NMR parameters with geometrical changes related to molecular vibrations and rotations.

The shielding and spin−spin coupling constants entering the effective spin Hamiltonian eq 1 are, in experiment, the averaged parameters for a vibrating and rotating molecule. The effects of rovibrational averaging are in many cases substantial—the shielding of F_2 being a prime example.[177,310] To compare accurately calculated molecular properties with experimental data, one should therefore take into account rovibrational effects (see e.g., ref 311 for a more general discussion). The property should be determined either for a specific rovibrational state, or for an average corresponding to a specific temperature. We shall in this section assume that the Born−Oppenheimer approximation[18] has been applied, and that the potential energy hypersurface and the rovibrational functions of interest are known with sufficient accuracy. In addition, we must describe the dependence of shielding or spin−spin coupling constants on small variations of the geometry in the neighborhood of the equilibrium. Vibrational averaging is therefore expensive, requiring the calculation of the spin-Hamiltonian tensors at a potentially large number of nuclear configurations, at least for systems other than diatomics, and in particular for nonrigid molecules.

A. Rovibrational Effects–General Theory

In the neighborhood of the equilibrium geometry r_e the value of any property P (such as the average of σ, J, or a particular tensor component) can be approximated as

$$P = P_e + \sum_i P_i S_i + {}^1/_2 \sum_{ij} P_{ij} S_i S_j + {}^1/_6 \sum_{ijk} P_{ijk} S_i S_j S_k + ... \quad (313)$$

where $P_{ijk...}$ are the derivatives of P with respect to the nuclear displacements, defined in terms of appropriate internal coordinates S_i. Let us consider first the simple case of a diatomic molecule, denoting the derivatives of P at r_e as P', P'', and so on, and the reduced coordinate as $\xi = (r - r_e)/r_e$. Equation 313 now becomes

$$P(\xi) = P_e + P'\xi + {}^1/_2 P''\xi^2 + ... \quad (314)$$

and, after averaging, we obtain for the rovibrational state v, J

$$\langle P \rangle_{v,J} = P_e + P' \langle \xi \rangle_{v,J} + {}^1/_2 P'' \langle \xi^2 \rangle_{v,J} + ... \quad (315)$$

where $\langle \xi^n \rangle_{v,J}$ stands for the average of ξ^n. An analogous expression is obtained for the temperature average, with $\langle P \rangle_T$ defined in terms of $\langle \xi^n \rangle_T$. It is presently not possible to calculate the derivatives P', P'', etc. analytically. The derivatives of σ and J are therefore determined numerically from the values computed at selected molecular geometries.

For small polyatomic molecules, following basically the same approach, one can start from eq 313 and derive an expression for P in terms of reduced normal coordinates q_r, q_s, etc. To obtain $\langle P \rangle_T$, one then needs the temperature averages $\langle q_r \rangle_T$, $\langle q_r^2 \rangle_T$, etc. and the data characterizing the potential hypersurface, such as harmonic and anharmonic force constants (for more details see Raynes et al.,[312,313] Lounila et al.,[314,315] Fukui et al.[316] and references therein).

More approximations are needed to establish rovibrational and temperature averages for larger polyatomic molecules. Most calculations have been rather incomplete, having been restricted to the analysis of σ or J as functions of specific geometry coordinate(s), rather than consideration of all contributions to the rovibrational effects. We discuss some examples in the following sections. It should be noted that some of the rovibrational effects are usually accounted for when an average experimental geometry is used instead of the optimized geometry corresponding to the potential minimum. This is also the principle behind the method of Åstrand et al.,[317] where an effective geometry that accounts for the major part of the rovibrational correction is determined.

Within the standard approach based on the Born–Oppenheimer approximation, the shielding constants are independent of isotopic species for a fixed molecular geometry. Similarly, the reduced spin–spin coupling constants are identical, the constants for isotopically substituted species differing only because of the differences in the nuclear magnetogyric ratios γ_K. Thus, it is only when rovibrational effects are considered that an estimate of the isotope effects on the shielding and the reduced spin–spin coupling constant is obtained. For a more detailed discussion and references to other works on isotope effects on shielding constants, we refer to the annual reviews of Jameson.[12]

Finally, we want to point out that the procedure of rovibrational averaging is independent of the approach used to compute the property (and energy) surfaces. Even though Hartree–Fock results have so far often been used as input for these studies, once an appropriate averaging scheme is developed, it can be applied to any property surface. However, none of the existing ab initio programs include an automated procedure for the calculation of rovibrational averages. For electric properties, a general recipe has been presented by Russell and Spackman.[318]

