

Relativistic Computation of NMR Shieldings and Spin-spin Coupling Constants

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1 Introduction

A long time has passed since the formulation of relativistic quantum mechanics. Meanwhile, it has become chemistry textbook knowledge that atoms and molecules containing heavy nuclei exhibit so-called relativistic effects which, e.g., cause mercury to be liquid and are responsible for the color and the chemical inertness of gold. A qualitative explanation based on the Bohr model for one-electron atoms is straightforward: Special relativity has to be considered when velocities are not anymore small compared to the speed of light. The Bohr formulae can be interpreted such that, in atomic units (see below), the electron in the ground state has a velocity of Z , with Z being the nuclear charge. The velocity of light, c , has a value of approximately 137 in the same units. This illustrates that electrons in heavy atoms can reach a substantial fraction of the speed of light, and it is therefore clear that core orbitals in heavy atoms show sizable relativistic effects. It has been somewhat surprising, though, that valence orbitals exhibit relativistic effects of the same order in c^{-2} as core orbitals, which cause significant changes in the chemical properties of heavy element compounds. Relativistic effects for valence orbitals are nowadays well investigated and understood. For elements of the 6th row of the periodic table (Cs - Rn), the correction terms are so large that nonrelativistic quantum chemical computations often do not yield even a qualitatively correct answer. It is generally accepted that relativistic computations have to be carried out for such atoms and their compounds. c^{-2} appears in the relativistic theory — due to its smallness — as an expansion parameter, by which perturbational orders of relativistic corrections are characterized. The nonrelativistic limit is approached for $c \rightarrow \infty$.

Nuclear shieldings and spin-spin couplings are very sensitive experimental probes for the electronic and geometrical structure of a compound. For the same reason, however, they are difficult to compute accurately. In the presence of heavy nuclei, this means that any attempt to achieve a reasonable agreement between theory and experiment has to consider relativistic effects in the computations. Both the current state of relativistic quantum chemical methods and the art of computing NMR parameters have advanced far enough that a large body of computational results for heavy element systems obtained with a variety of methods is available. Remarkable results have been achieved, e.g. the explanation of certain experimental trends such as the “halogen dependence”, or the ability to compute NMR parameters with the heavy nuclei as the probe. Therefore it is appropriate to give a short overview here of both the methodologies being used so far as well as of results that have been obtained for a number of heavy atom systems.

Concerning the methodology, we will focus on methods that are capable of treating both light and heavy nuclei with respect to NMR shieldings and spin-spin couplings on a first-principles basis (meaning *ab-initio* methods and approximate Kohn-Sham density functional theory (DFT)). Variational methods are emphasized, but the possibility of treating relativity as a perturbation is frequently mentioned. In particular for nuclear shieldings, certain chemical trends have successfully been ex-

plained upon inclusion of spin-orbit coupling to first order alone, and a number of such results are quoted in section 3. Concerning the spin-spin couplings, we focus on couplings involving a heavy nucleus. Dimensionless atomic units (unit of charge $e = 1$, electron mass $m = 1$, $4\pi\epsilon_0 = 1$, $h = 2\pi$, $c \approx 137.036$) are used in the theoretical section. The electronic g -factor is assumed to be exactly 2, as predicted by the Dirac equation, and not written explicitly.

Computed or experimental nuclear shieldings and chemical shifts are quoted in ppm (10^{-6}), spin-spin couplings either as reduced couplings K in SI units of $\text{kg m}^{-2}\text{s}^{-2}\text{A}^{-2}$, or as coupling constants J in Hertz (s^{-1}). The discussion of theoretical results and interpretations refer to a time-independent treatment of closed-shell molecules with fixed nuclei.

In Sec. 2, we outline the theoretical approach to heavy atom NMR. Illustrative results and interpretations for chemical shifts and spin-spin couplings presented in Secs. 3 and 4, respectively, are chosen in order to cover a range of chemical applications and trends and a number of different methodologies.

2 Relativistic theory of NMR shieldings and spin-spin coupling constants

In this section the theoretical methodology that allows for the relativistic computation of NMR parameters of molecules is outlined. Due to the vast amount of literature and the many different techniques in the field of relativistic quantum chemistry, no attempt has been made to give a complete overview. Instead, a hierarchy of currently common approximations from which magnetic properties can be extracted will be sketched in a pragmatic way. For details we refer to some of the books and review articles on relativistic quantum chemistry.¹⁻⁴

2.1 Relativity in quantum chemistry

“Ordinary” nonrelativistic quantum chemistry deals with the solution of the time-independent many-electron Schrödinger equation

$$\hat{\mathcal{H}}^{\text{nrel}}\Psi = \Psi E \quad , \quad (1)$$

with Ψ being the many-electron wavefunction of an atom or molecule with fixed nuclei, and E the total energy.

$$\hat{\mathcal{H}}^{\text{nrel}} = \sum_i \frac{\hat{p}_i^2}{2} + \sum_i V_{Ni} + V_{ee} + V_{\text{nuc}} \quad (2)$$

is the nonrelativistic Hamiltonian consisting of the nonrelativistic kinetic energy operator $\hat{p}_i^2/2$ for each electron i , the electron-nucleus attraction potential V_{Ni} for each electron, the nonrelativistic electron-electron Coulomb repulsion $V_{ee} = \sum_{j>i} 1/r_{ij}$, and the internuclear repulsion potential V_{nuc} . $\hat{p} = -i\nabla$ is the momentum operator in space representation. Since analytic solutions of equation (1) for many electron systems are not known, approximations have to be made. As a start-

ing point, the N -electron equation is usually separated into N effective one-electron equations for one-particle wavefunctions ψ (so called atomic or molecular orbitals) which depend on an effective potential V . For simplicity, we will implicitly refer to such effective one-electron equations (or true one-electron systems) in the following, by using the symbol ψ for the one-electron wavefunction or orbital. Particular details of common approximations are not discussed in this section.

In relativistic quantum chemistry, $\hat{\mathcal{H}}^{\text{nrel}}$ in equation (1) is replaced by its relativistic counterpart. All of the problems of the nonrelativistic many-electron theory are present in the relativistic formulation as well. Hence, similar techniques are common in order to find approximate solutions; in particular, use of orbitals is made. However, relativistic quantum chemistry has its own specific problems associated with it, one of them being the lack of a consistent relativistic many-particle Hamiltonian being derived from quantum electrodynamics. Therefore, relativistic many-electron atomic and molecular computations rely on the use of the four-component ‘‘no-pair’’ Dirac-Coulomb-Breit Hamiltonian or some approximation obtained from it:

$$\hat{\mathcal{H}}^{DCB} = \hat{P}^+ \left[\sum_{i=1}^N (c\boldsymbol{\alpha}_i \hat{\mathbf{p}}_i + \beta_i c^2) + V_{Ni} + V_{ee} + \sum_{j>i=1}^N \hat{\mathcal{H}}_{ij}^B + V_{\text{nuc}} \right] \hat{P}^+ . \quad (3)$$

Here, $\boldsymbol{\alpha}$ and β are 4×4 matrices introduced by Dirac in order to obtain a relativistic wave equation for spin-1/2 particles from the ‘‘classical’’ relativistic Hamilton function. In its standard representation, $\boldsymbol{\alpha}$ is written in terms of the well known Pauli spin-matrices $\boldsymbol{\alpha}_x$ (not to be confused with the symbol for the nuclear shielding tensor). The $\hat{\mathcal{H}}_{ij}^B$ (Breit interaction, see, e.g., reference 4) are relativistic corrections to V_{ee} that contain the so-called magnetic interaction and further account for the fact that the electron-electron interaction is not instantaneous but is transmitted with a finite speed. Use of the projection operators \hat{P}^+ cures some of the problematic features of the Dirac-Coulomb(-Breit) operator by restricting its solutions to the positive energy spectrum, the eigenfunctions of which are identified with the desired electronic states (no-pair approximation^{2,5}). We have to stress here that though $\hat{\mathcal{H}}^{DCB}$ is in general not truly Lorentz-invariant, it ‘‘provides an excellent approximation to the full theory’’.³

The main difference between the four-component relativistic and the nonrelativistic Hamiltonian is seen to be in the kinetic energy operator for an electron, which is $c\boldsymbol{\alpha} \hat{\mathbf{p}} + \beta c^2$ in equation (3) instead of $\hat{\mathbf{p}}^2/2$ in $\hat{\mathcal{H}}^{\text{nrel}}$. It takes into account the relativistic increase of electron mass due to high velocities, it includes the electron’s rest mass energy, it incorporates the electron spin, and also causes the spin-orbit coupling. Though electron spin needs to be considered in the nonrelativistic theory in an ad-hoc manner in order to account for experimental facts, a coupling between spin- and orbital degrees of freedom occurs only in the relativistic theory. For simplicity of notation, we will omit the \hat{P}^+ ’s in the following, and we will further not explicitly consider the Breit-interaction since it is actually being

neglected in many computations. Its relative importance to, e.g., total atomic energies was found to decrease with increasing nuclear charge from $\sim 50\%$ in He to $\sim 2\%$ in Hg relative to the one-electron relativistic corrections.⁶

A conceptually straightforward way of performing a relativistic molecular computation in order to obtain a starting point for a calculation of NMR properties is to use directly the time-independent Dirac equation

$$\hat{\mathcal{H}}^D \psi^D = \psi^D E \quad (4)$$

with

$$\hat{\mathcal{H}}^D = c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta c^2 + V \quad . \quad (5)$$

Note that we used here the aforementioned simple notation for (effective) one-electron equations. ψ^D is a four-component relativistic orbital. Because of $\boldsymbol{\alpha}$ and β being 4×4 matrices, the wavefunction has to be a four-component vector for which each component is a complex function of space. Due to the four components, such molecular computations are unfortunately quite expensive as compared to nonrelativistic ones, and the explicit inclusion of electron correlation is a formidable task.

Many attempts have been made to transform the four-component equation (4) into two-component form, in order to keep interpretations more simple¹ and to reduce the computational effort. Here we will give an account of some of these methods. Writing $\boldsymbol{\alpha}$ explicitly in terms of the 2×2 Pauli spin-matrices $\boldsymbol{\alpha}_s$, the Dirac equation (4) reads

$$(\hat{\mathcal{H}}^D - E)\psi^D = \begin{pmatrix} V - E & c\boldsymbol{\alpha}_s\hat{\mathbf{p}} \\ c\boldsymbol{\alpha}_s\hat{\mathbf{p}} & V - E - 2c^2 \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = 0 \quad . \quad (6)$$

The zero of the energy scale has been shifted in equation (6) to $+mc^2$, $m = 1$, the rest mass energy of the electron, so that bound states have negative energy as usual in nonrelativistic quantum chemistry. Here, φ and χ are the so-called ‘‘upper’’ and ‘‘lower’’ components of the four-component orbital ψ^D , each of them made up of two components. The functions φ and χ are also frequently referred to as the ‘‘large’’ and ‘‘small’’ components because of the $1/2c$ prefactor in equation (7) below.² From the second row of the matrix one obtains explicitly

$$\chi = X\varphi = \frac{1}{2c}k\boldsymbol{\alpha}_s\hat{\mathbf{p}}\varphi \quad , \quad (7)$$

with $k = (1 - [(V - E)/2c^2])^{-1}$, which yields the relation between the upper and the lower component.

¹However, so-called picture change effects occur, a discussion of which is beyond the scope of this overview. See, e.g., reference 7 and references cited therein

²Note however that, depending on the potential and the location, the ‘‘small component’’ can be much larger than the ‘‘large’’ one, e.g. for $p_{1/2}$ orbitals close to the nucleus

Because φ and χ are not independent from each other, it should be possible to obtain a relativistic two-component equation for φ or χ alone, the solutions of which contain the same information as ψ^D . In the ESC scheme (elimination of the small component), equation (7) is directly substituted in the equation obtained from the 1st row of the matrix in (6) and yields the two-component Hamiltonian:

$$\hat{\mathcal{H}}^{\text{ESC}} = V + \frac{1}{2}(\boldsymbol{\alpha}_s \hat{\mathbf{p}})k(\boldsymbol{\alpha}_s \hat{\mathbf{p}}) \quad . \quad (8)$$

In the nonrelativistic limit, $c \rightarrow \infty, k \rightarrow 1$, and then, with $(\boldsymbol{\alpha}_s \hat{\mathbf{p}})^2 = \hat{\mathbf{p}}^2$, the nonrelativistic Schrödinger Hamiltonian is recovered from the ESC operator (8):

$$\hat{\mathcal{H}}^{\text{nrel}} = V + \frac{1}{2}(\boldsymbol{\alpha}_s \hat{\mathbf{p}})^2 \quad . \quad (9)$$

Another way in which to obtain the nonrelativistic limit is to multiply (4) with $\hat{\mathcal{H}}^D$ before taking the limit $c \rightarrow \infty$. Though the ESC equation appears to be very illustrative, the Hamiltonian depends (through k) on the unknown energy and is not usable in actual linear variational calculations. In order to arrive at an energy-independent two-component equation, the Foldy-Wouthuysen (FW) transformation of $\hat{\mathcal{H}}^D$ to block-diagonal form is achieved by

$$\hat{\mathcal{H}}^{\text{FW}} = U \hat{\mathcal{H}}^D U^{-1} \quad . \quad (10)$$

In case $\hat{\mathcal{H}}^{\text{FW}}$ is block-diagonal, this completely uncouples the upper and lower component and yields the desired two-component equation and $\chi = X\varphi$, an energy-independent relation between upper and lower component (see equation (7)). U can be written in terms of X , see, e.g., the literature cited in reference 7. For many-electron systems, the exact form of X and U and therefore the exact form of $\hat{\mathcal{H}}^{\text{FW}}$ are not known. Different approximations for X yield different approximate two-component Hamiltonians in which the uncoupling of the two components is only achieved to a certain order in c^{-2} . These approximate two-component Hamiltonians are sometimes collectively denoted as “quasi relativistic”.

