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Restricted magnetically balanced basis applied for relativistic calculations of indirect nuclear spin–spin coupling tensors in the matrix Dirac–Kohn–Sham framework

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ABSTRACT

The relativistic four-component density functional approach based on the use of restricted magnetically balanced basis (mDKS-RMB), applied recently for calculations of NMR shielding, was extended for calculations of NMR indirect nuclear spin–spin coupling constants. The unperturbed equations are solved with the use of a restricted kinetically balanced basis set for the small component while to solve the second-order coupled perturbed DKS equations a restricted magnetically balanced basis set for the small component was applied. Benchmark relativistic calculations have been carried out for the X–H and H–H spin–spin coupling constants in the XH_4 series (X = C, Si, Ge, Sn and Pb). The method provides an attractive alternative to existing approximate two-component methods with transformed Hamiltonians for relativistic calculations of spin–spin coupling constants of heavy-atom systems. In particular, no picture-change effects arise in our method for property calculations.

1. Introduction

Nowadays it becomes a common point that relativity has an immense effect on NMR shielding tensor and indirect nuclear spin–spin coupling constants (SSCC) in heavy element compounds [1–4]. Often calculations of those properties serve as a very delicate probe to test different ways of treating relativistic effects and the basis set quality. In particular, calculation of SSCC provide a good test with respect to the basis set completeness in the core area, from one side, and to the ability of the basis to describe subtle effects of spin-polarization in molecules. Thus calculation of the NMR parameters at a four-component level with both Hartree–Fock (and nowadays – with post-Hartree–Fock) and DFT methods always were at the cutting edge of theoretical chemistry. During the last decade a number of four-component Hartree–Fock and two-component Hartree–Fock and DFT based approaches for calculation of SSCC were developed (see Refs. [5–11] and cited therein). A perturbational treatment of spin–orbit (SO) effects were also considered [12,13]. Due to inability of the Hartree–Fock level of theory to get reasonable accuracy in calculations of spin–spin couplings and because the use of four- and two-component post-Hartree–Fock methods would be extremely expensive, the major attention was switched to DFT based approaches. A number of applications were published using the zero-order regular approximation (ZORA) [2,3]. At present, it is by far the most often used method for relativistic SSCC calculations but other approaches, such as the infinite-order regular approximation with modified metric (IORAmm) [9] and the second-order Douglas–Kroll–Hess approximation [10] were also implemented recently. While the use of two-component approaches became recently very popular, their results still should be compared against those obtained at the four-component Dirac–Kohn–Sham level. So far there have been no DFT methods for relativistic four-component calculation of SSCC available [1]. Here we report on our development, implementation and pilot benchmark application of such a four-component Dirac–Kohn–Sham (DKS) approach.

One of the central problems in calculations of NMR parameters at the Dirac level is related to the fact that part of the contributions to shielding and SSCC appears as a sum over negative energy states. That makes accurate calculation of those parameters depending very much on the choice of a basis set for the small component. This problem can be cured by the use of a special basis depending on magnetic field or by applying a special transformation of the Hamiltonian (the latter also could be considered as a special choice of the basis) [14].

Recently we developed a new approach for calculation of NMR shielding and SSCC based on the use of restricted magnetically balanced (RMB) basis for the small component and implemented this approach at the Dirac–Kohn–Sham (DKS) level (this method was

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named as mDKS-RMB (matrix DKS with the use of RMB basis) [15]. In contrast to other known approaches for treating the negative energy states in the context of calculating NMR parameters, the use of RMB basis or Kutzelnigg's transformation [16] provides the assured variational stability of order $O(c^{-4})$. The rigorous proof of this statement is based on the generalized argumentation of Stanton and Havriliak [14,17]. mDKS-RMB efficiently solves the problems associated with summation over negative energy states and has a very rapid convergence with respect to the basis set used for the large component (the latter completely defines the basis for the small component) thus providing a very competitive alternative for such approaches as ODA and EFUTm [18] developed for NMR shielding tensor calculations. While there are possible difficulties with Kutzelnigg's transformation [16] for the magnetic field due to the magnetic moment of a nucleus (see Refs. [18,19] for more details), our approach is free of those problems. As we already mentioned in the previous paper [15] the mDKS-RMB method allows the use, as a primary perturbation, of either an external uniform magnetic field or magnetic field due to the magnetic moment of a nucleus. In the present work we report on our extension of the mDKS-RMB approach by developing and implementing a method for calculations of spin–spin coupling tensors. To the best of our knowledge this is the first ever use of restricted magnetic balance for calculation of spin–spin couplings. Despite the fact that the diamagnetic terms (connected with the summation over the negative energy states [16]) give usually a minor contribution to the couplings with most of the elements, such contributions could be rather significant for coupling with a heavy nucleus. Besides, it is always desirable to have a good reference method which treats all terms in the most robust way and which is able to provide solid data for benchmarking other less advanced approaches. Such accurate treatment of the diamagnetic term becomes especially important for implementations at the post-Hartree–Fock levels.