B. Geometry Dependence of Shielding Constants

For diatomic molecules, the accuracy of the calculations is often so high that any comparison with experimental data requires an analysis of rovibrational effects. In recent studies, Sundholm, Gauss, and Schäfer have calculated the spin–rotation constants and nuclear shieldings of a series of diatomic molecules using CCSD and CCSD(T) wave functions, GIAO's, and large basis sets.[177] These authors considered rovibrational corrections, as well as the small but nonnegligible effects of the Thomas precession eq 300 on the hydrogen spin–rotation constants. Sundholm et al. obtained not only purely theoretical estimates of the absolute shielding constants, but experimentally derived absolute shieldings as well, combining the experimentally determined spin–rotation constants with their calculated diamagnetic shielding constants (see eq 298). We have collected their results in Table 11. Sundholm et al. were able, through the use of systematic improvements in the wave function and the basis set, to estimate error bars of the calculated results. From Table 11, we note that the agreement with experiment is very good, except for the nitrogen and oxygen atoms. For these atoms, the inaccuracies in the experimental spin–rotation constants preclude a critical comparison with experiment. We note, however, that the theoretical calculations confirm the proposed reevaluation of the experimental ^{15}N shielding scale.[193] More recently, Sundholm and Gauss considered in a similar study the isotope and temperature effects on the shielding constants.[319]

For hydrogen fluoride, the results of Sundholm et al. have been corroborated by Åstrand et al.,[322,323] who used MCSCF wave functions together with GIAO's and a modified version of eq 314—using a better expansion point derived from an effective potential—to obtain highly accurate nuclear shieldings for this molecule. The rovibrational effects are found to be significant for fluorine, as $\sigma(^{19}F)$ at 300 K is 10.8 ppm smaller than the equilibrium value. For comparison, the effect is 10.42 in ref 177 and 10.0 ppm in a recent CHF calculation.[316]

In another study of a diatomic system, a calculation based on RPA and SOPPA shielding functions for

Table 11. Shielding Constants Enabling the Determination of Absolute Shielding Scales for Various Nuclei (in ppm)[a]

		absolute shielding constant			
molecule	nucleus	experimental/theoretical[b]	theoretical[c]	experimental[d]	ref of exp value
H_2	H	26.288(2)	26.298(20)	26.363(4)	320
HF	H	28.54(1)	28.48(6)	28.5(2)	186
	H[e]		28.62(1)		
	F	409.6(10)	409.2	410(6)	186
	F[f]		409.5(15)		
^{13}CO	C	0.9(9)	2.0(20)	1.0(12)	182
$C^{17}O$	O	−44.8(172)	−59.3(20)	−42.3(172)	185
$^{15}N_2$	N	−104.8(193)	−62.7(10)	−61.6	193
F_2	F	−231.6(10)	−225.5	−232.8(60)	321

[a] All numbers reported for 300 K, and taken from ref 177 unless stated otherwise. [b] Experimental numbers for the paramagnetic part as derived from spin−rotation measurements, and rovibrationally corrected CCSD(T) diamagnetic part of the shielding. [c] Rovibrationally corrected results: CCSD(T), ref 177; or MCSCF, refs 322 and 323. [d] Experimental absolute shielding scales as reported in the literature. [e] Reference 322. [f] References 322 and 323.

OH^- provided the initial data to analyze the rovibrational effects in $OH^-{\cdot}H_2O$.[324]

Large MCSCF calculations on the water molecule confirm the theoretically determined oxygen shielding in carbon monoxide (by comparison of the oxygen chemical shifts of the two compounds with experiment) and a new, purely theoretical, ^{17}O absolute shielding scale has been proposed.[325]

In a recent work, the isotope and temperature effects on the shieldings of ^{13}C and ^{77}Se were calculated.[315] Several different wave functions were used to obtain the property surfaces of carbon diselenide. The correlation effects were found to be important, and the best results (CASSCF and DFT) were in good agreement with experimental data for the ^{77}Se shielding. Since there are six isotopes of selenium, all of relatively high natural abundance, there is a large number of data to analyze for this system.

The temperature dependence of the shielding constants of all the nuclei in OCS has recently been computed in the MCSCF approximation.[326] For ^{13}C, the only nucleus for which the temperature dependence of the shielding may be determined on an absolute scale (using as a reference ab initio and experimental data for ^{13}C in methane), the ab initio results agree well with new experimental data given in the same work.

An example of what can presently be done for a polyatomic molecule is a study of CH_3Cl.[312] The temperature dependence of the shielding and isotope effects on σ (^{13}C) resulting from (multiple) substitution of ^1H by ^2H were predicted. The calculated effect due to substitution of ^{35}Cl by ^{37}Cl is in agreement with the known experimental result. Detailed shielding surfaces (at the SCF level) have also been calculated by Buckingham and Olegário[327] for the series CH_3X ($X = F$, Cl, Br).

Several shielding hypersurface calculations have been performed for proteins (see refs 328 and 329 and references therein). Knowledge of the shielding hypersurfaces can be helpful in the analysis of the structure of proteins, and the shielding as a function of torsional angles has been computed for a number of nuclei. One of the aims of such studies has been to find small basis sets that give reliable results, for instance locally dense basis sets. Such calculations are very time-consuming even at the SCF level, when, for example, 12^3 points need to be calculated to construct the hypersurface.