A rather simple approach is to expand (7) to zeroth order in c^{-2} . This yields $X \approx c\boldsymbol{\alpha}_s \hat{\mathbf{p}}/2c^2$, which results in the famous Pauli Hamiltonian⁸ after carrying out the transformation (10) with $U(X)$:

$$\hat{\mathcal{H}}^{\text{Pauli}} = \hat{\mathcal{H}}^{\text{nrel}} - \frac{\hat{\mathbf{p}}^4}{8c^2} - \frac{(\hat{\mathbf{p}}^2 V)}{8c^2} + \frac{i}{4c^2} \boldsymbol{\alpha}_s [(\hat{\mathbf{p}} V) \times \hat{\mathbf{p}}] \quad . \quad (11)$$

The second, third, and fourth term on the r.h.s. of (11) are the mass-velocity (MV), Darwin (DAR), and spin-orbit (SO) term, respectively, representing corrections of order c^{-2} to the nonrelativistic Hamiltonian. The Pauli operator has certain pathological features due to the fact that close to a nucleus where V is very large (it goes to $-\infty$ for point-like nuclei), $(V - E)/2c^2$ is not small and neglecting

this term in equation (7) is not justified. As a result, the Pauli operator contains severe singularities. Moreover, it is not variationally stable and permits only a perturbational treatment to first order. Higher order contributions yield diverging terms. Variational computations based on the Pauli operator have been frequently carried out, by using frozen cores and minimal basis sets in the core regions for valence orbitals, under which circumstances the variational instability can be kept somewhat under control in many cases. We will refer to such frozen core methods in Secs. 3 and 4 when speaking about variational Pauli computations. A *scalar relativistic* approach is obtained by omitting the SO term. This yields a one-component formalism analogous to the nonrelativistic scheme with pure α - and β - spin orbitals, that contain the — in many cases dominant — scalar relativistic effects. It is also possible to separate off a spin-orbit part in the Dirac equation.

One of the possible alternatives for the Pauli Hamiltonian is offered by the so-called ZORA (zeroth order regular approximation) method.⁹ Some authors refer to the ZORA Hamiltonian as the CPD (Chang-Pélissier-Durand) operator. It is obtained from the zeroth order of an expansion of k in powers of $E/(2c^2 - V)$ in equation (7). This expansion parameter remains rather small in particular where the potential V goes to $-\infty$. The two-component ZORA Hamiltonian resulting from the transformation (10) reads

$$\hat{\mathcal{H}}^{\text{ZORA}} = V + \frac{1}{2}(\boldsymbol{\alpha}_s \hat{\mathbf{p}})\mathcal{K}(\boldsymbol{\alpha}_s \hat{\mathbf{p}}) \quad (12a)$$

$$= V + \frac{1}{2}\hat{\mathbf{p}}\mathcal{K}\hat{\mathbf{p}} + \frac{i}{2}\boldsymbol{\alpha}_s[(\hat{\mathbf{p}}\mathcal{K}) \times \hat{\mathbf{p}}] \quad (12b)$$

with $\mathcal{K} = 2c^2/(2c^2 - V)$. Note the formal similarity to the ESC Hamiltonian in (8), with k replaced by \mathcal{K} . The nonrelativistic limit corresponds to $\mathcal{K} \rightarrow 1$, $(\hat{\mathbf{p}}\mathcal{K}) = 0$. The first and the second term in (12b) yield $\hat{\mathcal{H}}^{\text{nrrel}}$ plus scalar relativistic corrections, while the third term is the ZORA spin-orbit (SO) operator. For small V , $(\hat{\mathbf{p}}\mathcal{K}) \approx (\hat{\mathbf{p}}V)/2c^2$, and the ZORA spin-orbit term is similar to the Pauli spin-orbit term. Close to a nucleus, both operators differ substantially. The use of the ZORA method in heavy element computations is becoming increasingly popular, and the results are in most cases superior to those obtained with the Pauli operator. Conceptually, the ZORA operator has the disadvantage of not being invariant with respect to a change of the origin of the energy scale (gauge invariance), as can be seen from the fact that only V but not $(V - E)$ occurs in the operator. The standard choice for the potential is $V(\mathbf{r}) \rightarrow 0$ for $\mathbf{r} \rightarrow \infty$. Most of the resulting problems can be circumvented by a “scaling” procedure or by the use of frozen core potentials or model potentials for the construction of \mathcal{K} .

A different way of transforming the Dirac Hamiltonian to two-component form is used in the Douglas-Kroll (DK) method. Here, U in equation (10) is obtained via subsequent transformations

that uncouple the upper and lower components to some order n in c^{-2} written as

$$U_n = \sqrt{1 + W_n^2} + W_n \quad (13)$$

with W_n being anti-hermitian. For U_0 , the FW transformation for the free electron is used. To higher orders, equations for W_n have to be solved in order to achieve further uncoupling. Already with U_1 , most of the relativistic effects are recovered. We refer the reader to, e.g., reference 3 for details and original references. In particular due to the work of Hess and coworkers, the DK method has been established as a reliable tool in quantum chemistry for the computation of heavy element compounds. To some extent, the ZORA and the DK method to lowest order yield quite comparable results for many molecular properties. As an advantage, the DK method does not suffer from a gauge invariance problem, at the expense of a somewhat more complicated formalism, in particular if spin-orbit coupling and magnetic fields are included.

In order to arrive at a relativistic perturbation theory that avoids the infinities of the Pauli Hamiltonian to higher orders, so-called “direct” or “Dirac” four-component perturbation theory (DPT) can be employed. By a simple change of metric between upper and lower components in the Dirac-equation (6), an expansion of the resulting four-component equation in powers of c^{-2} is straightforward and leads to non singular first- and higher order expressions for E and ψ . A treatment of magnetic properties has been described in detail in the literature.¹⁰ However, higher order expressions become computationally rather expensive, while at the same time it is well known that first-order relativistic perturbation theory is not sufficient for such “relativistic” elements as, e.g., Au, Hg or Pb for the determination of bond energies or molecular geometries. It can be assumed that relativistic corrections of order c^{-4} are necessary as well for NMR parameters for such nuclei, in which case a variational procedure (Dirac, ZORA, DK) might be already easier to implement and computationally not much more or even less expensive.

As an alternative to the aforementioned methods which incorporate relativity directly into the calculations, the use of relativistic effective core potentials (ECPs) allows for consideration of relativistic effects in molecular computations. Inclusion of spin-orbit coupling is also possible in these methods. Recent benchmark calculations¹¹ have shown that ECPs can yield very reliable properties of heavy element compounds.

As already mentioned, the potential V in the equations in this section might not simply refer to the external potential (e.g. V_{Ni}) for one-electron systems but to an effective many-electron potential. In this case, V implicitly contains effects that are due to the electron-electron Coulomb repulsion $1/r_{ij}$. The explicit transformation of $1/r_{ij}$ to two-component form yields new relativistic operators of order c^{-2} instead, for example the two-electron spin-orbit operator. Use of the effective electronic potential in V in the one-electron SO operator accounts, to some extent, for these two-electron terms in a mean-

field sense. Transformation of the Breit interaction to two-component form yields further two-electron terms.

2.2 Nuclear shieldings and spin-spin couplings

A basic quantity that formally allows access to many properties of atoms and molecules is the total (electronic + nuclear repulsion) energy E of the system. It is readily available, to some degree of accuracy depending on the approximations that have been made, from quantum chemical computations, either from a relativistic or nonrelativistic formalism, based on variational or perturbational approaches. We will refer to the wavefunction or the set of orbitals that produced this energy as the “zeroth order solution”. In practice, it does not initially contain the effects from external magnetic fields or nuclear spins, but it might incorporate relativistic effects. Many observables, among them NMR shielding and spin-spin coupling tensors, can be defined as derivatives of the total energy of the system under investigation. The shielding tensor σ for a nucleus A is given by

$$\sigma(A) = \left. \frac{\partial^2 E}{\partial \mathbf{B}^{\text{ext}} \partial \boldsymbol{\mu}_A} \right|_{\mathbf{B}^{\text{ext}}=0, \boldsymbol{\mu}_A=0}, \quad (14a)$$

while the reduced nuclear spin-spin coupling tensor \mathbf{K} involving two nuclei A and B is obtained from

$$\mathbf{K}(A, B) = \left. \frac{\partial^2 E}{\partial \boldsymbol{\mu}_A \partial \boldsymbol{\mu}_B} \right|_{\boldsymbol{\mu}_A=0, \boldsymbol{\mu}_B=0}. \quad (14b)$$

Here, \mathbf{B}^{ext} is the applied external magnetic field, and $\boldsymbol{\mu}_A$ is the magnetic moment of nucleus A , related to its intrinsic angular momentum \mathbf{I}_A by $\boldsymbol{\mu}_A = \gamma_A \hbar \mathbf{I}_A$ with γ_A being the magneto-gyric ratio of the nucleus. We refer to some of the many excellent review articles focusing on the nonrelativistic computation of NMR parameters for details.^{12–15} Equations (14a,14b) conceptually serve as the starting point for a perturbational approach by which the energy derivatives can be evaluated once the zeroth order solution has been obtained. For the spin-spin coupling, the direct (through-space) coupling between two nuclei does not yield a contribution to the coupling constants for rapidly rotating molecules (i.e. for measurements in gas phase or in solution) and will not be discussed further. We implicitly refer to indirect spin-spin couplings throughout the rest of this work.

For the general case of two perturbations, described by the perturbation parameters κ and λ with Cartesian components $\kappa_x, \kappa_y, \kappa_z$ etc., the mixed second derivative of the total energy

$$E = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle \quad (15)$$

with respect to the perturbation parameters is given from standard double perturbation theory by equa-

tion (16) below. There it is assumed that the Hellmann-Feynman theorem holds w.r.t. the first perturbation λ for approximate zeroth-order solutions. In the NMR case, the nuclear magnetic moments or the external magnetic field are directly interpreted as the perturbation parameters due to their relative “smallness”.

$$E^{(1,1)} := \left. \frac{\partial^2 E}{\partial \kappa \partial \lambda} \right|_{\kappa=0, \lambda=0} = \langle \Psi^{(0,0)} | \hat{\mathcal{H}}^{(1,1)} | \Psi^{(0,0)} \rangle + 2 \operatorname{Re} \langle \Psi^{(0,1)} | \hat{\mathcal{H}}^{(1,0)} | \Psi^{(0,0)} \rangle \quad (16)$$

The superscripts denote the order of perturbation w.r.t. λ and κ , respectively. Because λ and κ are vectors, $E^{(1,1)}$ is a 2nd rank tensor. $\hat{\mathcal{H}}^{(1,0)} = \partial \hat{\mathcal{H}} / \partial \lambda |_{\lambda=0}$, $\Psi^{(0,1)} = \partial \Psi / \partial \kappa |_{\kappa=0}$, etc.. $\Psi^{(0,1)}$ represents the change of the wavefunction due to the presence of the perturbation denoted by κ , i.e. either the external magnetic field, or the magnetic field arising from one of the nuclear spins. $\Psi^{(0,1)}$ can be formally obtained from solving the first-order perturbed wave equation

$$(\hat{\mathcal{H}}^{(0,0)} - E^{(0,0)})\Psi^{(0,1)} + (\hat{\mathcal{H}}^{(0,1)} - E^{(0,1)})\Psi^{(0,0)} = 0 \quad , \quad (17)$$

showing that $\hat{\mathcal{H}}^{(0,1)}$ has to be known in order to compute $\Psi^{(0,1)}$. In DFT, formally similar expressions involving a sum over the Kohn-Sham orbitals instead of the many-electron wavefunction Ψ are used to compute σ and \mathbf{K} .