In the following section we will briefly describe our new approach for calculations of spin–spin coupling tensors within mDKS-RMB. Computational details are given in Section 3. Some benchmark calculations of SSCC will be discussed in Section 4, followed by conclusions in Section 5.

2. Theory

Before proceeding to the theory part, we would like to explain the notations used in the present work. Summation over repeated indices is assumed, and the following index notation is employed: *i, j* denote occupied positive energy spinors, *a* unoccupied positive and negative energy spinors, *p, q* all positive and negative energy spinors and λ, τ are basis function indices. Cartesian directions are indexed by *u, v*. Superscripts *L* and *S* denote the large and the small components, respectively. The Hartree system of atomic units is used throughout the paper if not noted otherwise. If necessary, subscripts 2×2 and 4×4 are used to stress that the corresponding matrices are two- and four-component, respectively.

By definition the indirect nuclear spin–spin coupling tensor $\mathbf{J}^{(M,N)}$ between two magnetic nuclei *M* and *N* is proportional to the reduced indirect spin–spin coupling tensor $\mathbf{K}^{(M,N)}$ (customarily written in SI units)

$$\mathbf{J}^{(M,N)} = h\frac{\gamma_M}{2\pi}\frac{\gamma_N}{2\pi}\mathbf{K}^{(M,N)}. \tag{1}$$

Here γ_M and γ_N represent the nuclear gyromagnetic ratios of the corresponding nuclei *M* and *N* and $\mathbf{K}^{(M,N)}$ is defined as the second derivative of the electronic energy $E(\vec{\mu}^M,\vec{\mu}^N)$ with respect to magnetic moments $\vec{\mu}^M$ and $\vec{\mu}^N$ of the nuclei *M* and *N*

$$\mathbf{K}^{(M,N)} = \left.\frac{d^2E(\vec{\mu}^M,\vec{\mu}^N)}{d\vec{\mu}^M d\vec{\mu}^N}\right|_{\vec{\mu}^M=\vec{\mu}^N=0}. \tag{2}$$

Since the magnetic fields due to the magnetic moments $\vec{\mu}^M$ and $\vec{\mu}^N$ have a minor effect on the electronic structure it is safe to use a second-order perturbation theory for calculation of the indirect nuclear spin–spin coupling tensor.

Let us start with the expression for the relativistic electronic energy in the presence of magnetic fields (due to magnetic moments of two different nuclei *M* and *N*). Using the principle of minimal coupling within the framework of the four-component Dirac–Kohn–Sham approach, this energy can be expressed as the sum of expectation values over occupied four-component spinors $\varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)}$

$$E(\vec{\mu}^M,\vec{\mu}^N) = \left\langle \varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)} \middle| D_{kin}^{00} + D^{01} + D^{10} \middle| \varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)} \right\rangle + E_{pot}^{(\vec{\mu}^M,\vec{\mu}^N)}. \tag{3}$$

The first term on the right hand side represents the relativistic kinetic energy of the system in the presence of the magnetic moments of the nuclei *M* and *N*,

$$D_{kin}^{00} \equiv (\beta - 1_{4\times 4})c^2 + c\vec{\alpha}\cdot\vec{p}, \quad D^{10} \equiv \vec{\alpha}\cdot\vec{A}_{\vec{\mu}^M}, \quad D^{01} \equiv \vec{\alpha}\cdot\vec{A}_{\vec{\mu}^N}, \tag{4}$$

where *c* is the speed of light, $\vec{p}$ is the momentum operator $\vec{p} = -i\vec{\nabla}$, $\vec{A}_{\vec{\mu}^M}$ is the vector potential due to magnetic nuclei *M* ($\vec{R}_M$ is the position of nucleus *M*)

$$\vec{A}_{\vec{\mu}^M} = \frac{\vec{\mu}^M\times\vec{r}_M}{r_M^3}, \quad \vec{r}_M = \vec{r} - \vec{R}_M. \tag{5}$$