C. Geometry Dependence of Spin–Spin Coupling Constants

Only a few studies of rovibrational effects on nuclear spin−spin coupling constants have appeared in the literature, despite the strong geometry dependence of the Fermi-contact operator.[30,249,330] The effects of rovibrational contributions in HD were discussed in section IX.A. The geometry dependence of the coupling constant of N_2 was investigated by Vahtras et al.[249] and by Malkina, Salahub, and Malkin.[30] Both studies showed that the small FC contribution changes sign when the geometry is slightly distorted from equilibrium.

A study of the dependence of the spin−spin coupling constant in HD on the internuclear distance was presented by Bacskay.[330] The paper addressed the observation that the spin−spin coupling is positive at the equilibrium geometry and that it increases rapidly with increasing bond length. As there is no coupling between the nuclear spins when the atoms are infinitely separated, the coupling must have a maximum. By using a FCI wave function and taking proper account of near-degeneracy effects as the bond is broken, a maximum of 4.33×10^7 Hz was found at about 11 a_0, after which the coupling decreases to zero at a separation of about 17 a_0. Although this large value of the coupling is unphysical, the calculated increase of the coupling constant with the vibrational level should be observable.

A careful analysis of the spin−spin coupling constant in HF has been presented by Åstrand et al.,[323] who found that the rovibrational correction was about 5% of the total coupling constant. Their rovibrationally corrected result for the vibrational ground state of the molecule, 500 ± 10 Hz, compares well with the most recent experimental determination of 500 ± 20 Hz.[256] For HCN and HNC, the dependence of the isotropic coupling and the anisotropies on the length of the triple bond has been discussed in a recent MCSCF study.[171]

The temperature dependence of both coupling constants in the water molecule has been recently studied by Wigglesworth et al.[253] The results obtained for the equilibrium geometry were discussed earlier and given in Table 7. The rovibrational effects computed using the SOPPA(CCSD) surface are fairly large, for $^1J(\mathrm{OH})$ +4.3 Hz and for $^2J(\mathrm{HH})$ +0.5 Hz, which indicates that at the level of accuracy achieved within both theory and experiment these effects have to be considered when comparing the results.

Detailed studies of property surfaces for $^1J(\mathrm{CH})$ and $^2J(\mathrm{HD})$ in isotopomers of CH_4 have been performed by Raynes, Oddershede and co-workers (see ref 118, 254, and 313 and references therein). The spin–spin coupling surface is much more complicated than the potential energy surface as there are, for instance, 3 first-order and 12 second-order coefficients for $^1J(\mathrm{CH})$ (whereas, in the same symmetry coordinates, there are only five harmonic force constants). The most recent SOPPA(CCSD) study[118] using 55 geometries includes an analysis of the temperature dependence of $^1J(\mathrm{CH})$ and $^2J(\mathrm{HD})$ and of the isotopic substitution effects. Similar rovibrational analyses, based on property surfaces obtained with SOPPA and MCSCF approximations, have been reported for the entire XH_4 series (X = C, Si, Ge, and Sn).[331,332]

There are several empirical formulas (starting with the Karplus equation) that describe the dependence of the vicinal coupling constant on the geometry, in particular for the $^3J(\mathrm{HH})$ coupling.[333] An advantage of ab initio theory is that one can compute the coupling for the required geometries and fit the parameters of an analytic formula to these results. In a number of papers (see refs 259, 271, and 334), the vicinal coupling constants in ethane (and, more recently, in ethane derivatives[335]) have been discussed and the constants C_0, C_n, and S_n in equations of the form

$$^3J(\mathrm{HH}) = C_0 + \sum_{n=1}^{m} (C_n \cos(n\phi) + S_n \sin(n\phi)) \quad (316)$$

have been determined. However, none of these calculations present definite results—the SCF approximation has been used in ref 334, the correlation effects have only been treated to low order in ref 271, and only the FC contribution was analyzed in ref 259. Although the bell-shape dependence of $^3J(\mathrm{HH})$ on the torsion angle is reproduced in these studies, larger basis sets and a higher level of correlation treatment are needed for high accuracy and reliability.

XIII. Intermolecular Interactions and Solvent Effects

The nuclear shielding and spin–spin coupling constants are highly sensitive probes of the electronic structure of a molecule. At the same time, these parameters, in particular the nuclear shieldings, are also sensitive probes of intermolecular interactions and solvent effects. An understanding of how the surroundings affect the NMR parameters will thus provide valuable help for understanding observed NMR spectra and thus extend the application range of NMR even further.

It would appear that the most systematic approach to study such effects is perturbation theory, treating the intermolecular interaction as an extra perturbation in addition to the magnetic field. However, the physically appealing perturbation treatment of weak intermolecular forces is a difficult subject by itself, and there are no applications to the study of NMR parameters of interacting systems. Although many concepts taken from the theory of intermolecular forces are used (e.g., analyzing the electric field due to the environment, partitioning the effects according to the type of interaction), we would like to stress that there is no systematic ab initio theory of NMR parameters in interacting atomic or molecular systems.