In the sum-over-states formulation it is assumed that the unperturbed ground-state $\Psi_0 = \Psi^{(0,0)}$ with $E_0 = E^{(0,0)}$ and *all* the excited states (energies E_i and wavefunctions Ψ_i) corresponding to the field-free Hamiltonian $\hat{\mathcal{H}}^{(0,0)}$ are known. The Ψ_i form a complete basis set in which $\Psi^{(0,1)}$ can be expressed as

$$\Psi^{(0,1)} = \sum_{a \neq 0} \Psi_a C_a \quad (18)$$

with yet unknown coefficients C_a . With the first-order equation (17), one obtains for the C_a after some manipulation

$$C_a = \sum_{a \neq 0} \frac{\langle \Psi_a | \hat{\mathcal{H}}^{(0,1)} | \Psi_0 \rangle}{E_0 - E_a} \quad , \quad (19)$$

and therefore for the nuclear shielding or spin-spin coupling

$$E^{(1,1)} = \langle \Psi_0 | \hat{\mathcal{H}}^{(1,1)} | \Psi_0 \rangle + 2 \operatorname{Re} \sum_{a \neq 0} \frac{\langle \Psi_0 | \hat{\mathcal{H}}^{(0,1)} | \Psi_a \rangle \langle \Psi_a | \hat{\mathcal{H}}^{(1,0)} | \Psi_0 \rangle}{E_0 - E_a} \quad . \quad (20)$$

We have to stress here that though equation (20) is *formally* correct, in practice not all (or any) of the excited states of $\hat{\mathcal{H}}^{(0,0)}$ are (or can be) known. However, equation (20) serves as a convenient basis for an interpretation of the final results and approximations to it can be easily identified within orbital

models. Employing variational perturbation theory, $E^{(1,1)}$ is in practice usually directly computed from the zeroth order solution based upon the set of occupied and unoccupied (virtual) orbitals that serve as a one-particle basis in most theoretical methods.¹⁶ In simple cases, for each occupied orbital a sum over virtual orbitals similar to (20) can be derived as the contributions to $E^{(1,1)}$, in which $E_0 - E_a$ is replaced by differences between occupied and virtual orbital energies, $\epsilon_i - \epsilon_a$. However, these orbital contributions also take into account for possible first-order change in the potential caused by the perturbation, and a possible dependence of the basis set on the perturbation. Neglecting any change in the potential V leads to so-called uncoupled equations that are much easier and computationally cheaper to solve.³ For interpretation purposes, the potential change is often negligible, in which case the orbital contributions can have exactly the form (20), but with Ψ_0 replaced by an occupied orbital ψ_i (with energy ϵ_i) and Ψ_a and E_a replaced by virtual orbitals ψ_a and their energies ϵ_a . In particular the HOMO-LUMO gap plays an important role here, since it leads to the largest individual $1/(\epsilon_i - \epsilon_a)$. Another factor is, of course, the magnitude of the $\langle \psi_i | \hat{\mathcal{H}}^{(0,1)} | \psi_a \rangle$ and $\langle \psi_a | \hat{\mathcal{H}}^{(1,0)} | \psi_i \rangle$ matrix elements. For chemical shifts (not shieldings) and spin-spin couplings, it turns out that $\langle \Psi_0 | \hat{\mathcal{H}}^{(1,1)} | \Psi_0 \rangle$, the diamagnetic term (see below), is often of only minor importance. It is possible to write the diamagnetic term in a sum-over-states form as well.¹⁷ *For simplicity of notation, we will refer to equation (20) as the working equation for evaluating σ and \mathbf{K} regardless of the actual method being used.*

Once the zeroth order solution is known, and the perturbation operators w.r.t. μ_A and \mathbf{B}^{ext} have been formulated, σ and \mathbf{K} can be computed based on equation (20) in some chosen computational approximation. For the relativistic case of heavy element systems, E , Ψ and the perturbation operators refer to a relativistic zeroth-order treatment. In case relativity is treated as a perturbation itself, this leads to at least 2nd + 3rd order perturbation expressions for σ and \mathbf{K} in which the order of derivatives is arbitrary. In this case, relativity can be conceptually regarded as a perturbation of an initially nonrelativistic expression for (14a), (14b).

In order to apply equation (20) for the computation of NMR shieldings or spin-spin couplings, the presence of the external magnetic field \mathbf{B}^{ext} and the magnetic field due the nuclear spins has thus to be considered in the theory. More specifically, within a chosen theoretical level (nonrelativistic, four-component, a variational two-component scheme, relativistic perturbation theory, ...) the Hamiltonian $\hat{\mathcal{H}}(\mathbf{B}^{\text{ext}}, \mu)$ is to be formulated in order to determine $\hat{\mathcal{H}}^{(1,1)}$, $\hat{\mathcal{H}}^{(1,0)}$ and $\hat{\mathcal{H}}^{(0,1)}$. Magnetic fields \mathbf{B} are usually incorporated into quantum chemistry by finding the corresponding magnetic vector potential \mathbf{A} which is related to the magnetic field \mathbf{B} by $\mathbf{B} = \nabla \times \mathbf{A}$, and making the so-called

³In DFT, neglecting the current-density dependence of the density functional leads to the mentioned uncoupled approach when the first-order perturbations of the orbitals due to the external magnetic field are evaluated.

minimal substitution for the momentum operator in the field-free Hamiltonian,

$$\hat{\mathbf{p}} \longrightarrow \hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} - q\mathbf{A} \quad , \quad (21)$$

with respect to a particle of charge q . We will use $q = -e = -1$ for an electron in the following.

The well-known gauge-invariance problem arises here, viz. a given magnetic field does not uniquely define the vector potential, since adding the gradient $\nabla f(\mathbf{r})$ of any scalar function to \mathbf{A} does not change \mathbf{B} , because $\nabla \times \nabla f(\mathbf{r}) = 0$. Often, f is chosen such that $\nabla \mathbf{A} = 0$ (Coulomb gauge). We will use this gauge in the following. A different gauge of \mathbf{A} can, e.g., be represented by choosing a different origin for the coordinate representation of \mathbf{A} . Though for a large class of variationally determined *exact* wavefunctions, expectation values do not depend on the chosen gauge, this is not generally true for approximate wavefunctions in a finite basis.¹⁶

For a point-like nuclear magnetic dipole, the vector potential is

$$\mathbf{A}_A^\mu = \frac{1}{c^2} \frac{\boldsymbol{\mu}_A \times \mathbf{r}_A}{r_A^3} \quad , \quad (22)$$

\mathbf{r}_A being the distance vector with respect to nucleus A , and r_A its length. Due to the strong inhomogeneity of \mathbf{A}_A^μ , the position of the nucleus A is generally used as the origin for \mathbf{A}_A^μ . The vector potential of an external, homogeneous magnetic field reads

$$\mathbf{A}^{\text{ext}} = \frac{1}{2} \mathbf{B}^{\text{ext}} \times \mathbf{r} \quad . \quad (23)$$

For a molecule with many atoms there exists no obvious gauge origin since \mathbf{r} refers to an arbitrarily chosen coordinate system. Nuclear shieldings obtained with wavefunctions approximated in a finite basis depend more or less strongly on the chosen origin. The \mathbf{A}^{ext} gauge problem is circumvented in, e.g., the GIAO (gauge-independent or gauge-including atomic orbitals) or the IGLO (individual gauge for localized orbitals) methods. In these methods, field dependent basis functions or molecular orbitals are employed to ensure gauge-invariance of expectation values. Such distributed gauge-origin methods are commonly used in computations of chemical shieldings. Another, less effective procedure is to supplement the basis sets by functions that are chosen such as to remove the gauge dependence to some extent without being of critical importance for the determination of the energy or the molecular structure. The gauge-origin problem has been extensively discussed in the literature, see, e.g., references 12, 13, 18 and literature cited therein for details.

Equation (22) is the most frequently used expression for the nuclear magnetic vector potential. However, it is known that for very accurate relativistic results, a finite nucleus model should be adopted both to obtain the zeroth order solution as well as in the NMR perturbation calculation. However, almost all of the results quoted later in this work have been obtained with the point-nucleus approxima-

tion, and the influence of finite-nucleus corrections on the final results does not seem to be of critical importance.

Substituting (21) into the nonrelativistic one-electron Schrödinger Hamiltonian, equation (9), yields the additional “magnetic” terms

$$\hat{\mathcal{H}}_{\text{nrel}}^{\text{mag}} = \frac{1}{2}(\mathbf{A} \hat{\mathbf{p}} + \hat{\mathbf{p}} \mathbf{A} + i \alpha_{\mathcal{S}}[\hat{\mathbf{p}} \times \mathbf{A} + \mathbf{A} \times \hat{\mathbf{p}}] + \mathbf{A}^2) \quad . \quad (24)$$

The expressions linear in \mathbf{A} are called the paramagnetic terms, while those proportional to \mathbf{A}^2 are called the diamagnetic terms. The second term on the r.h.s. of equation (24) describes the interaction of the electronic spin with a magnetic field and is not present if one starts with the one-component Schrödinger equation where $(\alpha_{\mathcal{S}} \hat{\mathbf{p}})^2$ of equation (9) is replaced by $\hat{\mathbf{p}}^2$ before the minimal substitution is made (this implies that the substitution $\hat{\mathbf{p}} \rightarrow \hat{\boldsymbol{\pi}}$ has to be made before transformation to two-component form and then the limit $c \rightarrow \infty$ is taken). In the ZORA or ESC case, formally very similar magnetic operators are obtained that contain relativistic corrections due to the presence of \mathcal{K} or k . For the ZORA case, see references 19, 20. For a derivation of the magnetic terms arising from the 2nd-order DK transformation and from the Pauli-Hamiltonian see references 21, 22. The ESC case is illustrated elsewhere.²³

Substituting $\hat{\mathbf{p}}$ with $\hat{\boldsymbol{\pi}}$ in the one-electron Dirac operator (5) yields a single paramagnetic term

$$\hat{\mathcal{H}}_{\text{D}}^{\text{mag}} = c \alpha \mathbf{A} \quad . \quad (25)$$

Since the nonrelativistic limit (24) as well as relativistic two-component Hamiltonians afford a diamagnetic term, this should be contained in a result for $E^{(1,1)}$ obtained from (25). It has been shown that a diamagnetic contribution to $E^{(1,1)}$ in equation (16) indeed arises in the four-component scheme due to the contributions from negative energy eigenfunctions of $\hat{\mathcal{H}}^{\text{D}}$, that are used as a basis set in a sum-over-states expression for $\Psi^{(0,1)}$ in equation (16),²⁴ even though there is only a paramagnetic perturbation operator (25).

Upon explicit substitution of $\mathbf{A} = \mathbf{A}^{\text{ext}} + \sum_A \mathbf{A}_A^\mu$ from equation (23), and equation (22) or a finite-size magnetic dipole version of it, $\hat{\mathcal{H}}^{\text{mag}}(\mathbf{B}^{\text{ext}}, \boldsymbol{\mu})$ is finally obtained. Taking the derivatives w.r.t. \mathbf{B}^{ext} and $\boldsymbol{\mu}_A, \boldsymbol{\mu}_B$ then yields $\hat{\mathcal{H}}^{(1,1)}$, $\hat{\mathcal{H}}^{(0,1)}$ and $\hat{\mathcal{H}}^{(1,0)}$ for a specific nonrelativistic or relativistic theoretical scheme. In the case of nuclear shieldings, it is most economic to take $\hat{\mathcal{H}}^{(1,0)} = \partial \hat{\mathcal{H}} / \partial \boldsymbol{\mu}_A |_{\boldsymbol{\mu}_A=0}$, while $\Psi^{(0,1)} = \partial \Psi / \partial \mathbf{B}^{\text{ext}} |_{\mathbf{B}^{\text{ext}}=0}$. In the nonrelativistic case, one obtains the one-electron operators

$$\hat{\mathcal{H}}_{\text{nrel}}^{\text{mag}}(\mathbf{B}^{\text{ext}}, \boldsymbol{\mu}) = \frac{1}{2} \mathbf{A}^{\text{ext}2} + \hat{\mathcal{H}}^{\text{OZ}} + \hat{\mathcal{H}}^{\text{SZ}} + \hat{\mathcal{H}}^{\text{OP}} + \hat{\mathcal{H}}^{\text{DS}} + \hat{\mathcal{H}}^{\text{FC}} + \hat{\mathcal{H}}^{\text{SD}} + \hat{\mathcal{H}}^{\text{OD}} \quad . \quad (26)$$