Matrices $\vec{\alpha}$ and β are 4×4 Dirac-matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \sigma_0 & 0 \\ 0 & -\sigma_0 \end{pmatrix}, \tag{6}$$

where vector $\vec{\sigma} = (\sigma_1,\sigma_2,\sigma_3)$ is composed of three 2×2 Pauli matrices and σ_0 is 2×2 identity matrix:

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{7}$$

Note, that in contrast to the non-relativistic theory, there are only contributions linear in $\vec{A}$ in Eq. (3). The second term on the right hand side of Eq. (3) represents the energy of non-relativistic electrostatic Coulomb interactions as well as the non-relativistic exchange-correlation functional (these terms depend on relativistic densities but the first order relativistic correction, namely the Breit term, and the dependence of the exchange-correlation energy functional on currents are omitted in the present study)

$$\begin{aligned} E_{pot}^{(\vec{\mu}^M,\vec{\mu}^N)} \equiv & \left\langle \varphi_i^{L(\vec{\mu}^M,\vec{\mu}^N)} \middle| E_{2\times 2}^{(\vec{\mu}^M,\vec{\mu}^N)} \middle| \varphi_i^{L(\vec{\mu}^M,\vec{\mu}^N)} \right\rangle \\ & + \left\langle \varphi_i^{S(\vec{\mu}^M,\vec{\mu}^N)} \middle| E_{2\times 2}^{(\vec{\mu}^M,\vec{\mu}^N)} \middle| \varphi_i^{S(\vec{\mu}^M,\vec{\mu}^N)} \right\rangle, \end{aligned} \tag{8}$$

$$\begin{aligned} E_{2\times 2}^{(\vec{\mu}^M,\vec{\mu}^N)} \equiv & -\sum_M \frac{Z_M}{r_M} 1_{2\times 2} + \frac{1}{2}\int \frac{\rho_0^{(\vec{\mu}^M,\vec{\mu}^N)}(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' 1_{2\times 2} \\ & + \left(\varepsilon_{xc}\left[\rho_k^{(\vec{\mu}^M,\vec{\mu}^N)}\right]\right)_{2\times 2}. \end{aligned} \tag{9}$$

Here Z_M is the charge of the *M*th nucleus and $\varphi_i^{L(\vec{\mu}^M,\vec{\mu}^N)}$ and $\varphi_i^{S(\vec{\mu}^M,\vec{\mu}^N)}$ are the large and small components of the *i*th occupied four-component spinor $\varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)}$, respectively. $\left(\varepsilon_{xc}\left[\rho_k^{(\vec{\mu}^M,\vec{\mu}^N)}\right]\right)_{2\times 2}$ is the non-collinear exchange-correlation energy density which depends on the total electron density $\rho_0^{(\vec{\mu}^M,\vec{\mu}^N)}$ as well as on three components of the spin density vector $\vec{\rho}^{(\vec{\mu}^M,\vec{\mu}^N)} = \left(\rho_1^{(\vec{\mu}^M,\vec{\mu}^N)}, \rho_2^{(\vec{\mu}^M,\vec{\mu}^N)}, \rho_3^{(\vec{\mu}^M,\vec{\mu}^N)}\right)$ in the presence of nuclear magnetic moments $\vec{\mu}^M$ and $\vec{\mu}^N$

$$\rho_k^{(\vec{\mu}^M,\vec{\mu}^N)} \equiv \varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)\dagger}\Sigma_k\varphi_i^{(\vec{\mu}^M,\vec{\mu}^N)}, \quad k = 0,1,2,3, \tag{10}$$

$$\Sigma_0 \equiv \begin{pmatrix} \sigma_0 & 0 \\ 0 & \sigma_0 \end{pmatrix}, \quad \vec{\Sigma} \equiv \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}. \tag{11}$$