Much of the work on intermolecular forces and solvent effects has been done at the SCF level, as such studies often involve large molecular systems (a discussion of the studies of the effects of intermolecular interactions on nuclear shieldings was recently given by de Dios[5]). However, in the SCF approximation the dispersion effects are not included, as known from perturbation theory of intermolecular forces.[336] Consequently, it is not appropriate to assume that dispersion is included in any SCF calculation of NMR parameters of interacting systems. Nevertheless, numerical evidence suggests that in many cases, the dominant effects observed in experiment can be recovered in SCF calculations, implying that nondispersive, short-range interactions dominate. This circumstance does not simplify the interpretation of the change of NMR parameters—the overlap and exchange effects are difficult to analyze and their dependence on internuclear distance is not easily described —but it does mean that the supermolecule SCF approach may be used to calculate the dominant changes in the shielding due to solute–solvent interactions.

A conceptually useful starting point for investigating the effects of a solvent on nuclear shieldings was presented by Buckingham,[337] who divided the solvent effects into four different contributions

$$\sigma_{\mathrm{solvent}} = \sigma_{\mathrm{b}} + \sigma_{\mathrm{a}} + \sigma_{\mathrm{w}} + \sigma_{\mathrm{E}} \quad (317)$$

Here σ_{b}, which denotes the change in the local magnetic field experienced by the nucleus due to the isotropic magnetizability of the solvent molecules, is proportional to the magnetizability of the solvent, σ_{a} is a similar change in the local magnetic field due to the magnetizability anisotropy of close-lying solvent molecules, σ_{w} is the change in the electronic structure of the solute due to van der Waals interactions with solvent molecules, and σ_{E} is the contribution from the electrostatic polarization of the solute's charge distribution. In ab initio calculations, the different contributions cannot easily be separated and defined. Although models of the various terms have been studied,[338] a rigorous partitioning of $\sigma_{\mathrm{solvent}}$ that recovers all the solvent effects and ensures no overlap between different contributions has not been formulated within ab initio theories.

It is useful to divide the effects of a surrounding medium on the observed NMR parameters into direct and indirect solvent effects, in a fashion similar to that for relativistic effects. The direct solvent effects result from the polarization of the electronic structure of the solute by the surrounding solvent, whereas the indirect effects are caused by the change in geometry (and changes in rovibrational contributions) that occurs upon solvation of the solute. Both may be important for a description of the observed solvation effect.

Most theoretical studies investigating solvent or crystal-structure effects employ the supermolecule model. However, very recently, some studies using continuum models—where the solvent is described by a surrounding dielectric medium—have been presented. We also note that an approach for calculating nuclear shieldings of infinite crystals has been presented within the framework of density-functional theory, using periodic boundary conditions.[339]

A. Intermolecular Property Surfaces

The first studies of intermolecular shielding surfaces using distributed gauge origins and taking account of electron correlation—as needed to recover dispersion effects—were done by Jameson and de Dios,[340] who used SOLO to calculate the intermolecular shielding surfaces of neon and argon dimers. They demonstrated that common gauge-origin methods give qualitatively wrong shapes of the intermolecular shielding surfaces, even at the correlated level. Approximate R^{-6} dependence was obtained for these systems at large atomic separations, whereas an approximate R^{-4} dependence was obtained for the argon shielding in the Na^+−Ar system. Jameson and de Dios later extended these studies of intermolecular potential energy surfaces to molecular systems such as Ar···NaH,[38] although then restricted to the SCF level. Subsequent investigations of the argon shielding constants[340,341] gave support to the use of noble gas shieldings as a probe of the Al/Si ratio in zeolites.

Barszczewicz et al.[342] have investigated the long-range effects of interatomic interactions on the noble gas isotropic and anisotropic shieldings in the He−He (FCI) and Na^+−Ar (SCF) systems. By careful consideration of basis-set superposition effects, an R^{-6} dependence was found for the isotropic He shielding, an R^{-4} dependence for the isotropic Ar shielding, and an R^{-3} dependence for the anisotropic shielding. It was shown that these expected asymptotic distance dependencies appear only at large internuclear separations.

B. Shielding and Spin–Spin Polarizabilities

Instead of expressing the shielding or spin−spin coupling constants as functions of internuclear separation, one may use the shielding and spin−spin coupling polarizabilities, which describe the dependence of σ (or J) on an electric field[282] (see also section X). The change of the NMR parameters in various environments can therefore be estimated from the electric field at the nucleus, obtained for example from molecular dynamics simulations or from a knowledge of the electrostatic potential of a protein backbone.