Here,

$$\hat{\mathcal{H}}^{OZ} = \frac{1}{2} \mathbf{B}^{\text{ext}} \cdot (\mathbf{r} \times \hat{\mathbf{p}}) = \frac{1}{2} \mathbf{B}^{\text{ext}} \cdot \hat{\mathbf{L}} \quad (27a)$$

$$\hat{\mathcal{H}}^{SZ} = \frac{1}{2} \mathbf{B}^{\text{ext}} \cdot \boldsymbol{\alpha}_s \quad (27b)$$

$$\hat{\mathcal{H}}^{OP} = \frac{1}{c^2} \sum_A \boldsymbol{\mu}_A \left(\frac{\mathbf{r}_A}{r_A^3} \times \hat{\mathbf{p}} \right) \quad (27c)$$

$$\hat{\mathcal{H}}^{DS} = \frac{1}{2c^2} \sum_A [(\boldsymbol{\mu}_A \cdot \mathbf{B}^{\text{ext}}) \left(\frac{\mathbf{r}_A}{r_A^3} \cdot \mathbf{r} \right) - (\boldsymbol{\mu}_A \cdot \mathbf{r}) (\mathbf{B}^{\text{ext}} \cdot \frac{\mathbf{r}_A}{r_A^3})] \quad (27d)$$

$$\hat{\mathcal{H}}^{FC} + \hat{\mathcal{H}}^{SD} = \frac{1}{2c^2} \sum_A \boldsymbol{\alpha}_s \left[\boldsymbol{\mu}_A (\nabla \cdot \frac{\mathbf{r}_A}{r_A^3}) - (\boldsymbol{\mu}_A \cdot \nabla) \frac{\mathbf{r}_A}{r_A^3} \right] \quad (27e)$$

$$\hat{\mathcal{H}}^{OD} = \frac{1}{2c^4} \sum_{B \neq A} \frac{(\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B) (\mathbf{r}_A \cdot \mathbf{r}_B) - (\boldsymbol{\mu}_A \cdot \mathbf{r}_B) (\boldsymbol{\mu}_B \cdot \mathbf{r}_A)}{r_A^3 r_B^3} . \quad (27f)$$

(27a) is the orbital Zeeman term, (27b) spin Zeeman, (27c) paramagnetic orbital, (27d) diamagnetic shielding, (27e) Fermi-contact + spin-dipole,⁴ (27f) diamagnetic orbital term, respectively. Note that the presence of c in the nonrelativistic magnetic operators does *not* denote any relativistic terms, but c emerges from the magnetic units in equation (22) and the fact that the fine structure constant equals $1/c$ in the chosen atomic units. As already mentioned, the operators in the ZORA or ESC case are formally quite similar to the nonrelativistic ones, but include \mathcal{K} or k and their derivatives, yielding different spatial contributions in particular for the FC term, but similar physical interpretations. We will therefore use the same names for the operators also when referring to these two-component relativistic schemes.

As compared to the nonrelativistic or two-component ones, the Dirac form of the one-electron magnetic operators look particularly simple:

$$\hat{\mathcal{H}}_D^{\text{mag}}(\mathbf{B}^{\text{ext}}, \boldsymbol{\mu}) = -\frac{c}{2} \mathbf{B}^{\text{ext}} \cdot (\boldsymbol{\alpha} \times \mathbf{r}) - \frac{1}{c} \sum_A \boldsymbol{\mu}_A \cdot \left(\boldsymbol{\alpha} \times \frac{\mathbf{r}_A}{r_A^3} \right) . \quad (28)$$

Taking the derivatives w.r.t. \mathbf{B}^{ext} and $\boldsymbol{\mu}_A$ in order to apply equation (20) is conceptually straightforward. Since (26) is connected to (28) as its nonrelativistic limit, the apparent simplicity of the four-component operators results in the many two-component terms through the coupling of the upper and lower components of the wavefunction by the Dirac operators. The ‘‘Gordon-decomposition’’ of the Dirac shielding tensor provides a route to interpret the four-component results in the more common way of paramagnetic and diamagnetic contributions.²⁵ See, e.g., reference 26 for numerical examples.

⁴The individual operators, in particular the well-known δ function for the FC term, are obtained by explicitly carrying out the differentiation of \mathbf{r}_A/r_A^3 in (27e)

Referring to the nonrelativistic scheme, equations (27a-27f), it can be seen that the OZ, OP and DS operators contribute to the nuclear shielding. Explicitly,

$$\begin{aligned} \hat{\mathcal{H}}^{(1,1)} &= \left. \frac{\partial^2 \hat{\mathcal{H}}^{DS}}{\partial \mathbf{B}^{\text{ext}} \partial \boldsymbol{\mu}_A} \right|_{\mathbf{B}^{\text{ext}}=0, \boldsymbol{\mu}_A=0} \\ \hat{\mathcal{H}}^{(1,0)} &= \left. \frac{\partial(\hat{\mathcal{H}}^{OP} + \hat{\mathcal{H}}^{FC} + \hat{\mathcal{H}}^{SD})}{\partial \boldsymbol{\mu}_A} \right|_{\boldsymbol{\mu}_A=0}, \quad \hat{\mathcal{H}}^{(0,1)} = \left. \frac{\partial \hat{\mathcal{H}}^{OZ}}{\partial \mathbf{B}^{\text{ext}}} \right|_{\mathbf{B}^{\text{ext}}=0} \end{aligned} \quad (29)$$

are used in equation (20). Here, the external field and the nuclear spin induce electronic paramagnetic orbital currents through $\hat{\mathcal{H}}^{OZ}$ and $\hat{\mathcal{H}}^{OP}$, respectively, the magnetic fields of which cause the paramagnetic nuclear shielding. The diamagnetic shielding contribution from $\hat{\mathcal{H}}^{DS}$ is due to the diamagnetic electronic currents induced in the electronic system. As already mentioned, we restrict the discussion here to the spin-compensated case (closed-shell molecules). Without spin-orbit coupling, the FC and SD term do not contribute to the nuclear shielding in closed shell systems, i.e. with pure spin-orbitals the contributions from spin-up and spin-down orbitals due to $\hat{\mathcal{H}}^{FC}$, $\hat{\mathcal{H}}^{SD}$ exactly cancel because the external magnetic field does not induce spin-density.

For nonrelativistic spin-spin couplings, one uses

$$\begin{aligned} \hat{\mathcal{H}}^{(1,1)} &= \left. \frac{\partial^2 \hat{\mathcal{H}}^{OD}}{\partial \mathbf{B}^{\text{ext}} \partial \boldsymbol{\mu}_A} \right|_{\boldsymbol{\mu}_A=0, \boldsymbol{\mu}_B=0} \\ \hat{\mathcal{H}}^{(1,0)} &= \left. \frac{\partial(\hat{\mathcal{H}}^{OP} + \hat{\mathcal{H}}^{FC} + \hat{\mathcal{H}}^{SD})}{\partial \boldsymbol{\mu}_A} \right|_{\boldsymbol{\mu}_A=0}, \quad \hat{\mathcal{H}}^{(0,1)} = \left. \frac{\partial(\hat{\mathcal{H}}^{OP} + \hat{\mathcal{H}}^{FC} + \hat{\mathcal{H}}^{SD})}{\partial \boldsymbol{\mu}_B} \right|_{\boldsymbol{\mu}_B=0}. \end{aligned} \quad (30)$$

Similar to NMR shieldings, the OP and OD terms introduce paramagnetic and diamagnetic electronic currents due to a nuclear magnetic moment that can further interact with the perturbations from another nucleus. The SD and in particular the FC term both yield nonzero contributions and cause a different coupling mechanism. These operators introduce a net electronic spin density at or around, say, nucleus A , which is transferred through the electronic system (chemical bonds) to nucleus B and interacts with its spin magnetic moment there. There is also a mixed term between the FC and the SD contribution, that contributes to the anisotropy of the \mathbf{K} tensor. Again, in the nonrelativistic case, where spin and spatial degrees of freedom are completely independent from each other, all ‘‘mixed’’ contributions to \mathbf{K} between orbital- and spin-dependent operators yield zero (e.g. the contribution due to $\hat{\mathcal{H}}^{FC}$ in $\hat{\mathcal{H}}^{(1,0)}$ with the one due to $\hat{\mathcal{H}}^{OP}$ in $\hat{\mathcal{H}}^{(0,1)}$ and vice versa in equation (20)). The same arguments concerning vanishing terms involving both spin- and orbital-dependent operators apply in the scalar relativistic case.

The situation is much different at the presence of spin-orbit (SO) coupling. Spatial and spin de-

degrees of freedom are then coupled and not anymore independent from each other. Not unexpectedly therefore, in, e.g., the Pauli, ESC, DK, or ZORA case including the one-electron spin-orbit (1e-SO) operator, mixed contributions involving both spin- and orbital-dependent operators occur for σ and \mathbf{K} in this case. In particular, the spin-dependent FC and SD terms contribute to the chemical shielding because, through SO coupling, an external magnetic field induces net spin-density even in a closed-shell system. Likewise, for spin-spin couplings, mixed terms between spin- and orbital dependent operators in $\hat{\mathcal{H}}^{(1,0)}$ and $\hat{\mathcal{H}}^{(0,1)}$ are no longer zero. In variational two-component procedures in which the zeroth order computation and the magnetic operators are based on the same formalism and no terms have been omitted initially, no new operators or new terms in the expressions for σ or \mathbf{K} arise due to SO coupling. In case that the (usually Pauli) 1e-SO operator is introduced as a first-order perturbation, the additional terms are formulated and calculated explicitly, which is convenient for interpretations. (The same holds for additional scalar relativistic corrections.) The operators arising from the minimal substitution $\hat{\mathbf{p}} \rightarrow \hat{\boldsymbol{\pi}}$ in the spin-orbit operator itself have thereby been overlooked for a long time.²² For nuclear shielding, the most important contribution due to spin-orbit coupling has been shown to arise from the FC term in the external magnetic field, while for spin-spin couplings, the FC-OP cross term appears to be dominant in the cases being investigated so far. See sections 3.1 and 4.2 for further comments and explanations. All the 1e-SO contributions are, of course, contained in the four-component treatment based on equation (28).

As already mentioned, transformation of the electron-electron interaction to two-component form yields various new terms, among them the two-component two-electron spin-orbit and spin-other-orbit operators (collectively being denoted here by “2e-SO”), which give rise to various additional magnetic contributions in the presence of magnetic fields. See, e.g., references 4, 16, 27 for theoretical details. Unless explicitly mentioned, we refer to the 1e-SO effects in the following. Actual program implementations may make use of an effective potential in the 1e-SO operator and the results may therefore contain two-electron SO effects to some extent.

2.3 Computational methods

While the importance of Hartree-Fock computations in quantum chemistry is generally decreasing in favor of either correlated ab-initio methods or DFT, it is still one of the common methods in the field of computation of heavy atom NMR parameters. A four-component implementation of Hartree-Fock shielding tensors and spin-spin couplings has been reported by Visscher and coworkers^{28,29} and an implementation for chemical shieldings by Nakatsuji and coworkers.^{26,30,31} Both implementations use a common gauge origin for the external magnetic field. Pioneering NMR Hartree-Fock calculations including scalar relativistic effects based on the Pauli operator or the DK transformation, and spin-orbit effects based either upon explicit consideration of the Pauli SO operator or the use of spin-orbit ECPs, have been reported by Nakatsuji et al.^{32,33} and by Fukui et al.^{21,22,34} Theoretically

somewhat less justified “mixed” methods such as using the scalar part of the DK operator together with Pauli SO for the zeroth order solution and nonrelativistic + Pauli SO operators for NMR shieldings have also been used with reasonable success.³⁵ The main disadvantage of the Hartree-Fock based methods is, of course, the neglect of electron correlation, that has been demonstrated to be of high importance for the determination of NMR parameters in general and of heavy atom spin-spin couplings in particular.

To the best of our knowledge, four-component post Hartree-Fock or DFT implementations of NMR parameters have not yet been carried out, but can be expected in the near future at least for the DFT case. Post Hartree-Fock MCSCF computations of heavy atom nuclear shieldings (employing GIAO) and spin-spin couplings have so far considered spin-orbit effects only, based on a perturbational first-order treatment of the Pauli SO operator.^{36–40} Scalar relativistic effects from the heavy atom were neglected in this case. This method is often suitable for NMR of light nuclei close to a heavy atom and has been successfully applied to small molecules. Likewise, SO ECPs are able to recover the important spin-orbit effects on neighbor atom shieldings that are being neglected by scalar relativistic ECPs.

The first-order SO approach has already been utilized in the pioneering computational approaches for the computation of nuclear shieldings in heavy atom compounds, involving simple semiempirical wavefunctions.^{41–44} For spin-spin couplings, relativistic effects have been first considered in form of correction factors applied on top of nonrelativistic Hartree-Fock or semiempirical wavefunctions.^{45,46} Four-component extended Hückel theory (REX) has been developed and extensively applied to both heavy atom shieldings and spin-spin couplings by Pyykkö and coworkers.⁴⁷

The restriction of excluding the heavy nuclei in the NMR computations applies technically to a common use of ECPs in heavy element computations. Existing methodology for NMR parameters that has been derived for all-electron calculations cannot be used without modification for NMR parameters of those atoms for which an ECP is used. In this case, either a NMR methodology directly derived from the pseudopotential formalism would have to be used, or at least the pseudo-orbitals need to be orthogonalized on the relativistic heavy atom cores before applying a standard all-electron code.

Density functional theory (DFT)⁴⁸ has been very successful in the field of heavy atom NMR computations. Methodological development for relativistic NMR computations has been performed in particular by Kaupp, Malkin, Malkina and coworkers^{49–51} (using the IGLO method for shieldings), and by Ziegler and coworkers (GIAO for shieldings).^{19,20,52–54} Taking into account that the electron density, the spin density and the current density define the one-electron magnetic contributions to σ and \mathbf{K} , and that these densities are (of course only in principle) obtained exactly from Kohn-Sham DFT,⁵⁵ its application to NMR parameters has a theoretically well founded base. From the experience gained so far it seems that the current-density dependence and also relativistic corrections of the exchange-correlation functional are not very large, and quite reasonable results can be obtained

with standard nonrelativistic local-density (LDA) or generalized gradient (GGA) approximations (in which, however, the density can be a relativistic one). The fact that electron correlation is to some extent accounted for in contemporary Kohn-Sham DFT, and due to its computational effectiveness with regards to the number of atoms that can be treated simultaneously, most of the relativistic NMR computations on larger systems such as transition metal complexes are currently based on DFT. For the heavy atom DFT NMR computations carried out so far, various relativistic methods have been utilized, among them perturbational use of the Pauli SO operator, variational computations with the Pauli operator and frozen cores excluding or including SO coupling, the use of the ZORA Hamiltonian, and use of scalar relativistic and spin-orbit ECPs.

We further note that some authors subdivide the relativistic effects of NMR parameters into “direct” and “indirect” effects, the latter being related to the change of the NMR parameters with respect to a change of the computed molecular structure due to relativity. It is known that small geometrical changes can result in sizeable changes of shieldings and couplings. The choice of experimentally determined structures, if available, for the computations is unambiguous and leaves only the “direct” effects to be discussed.

Apart from acronyms already specified in the previous sections, we will make use of the following abbreviations from now on: vPSO, vPSC, vPauli for variational Pauli SO only, scalar only, and scalar + SO, respectively. Similarly, pPSO, pPSC, pPauli denote first-order perturbational relativistic calculations. HF = Hartree-Fock. DKSC, DK = Douglas-Kroll, first order without and with SO corrections, respectively. MCSCF = multiconfigurational Hartree-Fock (ab-initio).

3 Heavy atom nuclear shieldings

Suggestions of the importance of relativistic corrections to nuclear shieldings and first numerical estimates for atoms date back to the 1960's. In 1969, Nakagawa argued that spin-orbit coupling will be an important factor for nuclear shieldings of light nuclei in the neighborhood of heavy halides.⁵⁶ Subsequently, semiempirical calculations of the respective SO effect in hydrogen and methyl halides were carried out by Morishima et al.,⁴¹ Volodicheva and Rebane⁴² and Cheremisin and Schastnev.⁴³ In the early 1980's, several authors published the formalism of nuclear shieldings within the four-component (Dirac) scheme.^{25,57,58} This work and its future importance was subsequently reviewed by Jameson⁵⁹ ⁵ See, e.g., reference 60 for a relativistic NMR application in solid-state physics. Already anticipated by Pyykkö⁵⁷ in his remark “A rigorous implementation of the present theory will [...] probably take some time”, four-component ab-initio (Hartree-Fock) calculations of NMR shieldings in molecules have been reported only rather recently.^{26,28,31}

⁵We also refer the reader to subsequent articles by Jameson, and Jameson et al., in this journal, who review the literature in the computational NMR field on a yearly basis. In particular the more recent articles show a large increase of publications based on relativistic methods.

Following the historical computational development we discuss spin-orbit (SO) effects on NMR shieldings prior to scalar relativistic effects.

3.1 Spin-orbit coupling effects

The proton chemical shift in the series of hydrogen halides HX ($X = \text{F, Cl, Br, I}$) and the ^{13}C shifts in CH_3X are probably the most thoroughly studied parameters in heavy atom NMR computations. The reason is that these molecules are among the smallest samples in which the strong SO dependence of NMR chemical shifts can be computed and compared to experiment. The HX and CH_3X series therefore serve as benchmarks for heavy atom NMR computations where, due to the smallness of the systems, high quality basis sets can be employed nowadays. The trend being obtained from the computations is always similar, regardless of which method has been used: excluding SO coupling does not recover the experimentally observed trend, but with inclusion of SO effects the calculated values follow the experimental trend. The numerical quality of the results is, of course, much dependent on the chosen method, and also somewhat on whether scalar relativistic effects have been additionally considered or not. Table 1 displays some of the results for the HX series that have been obtained during the last 3 decades. The data establish that the experimental trend can indeed be explained on the basis of SO effects only, while exclusion of SO effects does not reproduce the right trend even if scalar relativistic effects are considered.

Explanations of the SO contribution to nuclear shielding have been given in almost all of the articles quoted in Table 1 and many other papers. Qualitatively, let us consider the singlet (closed shell) ground state wavefunction without SO coupling first. As in equation (18), we assume that Ψ_0 and all the excited states of the Hamiltonian (without SO coupling) are available as a complete basis set. Expanding the spin-orbit coupled wavefunction in this basis means that, due to the nature of the SO operator, contributions also from excited triplet states will enter the SO wavefunction. Now the perturbed SO wavefunction in an external magnetic field, represented in the same basis, will have different coefficients for the singlet and triplet states and thereby the magnetic field can effectively induce a net spin density in the electronic system. The FC and SD operators also induce spin-density and therefore the contribution from these operators to the NMR shielding are no longer zero.

In the case of the shielding of a light nucleus L in the neighborhood of a heavy atom Y, the spin-density is induced by the external field around Y, transferred through the chemical bond(s) to the light nucleus L, and is there “detected” by the FC and SD perturbations (Heavy-Atom effect on the Light-Atom shielding, HALA, in contrast to the heavy atom effect on the heavy nucleus shielding itself, HAHA⁶¹). This suggests a qualitative similarity to the nonrelativistic FC/SD mechanism of nuclear spin-spin coupling, where the spin-density is not induced by the external field but by the FC and SD perturbation from another nucleus. This similarity has already been proposed in 1969 by Nakagawa et al.,⁵⁶ but no unambiguous numerical evidence could be provided. Recent DFT computations⁶²

on a number of systems convincingly demonstrate the correlation between $K(L,Y)$ and the spin-orbit contribution to $\sigma(L)$ induced by Y . In particular, a familiar Karplus-type dihedral angle relation known for three-bond spin-spin couplings has been obtained for the SO contribution to proton shielding in iodoethane that closely follows the behavior of ${}^3K(H,I)$. Many numerical results obtained by different authors show that the SD contribution to spin-orbit induced shielding can often be neglected, and the FC part is usually dominant. The same holds for nuclear spin-spin couplings (Sec. 4). Similar to spin-spin couplings, too, is that the magnitude of the FC contribution to nuclear shielding depends on the σ -character of the L–Y bond(s). This allows for similar chemical interpretations.^{51,62}

The case of $\delta({}^{13}\text{C})$ in methyl halides is not as spectacular as the hydrogen halides. Still, qualitative agreement with experimental data can only be achieved upon inclusion of SO coupling in the shieldings calculation, while scalar relativistic corrections are of minor importance. Benchmark data for these and other small molecules has been published, e.g., in references 32, 36, 43, 47, 49, 53, 63.

The importance of the influence of two-electron (2e-) SO operators or the Breit correction in the Dirac scheme has been investigated by some authors.^{30,36,50} For $\sigma({}^1\text{H})$ in HX and $\sigma({}^{13}\text{C})$ in MeX, the 2e-SO contributions were found to be small and of opposite sign to the 1e-SO shielding terms. The relative importance of the two-electron terms appears to be generally decreasing for these cases as the heavy atom becomes heavier, contributing about 30% to the (small) SO shift for F substituents and about 7% to the (large) SO shift for iodine substituents. Similar conclusions for the relative importance of the 2e-SO terms were obtained for the shielding of the heavy atom,³⁶ for which (see next section) the scalar relativistic effects should not be neglected. For increasingly heavy X, the scalar relativistic corrections may be of higher importance than the two-electron SO terms. See, e.g., the DK results in Table 1. On the other hand, the vPSC DFT values of reference 52 do not indicate such large scalar relativistic corrections. At the present level of accuracy that can currently be achieved by either nonrelativistic + pPSO or four component ab-initio methods, or relativistic DFT, the two-electron SO contributions appear to be rather negligible for heavy element molecules.

One of the major successes of relativistic NMR shieldings computations has been the explanation of the origin of the “normal” and “inverse” halogen dependence (NHD and IHD) in many compounds. Well known to experimentalists and theoreticians, shieldings of light atoms L bound to a halogen X quite often strongly increase as X becomes heavier (NHD) and its electronegativity decreases. Examples are HX, shown above, CH_3X , CH_2X_2 , etc., and many other main group compounds in particular in high oxidation states. However, counter examples are known, where the L nucleus becomes less shielded for decreasing electronegativity (and increasing nuclear charge) of X, at least for Cl (sometimes Br) compared to F. Sometimes, in those compounds the NHD is observed again for $\text{X} = \text{I}$ (and sometimes Br). Examples are SiX_4 , AlX_4^- , and many transition metal compounds. As in HX (Table 1), in the investigated cases the NHD is caused by the SO contribution to chemical shielding, while the nonrelativistic computations predict an IHD behavior. Figure 1 displays the Hartree-Fock

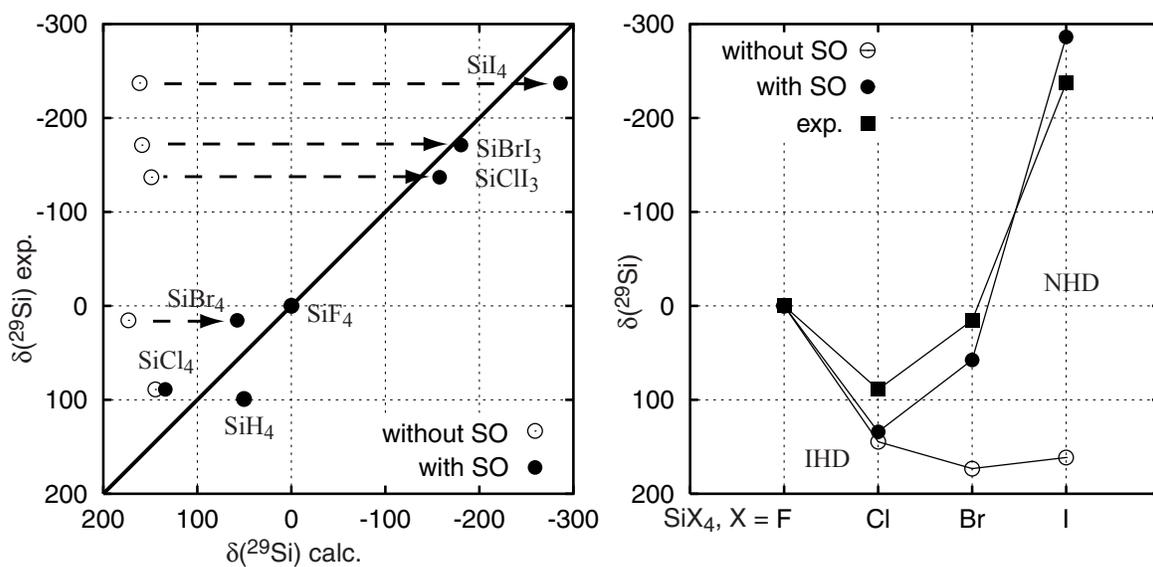


Figure 1: ^{19}Si chemical shifts with respect to SiF_4 in silane and some silicon halides, from Hartree-Fock data.³³ Scalar rel. and SO effects considered here via ECPs on the halide ligands. Left: experimental vs. computed Si shifts. Right: NHD and IHD along the SiX_4 series. See Sec. 3.1

data obtained for some silicon halides in 1995. Very similar results for these and other compounds were obtained in the same year by a semiempirical approach.⁴⁴ Extremely large SO corrections to the phosphorus chemical shift in PX_4^+ have been reported in reference 64 and were attributed to the pronounced s-character of the L–X bonds due to the high oxidation state of phosphorus. Similar NHD results can be found in many theoretical studies of the SO shielding contribution. The authors of reference 65 investigated a number of Ti tetrahalides and Nb hexahalides. Rather typical for early transition metal halides, almost vanishing net SO effects on the metal shielding were observed even for the tetra- and hexa-iodides, caused by a cancellation of positive SO contributions from the FC term and negative changes of the paramagnetic shielding at the presence of SO coupling. In this case, IHD for the series $\text{F} \rightarrow \text{I}$ is observed for the chemical shifts in agreement with experiment. This has been interpreted in terms of the different nature of the metal d-orbitals binding to the ligands as compared to (s- and) p-orbitals in the case of main group elements exhibiting NHD.