The calculation of shielding polarizabilities requires large basis sets to model all applied perturbations,[28,105,343,344] even when perturbation-dependent basis sets are used. Furthermore, the shielding polarizabilities are strongly dependent on electron correlation, even for shieldings that themselves do not display large correlation effects.[28,105,345] Nevertheless, the values obtained by different methods appear to be in fairly good agreement, at least for the first nonzero shielding polarizabilities. We shall return to the use of shielding polarizabilities in the study of solvent effects on nuclear shieldings in section XIII.F.

The dipole and quadrupole shielding polarizabilities of many nuclei in small molecules have been discussed by Augspurger et al.[346] From the calculated polarizabilities, the authors obtained an estimate of the dependence of the shielding on weak long-range electrical interactions in proteins. However, rather small basis sets were used and no account was taken of electron correlation. Considering the correlation dependence of the dipole shielding polarizabilities,[28,105] it is uncertain to what extent these results provide accurate estimates of the effects of the protein backbone on the nuclear shieldings.

Contreras and co-workers have used supermolecule calculations and finite electric fields to study the changes in the CH couplings in CH_4 and HCN in IPPP−CLOPPA (Inner Projections of the Polarization Propagator−Contributions from Localized Orbitals within the Polarization Propagator Approach)[347,348] based on an SCF reference wave function. Their investigations showed that the electric field generated by a close-lying molecule dominates the induced shift, although other effects must be considered as well for quantitative agreement.

C. Supermolecule Calculations

The simplest approach—at least conceptually—for evaluating the effects of a surrounding solvent (or a crystal structure) is supermolecule calculations, where some neighboring molecules are explicitly included in the calculation. However, because of the large number of molecules involved in such studies, supermolecule calculations of realistic systems have been restricted to the Hartree−Fock level, often using locally dense basis sets.[159] It is worth noting that basis-set superposition errors need to be considered in supermolecule calculations, in particular if comparisons are made with the monomer as a way of obtaining gas-to-liquid/solid shifts. Several SCF studies of intermolecular forces and solvent effects using supermolecule models have been presented. Here we mention for instance the studies of Jackowski and co-workers on di- and trimers of acetonitrile,[349,350] propionitrile trimers,[351] and ammonia[352,353] clusters, a study of ice,[160] and solid-state and liquid-state modeling of shieldings and spin−spin couplings in acetylene.[354,355]

D. Continuum Models

Although there is an extensive literature on various continuum models for describing the electrostatic effects of a surrounding dielectric medium (see the recent review by Tomasi and Persico[356]), differing mainly in the size and shape of the cavity, only two of these methods have been extended to investigate the effects of a dielectric medium on nuclear shieldings: the GIAO/(Multi-Configurational) Self-Consistent Reaction-Field (MCSCRF) method of Mikkelsen et al.[357] and the IGLO/Polarizable Continuum Model (PCM) SCF of Cremer et al.[358] For the spin−spin couplings, only the MCSCRF model has been used.[215]

The two continuum models used for molecular magnetic properties differ in their representation of the cavity. In the MCSCRF model, Mikkelsen et al.[357] use a simple spherical cavity for the molecule. The energy of interaction can then be written as a multipole expansion

$$E_{\text{solv}} = \sum_l g_l \sum_{m=-l}^{l} \langle T_{lm} \rangle^2 \tag{318}$$

and the summation may be truncated at any order l, where l represents the order of the spherical harmonics. The expressions for the charge moments $\langle T_{lm} \rangle$ can be found elsewhere.[356]

In the PCM approach of Tomasi and co-workers,[359,360] each atom is surrounded by a spherical cavity with its radius related to the van der Waals radius of the atom. The cavity surface is divided into a number of small surface elements, where the reaction field from the solvent is modeled by distributing point charges onto the surface elements. The magnitudes of the point charges are determined on the basis of the dielectric constant of the medium.

One of the first applications of continuum models to the study of nuclear shieldings was an attempt by Bühl et al. to reconcile the theoretical and experimental shieldings for ^{11}B in H_3BNH_3.[361] When optimizing the geometry of the molecule in the presence of a dielectric continuum using an ellipsoidal cavity, the shielding changed from −15.7 ppm at the gas-phase geometry (relative to the ^{11}B shielding in BF_3OEt_2) to −20.5 ppm at the optimized solvated geometry using the dielectric constant of water, 78.5. Cremer et al.[358] included the direct polarization effect on the shieldings using the IGLO−PISA model. For the ^{11}B shielding, they obtained −19.5 ppm, to be compared with the experimental value of −23.8 ppm.

Several applications of the PISA/IGLO approach have been presented at the SCF level by Cremer and co-workers, who studied the effect of a surrounding solvent on the shielding of a number of molecules.[362,363] In particular, by comparing calculated shifts obtained with the PISA/IGLO model to experimental observations, they have concluded that trivalent silylium ions (R_3Si^+) in solution do not exist, even in weakly coordinating solvents.[362]

Using a spherical cavity, Mikkelsen and co-workers have studied the dependence of nuclear shieldings and magnetizabilities on the cavity size, the dielectric constant, and the order of the multipole expansion for a series of small molecules.[357] It was demonstrated that the Onsager model (truncation of eq 318 at order $l = 1$) in most cases is unable to recover more than half of the change observed at order $l = 10$. In general, the multipole expansion had to include terms to order six before it was converged. It was furthermore shown that both direct and indirect solvent effects give significant contributions to the solvent shift, which may in some cases be as large as the correlation corrections.