If one bases the interpretation for the IHD on equation (20), the decreasing HOMO-LUMO-gap due to decreasing electronegativity of the halogen in the series $\text{X} = \text{F} \rightarrow \text{I}$ results in a larger magnitude of the paramagnetic shielding, if the matrix elements in the sum over excited states are assumed to be approximately constant⁶. Since the nonrelativistic paramagnetic shielding contribution is typically

⁶In reference 66, excellent linear correlation of ^{95}Mo chemical shifts with the lowest magnetically allowed d-d* excitation

negative, this results in increasingly positive chemical shifts (IHD). From the investigations quoted above it becomes clear that the NHD, on the other hand, is due to the more pronounced influence of spin-orbit coupling, which often increases the shielding and therefore causes increasingly negative chemical shifts. The diamagnetic shielding, as a core property, is usually found to be of small influence concerning the chemical shifts. From the relativistic nature of the NHD it becomes clear why previous explanations of the NHD that only take the (nonrelativistic) paramagnetic shielding into account have not generally been convincing.

Density functional theory (DFT) has been particularly successful in the case of transition metal compounds, and generally in cases for which electron correlation has a strong influence on the NMR shielding, and where and a correlated ab-initio method including relativistic effects has not been available or has not been applicable due to the size of the system. See also the section on spin-spin couplings. An example where electron correlation is believed to be very important is the ^{13}C shift in the series of CX_3^+ . Nonrelativistic DFT and MP2 calculations show very similar results exhibiting IHD. This trend is also observed, but strongly overestimated, by nonrelativistic Hartree-Fock calculations, indicating the importance of electron correlation. Further inclusion of SO coupling in the DFT calculations recovers the experimentally observed NHD for $\text{X} = \text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ with good accuracy.⁶⁷

Most of the relativistic DFT studies of transition metal compounds include scalar relativistic effects and are discussed in the next section.

3.2 Including scalar relativistic effects

From a computational point of view, the most simple way of including scalar relativistic effects in a NMR shieldings calculation is to use an available scalar relativistic ECP on the heavy atom. In case HALA effects are studied, existing nonrelativistic NMR code can be (and is) used without modifications. Many studies have been carried out using this approach, see, e.g., references 51,68 for overviews of density functional applications in particular to transition metal complexes. In view of the importance of SO corrections to σ as seen in the previous section, however, the range of applications of this method seems to be limited. Spin-orbit ECPs have been applied to a number of NMR ligand shieldings including heavy main group and transition metal compounds.^{33,63} Restrictions with respect to HALA effects also apply to the purely scalar relativistic approach of reference 52, in which HX and a number of transition metal complexes are studied. However, the method is capable of treating the heavy metal shift (and HAHA effects) itself, with reasonable accuracy as shown for the W shifts in Table 2. In reference 69, an overview of this variational scalar Pauli method is given. Among other data, a large number of ^{125}Te shifts are presented. In comparison with experiment, the relativistic computations achieved good accuracy, therefore SO effects can be regarded as mostly unimportant for Te chemical

energy has been observed for a number of Mo complexes

shifts. An increase of the scalar relativistic effects of the chemical shielding of the heavy nucleus X with $\sim Z^{3.5}$ has been found from SCDK calculations for the HX series.²¹ This underlines the importance of scalar relativistic corrections for heavy nucleus shieldings. Computational methods that include both scalar relativistic and SO effects and have been applied to both light and heavy nucleus shieldings are, of course, the four-component methods,^{26,28,30} and, e.g., Douglas-Kroll including SO effects,⁷⁰⁻⁷² Pauli including SO,^{22,53} or the ZORA approach.^{19,73} A collection of transition metal tetroxo- and hexacarbonyl complexes appears to represent a benchmark test set for DFT NMR implementations. Oxygen shifts of group 6-8 transition metal tetroxo-complexes were studied, e.g., in references 52, 74 with a scalar relativistic approach. The rather good agreement with experimental shifts suggests that SO coupling does not play an important role in this case. Scalar relativistic effects on the ligand shifts appeared to be of high importance only for the 5d metals and are almost negligible for the 3d metals. The metal shifts in the same set of complexes were studied by variational scalar+SO Pauli and ZORA spin-orbit DFT.⁷⁵ Unfortunately, no oxygen shifts were reported there for comparison. The results for the metal shifts have been satisfactory, with ZORA emerging as the superior method in this case. Table 2 displays some ^{183}W shifts that were obtained by DFT methods and by a Hartree-Fock approach⁷⁰ including scalar + SO effects. The results indicate that scalar and SO effects are probably of equal importance for the W shifts. In reference 76, a larger number of W shifts than quoted in Table 2 have been computed by both variational vPauli and by ZORA DFT. ZORA resulted in a mean error of approximately 3% of the total shift range of 7000 ppm for the investigated samples when compared to experiment. The Pauli approach performed worse in this case, with an error of about 6%. ZORA produced a similarly accuracy for a number of ^{207}Pb chemical shifts reported in the same study (4% error compared to the covered shift range), whereas the mean error from the Pauli approach was found to be four times larger in this case. The ZORA computations predicted an enormous SO shift of the Pb shielding of PbI_4 of more than -8000 ppm — a number yet to be supported by experimental results.

Carbon chemical shifts for 5d transition metal carbonyl complexes studied with DFT are displayed in Table 3. SO effects play a less significant role for the ^{13}C chemical shift in these complexes as compared to HX, but systematically improve the computed results. The SO shifts do not easily follow intuitive arguments based on the size of the HOMO-LUMO gap (HLG).⁵³ From equation (20) the individual contributions to the shielding can be expected to decrease with increasing HLG along a row of the periodic table. Despite the fact that the HLG increases from approximately 2 to 6 eV from $[\text{Hf}(\text{CO})_6]^{2-}$ to $[\text{Ir}(\text{CO})_6]^{3+}$, the spin-orbit contribution to the nuclear shielding and to the chemical shift is nevertheless seen to be increasing from Hf to Ir. As illustrated in reference 53, the trend can be rationalized on the basis that, due to the relative energies of the metal d_σ , d_π and the CO σ and π^* orbitals, the bonding in Hf carbonyl is dominated by $d_\pi-\pi_{\text{CO}}^*$ interaction, whereas the bonding in Ir carbonyl is dominated by $d_\sigma-\sigma_{\text{CO}}$ interaction. CO is more likely to σ -donate charge to the highly

positively charged Ir, whereas metal-ligand π -back-donation dominates in the Hf complex. Only in the former case though, spin density can be effectively transferred to the carbon nucleus, therefore the magnitude of the SO induced carbon shift is increasing along the 5d transition metal carbonyl series despite the increasing HLG. It has been shown previously that the decreasing $\delta(^{13}\text{C})$ along the series at the scalar relativistic level is due to a complex interplay of different factors in which the amount of π -back-donation is predominant.^{77,78}

In a ZORA DFT study of ^{195}Pt chemical shifts,⁷⁹ the authors also found that simple arguments based on the magnitude of $1/(\epsilon_i - \epsilon_a)$ are not always able to provide an explanation of the observed trends. The magnitude of the matrix elements in the numerator of the sum in equation (20) has to be considered as well and needs to be explained by intuitive chemical arguments. In the case of Pt shifts, NHD is observed in many cases. An analysis of the computational data shows that both the SO contributions and the paramagnetic shielding approximately equally contribute to the NHD. For the paramagnetic shielding, this was attributed to a preference of the soft acid Pt(II) to bind to the soft base I instead of Cl. The authors in reference 79 could numerically and graphically illustrate that this results in a smaller magnitude of the (negative) paramagnetic shielding for iodine ligands due to smaller paramagnetic matrix elements in equation (20) that overcompensate the opposite HLG influence. The overall accuracy of the ZORA DFT method for Pt-shieldings resulted in a mean error of approximately 10% of the investigated chemical shift range for 23 samples.⁷⁹

Mercury shieldings have been computed by DFT and Hartree-Fock methods.^{19,71,72} Table 4 lists some results that have been obtained. As can be seen from the data for HgMeX and HgX_2 , the mercury halide compounds exhibit NHD, largely caused by the SO effects on the nuclear shieldings.^{19,71} Large “coupling” between scalar and SO corrections to mercury shifts were noted in reference 71. This means that the inclusion of both relativistic mechanisms is important in order to achieve reasonable results, because the SO correction based on a nonrelativistic zeroth order solution is much different from the one obtained from a scalar relativistic one. It is well known that scalar relativistic effects substantially stabilize and contract the 6s orbital in Hg, while the Hg 5d shell is destabilized and spatially expanded as compared to nonrelativistic computations. In effect, the scalar relativistic Hg–ligand bonds are much different from the nonrelativistic ones, meaning that the s- and d-contributions in the occupied and virtual metal-ligand orbitals, that determine to some extent the magnitude of the SO corrections to the chemical shifts, will be very different as well. In reference 71, the rather unsatisfactory performance of the computations, in particular the strong overestimation of the SO shift corrections for the HgX_2 series (Table 4, large basis set) was attributed to the missing treatment of 2e-SO terms. The authors proposed that 20 to 40 % of the 1e-SO contribution to the chemical shift may be canceled by the two-electron contributions, which seems to be excessive taking the previously quoted findings about the relative importance of the two-electron SO terms for heavy atom compounds into account. Considering the reasonable overall performance of the DFT calculations for Hg shifts

(they do not include 2e-SO operators explicitly), the inaccuracies of the Hartree-Fock results for HgX_2 could also be attributed to the missing treatment of electron correlation. Another problem might be the inconsistent treatment of relativity, viz. the use of the problematic Pauli SO operator in conjunction with the scalar relativistic DK Hamiltonian. This has been criticized by Fukui.²¹

For the series $\text{Hg}(\text{LCH}_3)_2$, $\text{L} = \text{C}, \text{Si}, \text{Ge}$, which has been computed with a DK transformed Hamiltonian including SO coupling, it was found that the rather small magnitudes of Hg chemical shifts are caused by cancellation of large relativistic and nonrelativistic contributions.⁷² Even the usually negligible SD contribution to the chemical shift is here comparable in magnitude to the shift itself. In that respect, the achieved results must be regarded as quite accurate and testify to the accuracy of the relativistic treatment with the DK Hamiltonian. The authors also consider missing solvent effects as a possible source of error, an issue that has already been addressed regarding mercury chemical shifts.¹⁹ Experimentally confirmed, the solvent dependence of, e.g., the Hg shift in HgI_2 can amount to more than 1000 ppm (pyridine vs. THF). It has been computationally demonstrated in reference 19, that direct coordination of the metal by a nucleophilic solvent (pyridine, simulated by NH_3 in the ZORA computations) is largely responsible for the large experimentally solvent effects on chemical shifts. The computations were able to qualitatively simulate a strong positive contribution to $\delta(^{199}\text{Hg})$ due to the coordination of the solvent to Hg. The resulting geometry change (bending of X-Hg-X by approximately 30 degrees) upon complexation was found to increase the magnitude of the chemical shift by ~ 600 ppm for HgCl_2 , while the direct interaction of the solvent with the heavy atom caused a large decrease of δ by ~ -1100 ppm. THF was supposed to coordinate much less strongly to Hg and not to cause a significant change of the linear structure of HgX_2 . A possible influence on the chemical shift due to THF that might account for the differences between theory and experiment in Table 4 has therefore not been investigated.

It should be noted here, that absolute shielding values of, e.g., 8020 ppm from ZORA DFT,¹⁹ and of 15128 ppm from spin-orbit DK Hartree-Fock⁷² for ^{199}Hg in $\text{Hg}(\text{CH}_3)_2$ have been reported. While the paramagnetic and diamagnetic shieldings are approximately equal in both methods, the reported spin-orbit corrections differ by ~ 7000 ppm. The differences obviously largely cancel regarding the chemical shift and demonstrate that due to cancellation of systematic errors, chemical shifts are much easier to compute accurately than absolute shieldings in particular for such heavy nuclei. We therefore do not list reported absolute shielding values in the tables.

Chemical shifts in compounds containing elements as heavy as uranium have been investigated^{73,80} with DFT. In reference 80, variational Pauli and ZORA calculations have been employed together with standard GGA functionals, as well as a scalar relativistic ECP in conjunction with the B3LYP hybrid functional. ^{19}F chemical shifts in a number of U-halide complexes were obtained with moderate absolute accuracy with both the ZORA and the Pauli approaches, while certain trends between different compounds could not be reproduced by the GGA functionals. SO effects for the F shifts were found

to be of low importance (typically ~ 30 ppm for Pauli and somewhat less for ZORA, as compared to experimental shifts between 750 and 790 ppm) The scalar relativistic ECP/B3LYP did yield systematically between 80 and 270 ppm too large chemical shifts, but certain trends were better reproduced. From this, the authors concluded that the ECP approach is beyond its limit for actinide NMR and that improved XC functionals are needed for the non-hybrid DFT methods in order to reproduce chemical trends among a series of compounds more accurately. A clearly better performance of ZORA vs. Pauli could not be observed in this study.

Many of the studies cited so far provide relativistic effects also on the shielding tensor anisotropy, $\Delta\sigma$. See references 28, 36, 37 for examples. The practical application of these quantities for heavy atom systems is, however, rather limited so far. We therefore refer to the literature for detailed discussions of relativistic effects on $\Delta\sigma$, and only mention here that huge effects have been reported so far.

4 Heavy atom spin-spin couplings

Nuclear spin-spin couplings are not very easy to compute accurately, in particular for heavy elements, but can often be measured with high precision. Unlike the case of chemical shifts, where systematic errors in the computation may cancel when the shifts are obtained from the difference of the two computed shielding values of the probe and the reference compounds, there is no such cancellation of errors for spin-spin couplings. Another problem is that the interest is often in couplings involving the heavy nucleus itself, and scalar relativistic effects can be enormously large. Therefore, attempts to calculate spin-spin couplings similarly to the NMR shieldings case just by considering the Pauli SO operator to first-order did not yield very satisfactory results for couplings involving a heavy nucleus.³⁸⁻⁴⁰ However, this method seems to be applicable for the study of HALA effects in some cases.³⁸ Likewise, ECPs can be employed for this type of applications (e.g. in reference 81). However, in the following we will focus on couplings to a heavy nucleus itself. As compared to chemical shieldings, much less computational data is yet available.

4.1 (Mostly) scalar relativistic effects

Scalar relativistic effects are usually believed to yield the major influence on heavy nuclear spin-spin couplings. The reason for this is related to the fact that the FC term (27e) was found to represent the dominant contribution for an overwhelming number of couplings that have been investigated (of course, counter examples are known). In its usual nonrelativistic form for point-like nuclei, the FC term originates from the value of the induced spin-density *directly at* the nuclei, while its relativistic generalizations probe the space very close to the nuclei.^{20,29} There in particular, the electron density is substantially modified due to the scalar relativistic operators (MV + DAR in the Pauli formalism,

equation (11)), and a huge influence on the FC perturbations can be expected. This has been noted in 1968⁸² regarding the contact term in NMR spin-spin coupling and is already known since 1930⁸³ from the theory of atomic hyperfine splittings.

The authors of references 45 and 46 introduced relativistic correction factors (RCFs) for hyperfine integrals of atomic orbitals (AOs), which account for the relativistic increase of the electron density at the respective nucleus. The RCFs can then be used in a nonrelativistic molecular computations to scale the AO integrals entering the FC expression for the coupling tensor in equation (20). The authors of reference 84 reported a somewhat related procedure that is applicable to couplings involving one heavy nucleus, based on the variational scalar Pauli treatment. The semiempirical approaches described in, e.g., references 85–88 also make use of integrals based on four-component atomic computations in an otherwise nonrelativistic formalism.

To give the reader an idea of the magnitude of the RCFs, we note that, e.g., a value of 2.4386 has been reported⁴⁵ for the Hg 6s orbital. This means that, if the coupling Hg-L (L = light nucleus) is dominated, as it is often the case, by the FC contribution and by the 6s orbital on the Hg side, the coupling relativistically increases by almost a factor of 3. Likewise, Hg-Hg and other couplings between 6th row elements can be expected to relativistically increase by almost an order of magnitude. Even for rather light 4th row nuclei, non-negligible relativistic effects on coupling constants of $\sim 10\%$ can be expected. This should be compared to the celebrated huge relativistic bond contraction of many Au(I) compounds, which is of the order of 10% .

A problem connected with the RCFs is that they do not account for relativistic changes of the molecular orbitals that determine the spin-spin coupling. Such changes would be obtained from a variational or higher than first-order perturbational relativistic molecular computation. The RCFs are also not able to describe relativistic effects of L-L' couplings in the neighborhood of a heavy nucleus for the same reason. In many cases, relativistic changes of the zeroth order solution may either enhance or quench the strong relativistic effects of the AO integrals and lead to much different answers than obtained from the RCFs. In these, and other cases for which the coupling is not dominated by the FC term, a consistent first-principles variational or perturbational scheme for molecules is desirable.

The four-component formalism of nuclear spin-spin couplings has been subsequently published by Pyykkö, who provided a simple LCAO example for $K(\text{Hg-C})$ in dimethylmercury.⁸⁹ The results are very typical for heavy-atom spin-spin couplings. They exhibit a huge relativistic increase of $K(\text{Hg-C})$ by a factor of 2.7, with the new mixed contributions due to spin-orbit coupling being almost negligible for the isotropic coupling and yielding a somewhat larger contribution to the anisotropy ΔK of the coupling tensor. ΔK thereby increased even stronger by a factor of 3.3 due to relativity. A formulation for spin-spin couplings within the four-component scheme based on the polarization propagator method has been published by Aucar and Oddershede.⁹⁰ An implementation for spin-spin couplings within the relativistic extended Hückel theory (REX) was applied to many systems and often recov-

ered the experimentally observed trends and provided explanations.⁹¹ Recently, ab-initio Hartree-Fock four-component implementation and benchmark results for HX, H₂Y, (Y = O, S, Se, Te), and some plumbanes have been reported.^{24,28,29} Also rather recently, the two-component ZORA DFT approach for spin-spin couplings has been formulated and implemented by the present authors.^{20,54} Earlier semiempirical approaches based on the MNDO, AM1 and PM3 Hamiltonians, and ab-initio methods including the Pauli SO operator, have already been mentioned. See reference 23 for a review on hyperfine interaction in metals from the solid-state physics point of view.

The series YH₄, Y = C, Si, Ge, Sn, Pb, has been studied as benchmark systems in many of the references cited so far. The results show a strong scalar relativistic increase in the FC contribution to the Y-H coupling, that amounts to roughly a factor of two in the case of Y = Pb. Table 5 displays spin-spin couplings in plumbanes obtained from different theoretical methods. Nonrelativistically, the FC term to the couplings is dominant and all other contributions are almost negligible. In the relativistic case, the situation is not much different. The new mixed contributions due to SO coupling are not negligible, but rather small.^{40,54,91} The scalar relativistic corrections to FC terms of the Pb-L couplings clearly dominate the picture and it can be seen from Table 5 that the total relativistic corrections to the Pb-L couplings are very substantial. The correlated ab-initio study of Kirpekar et al.,⁴⁰ only including SO effects, was not able to achieve qualitative agreement with experiment, but could provide evidence that SO effects on $K(\text{Pb-H})$ in PbH₄ are indeed not very large (and negative in this case). The largest SO contribution is here due to the OP-FC cross term (which is zero in the nonrelativistic limit).^{40,54} Therefore, large SO effects on the coupling constants can be expected only for those systems where SO coupling is of high importance (typically heavy p-block elements such as Tl, Bi, Pb), and both the FC and the paramagnetic coupling contribution are not very small already at the non- or scalar-relativistic limit. This is not the case for the plumbanes, and therefore the scalar relativistic effects on the FC term dominate the picture. This also rationalizes the quite accurate results for PbH₄ and PbMe₄ in references 84, 86. Compared to other studies of 6th row element one-bond couplings, the data in Table 5 appears to be rather typical and qualitatively similar results have been, e.g., obtained for couplings involving W, Pt and Hg in a number of heavy metal complexes.^{20,84} As for the plumbanes in Table 5, chemical trends for very similar compounds are often already reproduced at the nonrelativistic level while magnitudes of coupling constants typically increase by a factor of two due to scalar relativistic corrections. Already at the scalar relativistic level, good agreement with experiment has been achieved for most of the systems in references 20, 84.

From the data in Table 5, the importance of electron correlation for obtaining reasonable estimates of spin-spin coupling constants becomes obvious. The effect of correlation at the nonrelativistic ab-initio level is seen from a comparison of the nrel. number in parentheses listed for the Dirac approach with the one from the MCSCF computation. Based on a respective nonrelativistic ratio for SiH₄, the authors of reference 29 estimated a Pb-H coupling constant in PbH₄ of $\sim 138 \cdot 10^{20} \text{ kg m}^{-2} \text{ s}^{-2} \text{ A}^{-2}$

for a correlated approach. This is very close to the ZORA DFT result and underlines on the one hand the sensitivity of spin-spin coupling constants w.r.t. the quality of the zeroth order solution and on the other hand the fact that standard DFT functionals partially account for the influence of correlation. The semiempirical methods try to incorporate these effects via their parametrization. As seen from Table 5, the results for PbH_4 and PbMe_4 are in rather good agreement with experiment. However, the Pb-Cl coupling in PbCl_4 appears to be strongly underestimated by the AM1 method. The authors list a better coupling constant of $-80.6 \cdot 10^{20} \text{kg m}^{-2} \text{s}^{-2} \text{A}^{-2}$ obtained with the PM3 semiempirical Hamiltonian in reference 86, but on the other hand $K(\text{Pb-H})$ in PbH_4 is overestimated by more than a factor of five with PM3. In a comparison of theory and experiment for the YCl_4 series, $\text{Y} = \text{C}, \text{Si}, \text{Sn}, \text{Pb}$, the semiempirical methods systematically underestimate the magnitude of the Y-Cl coupling constant, with the PM3 results being substantially larger than the AM1 (and MNDO) results. REX performs rather well in comparison.⁹¹ The strong overestimation of some coupling constants in the semiempirical methods has been attributed to the “triplet instability” problem that also plagues the Hartree-Fock approaches.¹² The DFT methods seem to be much more robust in this case. Both scalar and SO ZORA DFT have predicted a negative Pb-C coupling constant for PbMe_4 despite the fact that the nonrelativistic ZORA limit, other computations, and the quoted experimental coupling (from 1978) agree on a positive value. In all other cases we have investigated so far, ZORA did yield the experimentally predicted sign of K and in most cases the magnitudes were reproduced with good accuracy.

As already mentioned in Sec. 3, solvent effects can substantially influence NMR parameters for heavy atom compounds. In particular, it was found that complexation of the heavy atom by solvent molecules, if possible, yields huge effects on shieldings of the heavy nucleus. It is therefore not very surprising, that this is the case for NMR spin-spin couplings as well. More surprising, though, is the magnitude of the effects even for rather weakly coordinating solvents that do not cause a significant change of the geometry of the compound under investigation. In reference 92, a number of linear mercury and square-planar platinum complexes have been investigated. Even for such weakly coordinating solvents such as CHCl_3 or CH_2Cl_2 , a significant shift of the FC contribution to the spin-spin coupling has been observed. Experimental trends for different solvents (CHCl_3 vs. DMSO) have been quantitatively reproduced. The solvent coordination effect has been analyzed in detail for $\text{Hg}(\text{CN})_2$. $K(\text{Hg-C})$ increases from 237.9 to 443.4 to $576.2 \cdot 10^{20} \text{kg m}^{-2} \text{s}^{-2} \text{A}^{-2}$ at the nonrelativistic, scalar ZORA relativistic, scalar rel. + 4 CH_3OH solvent molecules level, respectively (DFT, VWN functional). SO corrections were very small in the samples studied in reference 92. It was found that charge donation from the solvent into the metal-ligand σ bonds is responsible for the large positive shift of $K(\text{Hg-C})$. It does not seem very likely that unspecific solvent effects for coordinatively saturated complexes are of such high importance, but they will be not negligible for high-accuracy computations. In reference 93, complexation the complex $[(\text{NC})_5\text{Pt-Tl}(\text{CN})]^-$ by water was found to