Åstrand et al. have used the MCSCRF approach to investigate the solvent dependence of the $^2J(^1H^1H)$ and $^1J(^1H^{125}Se)$ couplings in H_2Se, as well as the shielding constants[215] of this molecule. These authors demonstrated that polarization as well as geometry effects may dominate the effects of a dielectric medium on spin−spin couplings. Whereas the effect on the selenium−proton coupling is almost a pure polarization effect, the change in geometry—despite being small—dominates the change in the proton−proton coupling. In both cases, the change in the Fermi contact term dominates.

The study of Åstrand et al. demonstrates that dielectric medium effects on spin−spin couplings may be large, almost 15% for the proton−selenium coupling. However, this molecule is not well suited for a critical evaluation of the continuum model for describing medium effects on spin−spin couplings, since relativistic effects (see section XI.A) and the strong geometry dependence of the NMR parameters in this molecule make a direct comparison with solution-phase experiments difficult. Nevertheless, if we combine the relativistic corrections to the coupling constants estimated by Aucar et al.,[364] −47.6 Hz and +1 Hz for $^1J(^1H^{125}Se)$ and $^2J(^1H^1H)$, respectively, with the MCSCRF results (in a dielectric medium) of Åstrand et al. of about 120 Hz and −15.4 Hz, we get reasonably good agreement with the experimental numbers[365] of 63.4 ± 0.5 Hz ppm and −13.5 ± 0.3 Hz, respectively.

E. Combined Molecular Dynamics/Quantum Chemistry Approaches

In liquids, the molecules are freely tumbling. Although the intermolecular interactions may be described in an average sense using continuum models, a proper treatment and understanding of the molecular properties of liquids require that this molecular motion is explicitly taken into account using for example molecular dynamics.

Various intermolecular potentials were used in molecular dynamics simulations of liquid water at different temperatures and pressures by Malkin et al.[366] At selected time steps, small representative clusters of water molecules were extracted and used to calculate the nuclear shieldings of the central water molecule using the SOS-DFT/IGLO method. By averaging over the different selected water clusters, the temperature dependence and gas-to-liquid shifts of the nuclear shieldings in water were obtained (for discussion of their results, see section XIII.F).

An interesting approach to the calculation of solvent shifts of nuclear shieldings was recently presented by Nymand, Åstrand and Mikkelsen.[367,368] In their approach, the electric fields and electric field gradients obtained in molecular dynamics simulations were combined with shielding polarizabilities using intermolecular perturbation theory. This approach avoids the problems faced in supermolecule

Table 12. Gas-to-Liquid Shifts (dσ) and Shielding Anisotropies, $\Delta\sigma$, for the Nuclear Shieldings of Water Using Various Theoretical Models (in ppm)[a]

method	ref	dσ (O)	dσ (H)	$\Delta\sigma$ (O)	$\Delta\sigma$ (H)
GIAO/SCRF (l =1)	371	7.9	−0.86		
GIAO-SCF/$(H_2O)_5$		−25.6	≈−4.0		
GIAO-SCF/molecular dynamics		−20.3	−2.28		
GIAO-SCF/$(H_2O)_5$	160			34.24	
GIAO-SCF/$(H_2O)_{17}$				35.17	
GIAO/SCRF (l = 10)[b]	372	9.4	−0.95	54.7	21.56
GIAO-SCF/$(H_2O)_5$		−17.8	−3.55	33.5	31.15
GIAO/semicontinuum/$(H_2O)_5$		−16.4	−3.97	33.1	31.73
IGLO/DFT/molecular dynamics	366	−37.6 ± 2.1	−3.2 ± 0.2		
GIAO-SCF, intermolecular perturbation theory	368	−7.1	−3.04		
experiment	373,374	−36.2	−4.26		
	375			28.7 ± 1	
	376			34.2 ± 1	

[a] The isotropic values are reported as $\sigma(X)^{\text{gas}} - \sigma(X)^{\text{liquid}}$. The shielding anisotropies $\Delta\sigma$ are defined according to eq 291. [b] The calculations of ref 372 are all SCF calculations using GIAO's, with (1) a dielectric continuum model using a spherical cavity and truncation of the multipole expansion at $l = 10$, (2) a supermolecule model where the central water molecule is surrounded by the four closest neighboring water molecules, and (3) a semicontinuum model where the supermolecule cluster is embedded in the dielectric medium as in 1.

calculations, and allows for systematic improvements in the treatment of electron correlation. However, the method requires accurate shielding polarizabilities and changes in the geometry of the solvated molecule are not accounted for.