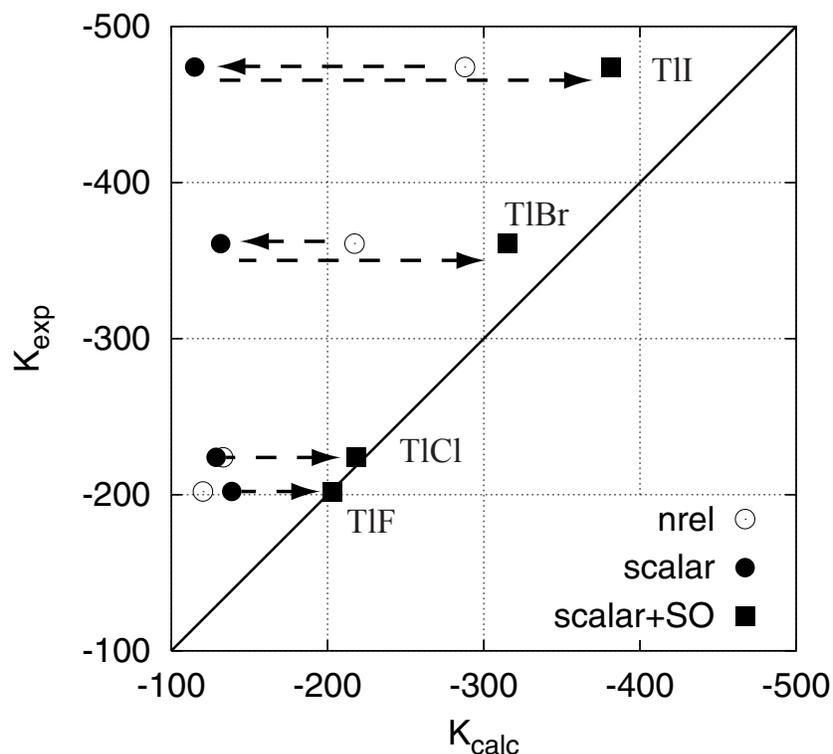


Figure 2: Reduced spin-spin coupling constants in thallium halides TlX from ZORA DFT computations (reference 54, BP86 functional), in $10^{20} \text{ kg m}^{-2} \text{ s}^{-2} \text{ A}^{-2}$. Calculated vs. experimental values. Experimental data compiled in reference 94

explain a rather unintuitive experimental result for the Tl-C couplings. In aqueous solution, ${}^2K(\text{Tl-C}) \gg {}^1K(\text{Tl-C})$ has been observed experimentally. In the same complex, the huge Pt-Tl coupling (expt. $\sim 57 \text{ kHz}$ in water) has been shown to increase by more than 20 kHz upon coordination by solvent molecules in the ZORA DFT computations.

4.2 Spin-orbit effects

Not many cases have been investigated so far, where SO coupling is of essential importance for heavy nucleus spin-spin coupling constants. Very often it is possible to achieve a good comparison between theory and experiment already at the computationally much cheaper and easier to interpret scalar relativistic level. As a counter example, we would like to emphasize the case of Tl halides, TlX. Figure 2 shows the coupling constants that have been obtained with the ZORA DFT approach⁵⁴ on different levels of approximation. Clearly, SO effects yield the dominant contribution to the coupling constants for TlI and a completely wrong trend for the series is obtained at the scalar relativistic

level. The explanation of the SO effects follows the one for the chemical shieldings. Mixed terms between the spin-dependent FC and SD operators and the orbital dependent OP operator are not zero anymore in the presence of SO coupling. Through SO coupling, the spin-density that is induced by the FC perturbation at a nucleus “leaks” through into the orbital shapes and causes orbital current densities that yield non-zero coupling contributions with the orbital currents induced by the OP term at the other nucleus. Likewise, the OP operator induces spin-density in the SO coupled system. As for nuclear shieldings, the FC-OP cross term was found to be dominant and the SD-OP term was small.^{39,40,54} For TlX, the paramagnetic contribution is dominant at the nonrelativistic level and the FC term represents the second largest contribution. This leads to the large FC-OP cross terms at the SO coupled level. In the case of TlI, this cross term represents the largest individual relativistic correction to the coupling constant and is essential in order to obtain the correct trend for the TlX series.⁵⁴ The DFT approach appears to be of somewhat reduced accuracy for the case of TlBr and TlI which has been largely attributed to deficiencies in the GGA functional.⁵⁴

The authors of reference 38 concluded from a study of $K(\text{H-H})$ in H_2Y ($\text{Y} = \text{O}, \text{S}, \text{Se}, \text{Te}$) that the SO effects may generally yield the dominant contribution for HALA effects as it is the case for many nuclear shieldings. A large relativistic change of $K(\text{H-H})$ in PbH_4 has been observed from four-component Hartree-Fock computations²⁹ where SO effects are naturally present. On the other hand, reference 40 reports rather small SO corrections to $K(\text{H-H})$ in PbH_4 , based on a nonrelativistic Hartree-Fock wavefunction. Furthermore, huge changes of the FC term due to electron correlation were found. Clearly, more relativistic studies including both scalar and SO effects are needed in this case in order to draw a definite conclusion.

Available studies have shown that even in those cases where the SO effect on the coupling constant is rather small, the anisotropy ΔK can be quite strongly influenced by SO coupling. Relativistic changes of ΔK have been reported in several of the papers cited so far, e.g. in references 24, 28, 38, 54, 87, 91. However, the applications of ΔK studies for the heavy atom case are, as in the $\Delta\sigma$ case, very limited so far. However, it is already established that future investigations of ΔK and interpretations of respective experimental findings will need to include relativistic effects if heavy atom systems are studied, and both scalar and SO effects will be of importance in this case. Experimental data for the TlX series has, along with a number of other light and heavy diatomic systems, been investigated in reference 94 and periodic trends of K and ΔK have been analyzed. ΔK can generally be expected to increase with increasing charge of the heavy nuclei involved, with very large anisotropies for couplings with 6th row atoms in particular at the right end of the periodic table.

5 Summary

It is nowadays possible to compute relativistic heavy nucleus NMR parameters by a variety of different approaches at different levels of accuracy and computational expense. A number of available quantum chemical program systems are capable of such computations. From the numerical evidence provided so far by many computational studies of NMR parameters in heavy atom systems, it becomes obvious that relativistic effects can be responsible for the main chemical trends that have been observed experimentally. In particular, spin-orbit coupling must be considered for shieldings of light nuclei in the neighborhood of heavy p-block elements. Both scalar and spin-orbit relativistic corrections are important for shielding tensors of heavy nuclei and ligand shieldings in heavy transition metal complexes. It is imperative to use scalar relativistic corrections in order to compute reliable magnitudes for spin-spin couplings involving heavy nuclei. Spin-orbit corrections to spin-spin couplings can be very substantial if both the paramagnetic and the Fermi-contact contributions to the coupling are large and a heavy p-block element is involved.

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Table 1: Proton chemical shifts in hydrogen halides HX

$-\delta(^1\text{H})^a$	X =	Cl		Br		I	
		nrel ^{d)}	rel	nrel	rel	nrel	rel
Method / Year							
semiemp. pPSO / 1973 ⁴¹		8.02	8.24	11.24	13.85	13.08	20.92
semiemp. pPSO / 1978 ⁴²		2.1	2.7	5.75	10.0	3.22	16.8
REX / 1987 ⁴⁷			0.45		3.35		11.01
HF pPSO / 1995 ³²		2.43	3.17	2.57	7.72	3.07	18.93
HF DK + vPSO / 1996 ³⁵		1.92	2.69	2.36	7.87	0.04	19.93
DFT pPSO / 1996 ⁴⁹		1.68	2.31	1.23	5.34	1.61	13.24
DFT vPSC / 1997 ⁵²		1.4	1.5	1.7	1.8	2.1	2.3
MCSCF pPSO / 1998 ³⁶		1.98	2.57	2.19	6.04	2.74	14.68
DFT vPauli / 1998 ⁵³			1.43		5.34		11.79
HF SCDK / 1999 ³⁴		2.08	2.17	2.39	3.06	2.62	4.95
HF Dirac / 1999 ²⁸		2.39	3.13	2.82	8.21	3.32	20.11
HF Dirac / 1999 ²⁶			2.68		4.91		10.71
DFT ZORA / 2001 ^{b)}		1.57	2.45	1.84	5.31	2.19	13.6
DFT SO-ECP / 2001 ⁶³		1.68	2.39	1.21	6.42	1.61	14.87
exp (± 0.02) ^{c)}			2.58		6.43		15.34

^{a)} In ppm, with respect to HF, all values $\times(-1)$

^{b)} this work, DFT ZORA

^{c)} Experimental values as quoted in.⁵³ Uncertainty due to the experimental value for HF (measured w.r.t. CH₄)

^{d)} nonrelativistic values listed if reported in reference

Table 2: Some ¹⁸³W chemical shifts

Compound	δ exp. ^{a)}	DFT vPSC ⁵²		DFT vPauli ⁷⁶	DFT ZORA ⁷⁶	HF SCDK + vPSO ^{70 b)}	
		nrel	rel	rel	rel	nrel	rel
W(CO) ₆	-3446	-4075	-3703	-3306	-3876		
WF ₆	-1121			-107	-630	-1795	-1135
WCl ₆	2181			1773	1932	2266	2686

^{a)} with respect to WO₄²⁻, as compiled in Ref.⁷⁶

^{b)} reported in⁷⁰ with respect to WF₆

Table 3: ^{13}C chemical shifts in 5d transition metal carbonyls, from DFT calculations

Compound	δ exp. ^{a)}	vPSC ⁷⁸	vPauli ⁵³	SO ECP ⁶³
$[\text{Hf}(\text{CO})_6]^{2-}$	244	228.3	234.5	228.2
$[\text{Ta}(\text{CO})_6]^-$	211	211.8	214.8	206.0
$\text{W}(\text{CO})_6$	192	197.7	196.7	188.6
$[\text{Re}(\text{CO})_6]^+$	171	183.9	176.2	173.7
$[\text{Os}(\text{CO})_6]^{2+}$	147	172.4	149.5	153.9
$[\text{Ir}(\text{CO})_6]^{3+}$	121	153.6	125.8	130.9
$[\text{Au}(\text{CO})_2]^+$	174		165.3	164.0
$[\text{Hg}(\text{CO})_2]^{2+}$	169		158.2	154.0

^{a)} as compiled in Refs.,^{53,63} with respect to TMS

Table 4: ^{199}Hg chemical shifts

Compound ^{a)}	δ exp. ^{b)}	DFT ZORA ¹⁹	HF DK
$\text{Hg}(\text{SiH}_3)_2$	+196		+232 ⁷²
$\text{Hg}(\text{GeH}_3)_2$	-147		-289 ⁷²
$\text{HgMe}(\text{CN})$	-766	-861	
$\text{Hg}(\text{CN})_2$	-1386	-1724	
HgMeCl	-861	-943	
HgMeBr	-915	-1068	
HgMeI	-1097	-1025	
HgCl_2	-1519	-1556	(-1519) ^{c)}
HgBr_2	-2213	-2684	-2134 / -3191 ^{c)}
HgI_2	-3447	-3506	-2371 / -4130 ^{c)}
$\text{HgCl}_2(\text{NH}_3)_2$ ^{d)}	-1280 ^{e)}	-1086	
$\text{HgBr}_2(\text{NH}_3)_2$ ^{d)}	-1622 ^{e)}	-1858	
$\text{HgI}_2(\text{NH}_3)_2$ ^{d)}	-2355 ^{e)}	-2836	

^{a)} (Me = CH_3)

^{b)} with respect to HgMe_2 , as compiled in Refs.^{19,72} Solvent for HgX_2 has been THF.

^{c)} SCDK + vPSO, Reference.⁷¹ Data reported with respect to HgCl_2 , therefore the value for HgCl_2 has been set equal to the experimental shift here. Results were obtained with two different basis sets. The shifts corresponding to the external field projectors are displayed.

^{d)} NH_3 to simulate the solvent pyridine in the computations

^{e)} Experimental values for HgX_2 in pyridine

Table 5: Reduced Pb-L spin-spin coupling constants in plumbanes, in $10^{20} \text{kg m}^{-2} \text{s}^{-2} \text{A}^{-2}$.

Compound	PbH ₄	PbMe ₂ H ₂	PbMe ₃ H	PbMe ₄	PbCl ₄
Coupling ^{a)}	Pb-H	Pb-H	Pb-H	Pb-C	Pb-Cl
REX ⁹¹	84.4 (37.3)			46.5 (16.4)	
AM1 ⁸⁶	97.2			33.5	-32.0
DFT vPSC ⁸⁴	85.1			20.7	
DFT ZORA ^{20,54}	122.8 (59.9)	98.3 (57.8)	89.1 (56.6)	-26.8 ^{b)} (10.4)	-321.5 ^{b)} (-211.6)
HF Dirac ²⁹	181.9 (71.1)		166.8		
MCSCF pPSO ⁴⁰	48.3 (56.2)				
expt. ⁹⁵	112 ^{c)}	98.7	92.3	39.6	288.9 ^{d)}

^{a)} nonrelativistic values in parentheses, Me = CH₃

^{b)} PbMe₄: this work, PbCl₄: scalar ZORA

^{c)} extrapolated from PbMe₂H₂ and PbMe₃H

^{d)} not directly measured, sign not determined

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