Lau and Gerig have used molecular dynamics to study the interactions between solvent and solute, the solvent effects on the shielding being modeled with empirical formulas for interatomic dependence on nuclear shieldings, using data from ab initio calculations. They were able to reproduce quite accurately the experimental solvent shifts for neon[369] and for the fluorine atom in fluorobenzene.[370]

F. A Case Study of Solvent Effects: The Gas-to-Liquid Shifts in Water

The gas-to-liquid shifts (one of the best indicators of intermolecular interactions) and the shielding anisotropies of water have been given a prominent place in solvent calculations. In Table 12, we have collected some recent results, including the SCRF and molecular dynamics studies of Chesnut and Rusiloski,[371] the molecular cluster calculations by Hinton et al.,[160] the continuum and semicontinuum results of Mikkelsen et al.,[372] the combined IGLO/DFT/molecular dynamics study of Malkin et al.,[366] and the results of Nymand and Åstrand, obtained using molecular dynamics and intermolecular perturbation theory.[367,368]

From the table, we note that the continuum models are inadequate for this problem, giving the wrong sign for the liquid shift of the oxygen shielding. This result is not unexpected, considering the strong hydrogen bonds in liquid water, which are not accounted for in the continuum model. We also note the excellent agreement for the oxygen liquid shift in the DFT/molecular dynamics approach of Malkin et al., although the rather poor estimate of the gas-phase oxygen shielding (326 ppm compared with recent highly accurate estimates of 337 ppm[62,325]) raises some questions as to the reliability of these calculations. In contrast, the rigid cluster models recover only about one-half of the observed liquid shift. Surprisingly, this situation changes for the hydrogen gas-to-liquid shift, where the rigid clusters give better agreement with experiment than do the molecular dynamics studies. The results of Nymand et al. are also fairly good for the hydrogen shielding—although by no means comparable to the semicontinuum results—whereas the oxygen gas-to-liquid shift is poor. However, in this investigation and in the rigid cluster models no account was made of the change in molecular geometry, which may explain part of the large discrepancies observed for these models.

A discussion of calculated and measured effects of hydrogen bonding on the shieldings in water and many other systems has been given in a recent review.[377]

XIV. Conclusions

The general expressions for the nuclear shielding and indirect spin−spin coupling constants were established by Ramsey almost half a century ago. However, the development and progress of ab initio methods for the calculation of molecular properties (as applied for instance in studies of electric polarizabilities and molecular Hessians) was not immediately reflected in the calculation of NMR parameters because of the problems specific to the shielding constants (the gauge dependence of the approximate results) and to the spin−spin coupling constants (the triplet nature of the perturbation). These problems have now been largely solved, and increasingly accurate and reliable results can presently be obtained within various approximations, often using generally available codes.

The simplest calculations are those of the shielding constants at the SCF level. For many purposes, the SCF approximation is sufficiently accurate and may often successfully complement experimental observations. The SCF approach is a black-box method, requiring practically no input from the user apart from the molecular structure and choice of basis set. A large number of SCF programs is available for the calculation of nuclear shieldings. Direct and parallel codes enable calculations on very large molecules and the determination of the basis-set limits for smaller molecules. The SCF calculation of shieldings is not significantly more costly than the determination of the molecular energy and nuclear shieldings have been obtained at the SCF level for over 30 different nuclei of experimental interest.

If the SCF approximation is not applicable—for instance, when the shieldings of nitrogen, oxygen, or fluorine nuclei with lone pairs are calculated—or when high accuracy is required, various correlated approaches are available. Gauge-invariant calculations of nuclear shieldings have in recent years been implemented for many correlated wave functions. The choice of correlated method should be be based on several considerations: (1) the level of accuracy desired, (2) the size of the molecule investigated, and (3) the electronic structure of the molecule. Applying correlated wave functions one can often reduce the errors of SCF approximation by an order of magnitude or more. When highly accurate results are needed, it is desirable to analyze residual errors due to the truncation of the orbital space and approximations in the treatment of the correlation effects. These errors may be estimated using correlation-consistent basis sets and, for correlation effects, applying the hierarchies of perturbation and coupled-cluster theories. An estimate of the convergence of the correlation treatment may be obtained also from a series of MCSCF calculations. Recent development of direct codes for GIAO-MP2 calculations opens the way for studies of the shieldings in large molecules at the correlated level.

Perturbation theory methods similar to those for shieldings can be applied to compute spin–spin coupling constants. However, because of the complicated interactions involved, the number of computer codes available to calculate these constants is significantly smaller than the number of codes for gauge-invariant calculations of nuclear shieldings. Nevertheless, codes are available for calculations of spin–spin coupling using different correlated wave functions, and applications of these codes show that systematic improvements in the calculated spin–spin coupling constants are obtained with increasing level of sophistication of the calculation. Even when it is difficult to describe fully the correlation effects or to achieve convergence of the basis set, one can in many cases estimate the residual errors in the calculated coupling constants.

As for the shieldings, nuclear spin–spin coupling calculations are more difficult for molecules with double bonds (where the occupied and unoccupied π orbitals may form a “quasi-degenerate” pair) and when the coupling to an atom with lone pair(s) is studied. When only single bonds are present, an SCF wave function may provide a reasonable approximation to the spin–spin coupling constants. However, SCF results by themselves are of little use for the coupling constants when comparison with experiment is impossible, and the validity of the restricted SCF approximation should at least be checked against a simple correlated approach (such as an MCSCF wave function or a coupled-cluster calculation in a small basis).

For both the nuclear shieldings and the spin–spin coupling constants, ab initio theory has reached a level of accuracy that in many cases makes it a valuable complement to experiment. In studies that are experimentally difficult, theory may provide data that are not experimentally obtainable or which have large experimental uncertainty of systematic (model interpretation) or indeterminate nature. Typical examples are gas-phase analyses of small molecules (when accurate results for an isolated molecule are required), studies of unstable species such as carbocations, or studies of tensor properties such as the anisotropy and antisymmetry of shielding and spin–spin coupling tensors.

At the same time, the increased accuracy of ab initio calculations permits and necessitates a consideration of rovibrational corrections to the computed properties. Another important effect—in particular for the shieldings—is due to the solvent, since most NMR experiments are performed in the liquid phase. The theoretical development and application of various methods that describe solvent effects bring in an increasing amount of data. However, this is a field which still is under development. For a better understanding of the effects of intermolecular interactions and for the development of a theoretical description of solvent effects, further studies on small systems, such as the water dimer, are needed.

Despite the large number of data that have become available in recent years from theoretical calculations of NMR parameters, no simple, general relationships between the NMR parameters and the electronic structure of a molecule have been established. Even qualitative estimates of shielding or spin–spin coupling constants often require one to go beyond the standard molecular-orbital model of the SCF approximation. Although the main effects of electron correlation are recovered by all the modern methods, the interpretation is usually more complicated than an analysis of the SCF results. It should be kept in mind that although some of the new methods and programs enable black box-type calculations, an understanding of the correlation effects in the systems studied helps in using the programs efficiently and to obtain reliable results. It may also help unravel the characteristics of the electronic structure that govern the nuclear shieldings and coupling constants in the molecule of interest.

For a theoretical chemist, the computation of NMR parameters provides a stringent test of modern ab initio methods. Using the same reference wave function, one can simultaneously perform calculations of numerous properties measured in a single NMR spectrum. This has practical advantages as well, since, at a sufficiently high computational level, agreement of the calculated and experimentally observed parameters gives support to the accuracy of the other calculated shieldings or couplings, which may not be known experimentally.

One of the main advantages of modern ab initio methods is that the accuracy of the results can be determined from the level of calculation. The errors in the calculated properties can be estimated, and a comparison with experiment is not necessarily required to judge the quality of the results. Theoretical calculations can therefore be used independently to study the NMR parameters in idealized environments providing, together with the information contained in the wave function, valuable data for an understanding of the behavior of nuclear shieldings and spin−spin couplings. Applications of ab initio methods to predict, analyze, or interpret experimental data are now becoming commonplace. With the development and increasing availability of more reliable computational methods, the role of these applications in the study of NMR spectra is likely to increase in the future.

XV. Abbreviations

CASSCF	complete active space self-consistent field
cc-pVXZ	correlation-consistent polarized valence x zeta, x = D, T, Q, etc.—double, triple, quadruple, etc.
CCSD	coupled-cluster, single and double excitations
CCSD(T)	couple-cluster single and double excitations with perturbative correction for triple excitations
CHF	coupled Hartree−Fock
CI	configuration interaction
CSGT	continuous set of gauge transformations
CTOCD	continuous transformation of the origin of the current density
DFT	density functional theory
DSO	diamagnetic spin−orbit
EOM	equations of motion
ECP	effective core potential
FC	Fermi contact
FCI	full configuration interaction
FF	finite field
FPT	finite perturbation theory
GIAO	gauge invariant (including) atomic orbitals
IGLO	individual gauges for localized orbitals
IGAIM	individual gauges for atoms in molecules
LORG	localized orbitals/localized origins
MBPT	many-body perturbation theory
MCSCF	multiconfiguration self-consistent field
MPPT	Møller−Plesset perturbation theory
MP2, MP*n*	second, *n*th order versions of MPPT
PSO	paramagnetic spin−orbit
PP, PPA	polarization propagator (approximation)
QCI (SD)	quadratic configuration interaction (single and double excitations)
RPA	random-phase approximation
RASSCF	restricted active space self-consistent field
RECP	quasirelativistic effective core potential
SCF	self-consistent field
SD	spin−dipole
SDQ-MP4	fourth-order Møller−Plesset perturbation theory including single, double, and quadruple excitations
SOLO	second-order PPA using LORG
SOPPA	second-order polarization propagator approximation

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