

Resolution of identity Dirac-Kohn-Sham method using the large component only: Calculations of g -tensor and hyperfine tensor

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A new relativistic two-component density functional approach, based on the Dirac-Kohn-Sham method and an extensive use of the technique of resolution of identity (RI), has been developed and is termed the DKS2-RI method. It has been applied to relativistic calculations of g and hyperfine tensors of coinage-metal atoms and some mercury complexes. The DKS2-RI method solves the Dirac-Kohn-Sham equations in a two-component framework using explicitly a basis for the large component only, but it retains all contributions coming from the small component. The DKS2-RI results converge to those of the four-component Dirac-Kohn-Sham with an increasing basis set since the error associated with the use of RI will approach zero. The RI approximation provides a basis for a very efficient implementation by avoiding problems associated with complicated integrals otherwise arising from the elimination of the small component. The approach has been implemented in an unrestricted noncollinear two-component density functional framework. DKS2-RI is related to Dyal's [J. Chem. Phys. **106**, 9618 (1997)] unnormalized elimination of the small component method (which was formulated at the Hartree-Fock level and applied to one-electron systems only), but it takes advantage of the local Kohn-Sham exchange-correlation operators (as, e.g., arising from local or gradient-corrected functionals). The DKS2-RI method provides an attractive alternative to existing approximate two-component methods with transformed Hamiltonians (such as Douglas-Kroll-Hess [Ann. Phys. **82**, 89 (1974); Phys. Rev. A **33**, 3742 (1986)] method, zero-order regular approximation, or related approaches) for relativistic calculations of the structure and properties of heavy-atom systems. In particular, no picture-change effects arise in the property calculations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2173995]

I. INTRODUCTION

The direct numerical solution of the Dirac equation in a four-component framework remains a complicated task even for moderate-size molecular systems. Therefore, various approximate two-component methods with transformed Hamiltonians were suggested, e.g., the Douglas-Kroll-Hess^{1,2} (DKH) and zero-order regular approximation³ (ZORA) approaches (see Ref. 4 for reviews). Most two-component methods (ZORA and finite-order DKH) involve various approximations, which are not in all cases fully under control. The implementations may nevertheless be computationally demanding. Several attempts have been made recently to improve the existing methods and/or to render them more efficient.⁵

Here we reconsider the possibilities of solving the Dirac equation at the Kohn-Sham level of theory using a basis for the large component only, while avoiding drastic approximations. We start from the basic work of van Lenthe *et al.*⁶ They implemented the Dirac-Kohn-Sham method using a basis for the large component only (in the following we will call this method DKS2) but found the approach computation-

ally too demanding, as one-electron equations for each occupied molecular orbital (MO) had to be solved separately due to the dependence of the Fock matrix on the corresponding one-electron energies. While the inversion of a matrix is not a time-consuming step, the recalculation of the Fock matrix for each occupied MOs (inevitably involving numerical calculation of complicated integrals with the potential and other operators in the denominator) was the computational bottleneck.⁶ The problem may be avoided using ZORA,³ which can be viewed as an approach where the energy dependence of the Fock matrices is removed simply by neglect of the one-electron energies in the denominator. The price for this simplification is that the basic equation being solved is no longer the original Dirac equation, but rather an approximation to it with serious drawbacks (see Ref. 7 for a critical discussion of the ZORA approximation). Besides, the existing implementations of ZORA and of ZORA-based approaches usually consider only "collinear" exchange-correlation potentials which do not contribute to $\alpha\beta$ and $\beta\alpha$ blocks of the two-component Kohn-Sham matrix (this holds also for the original DKS2 work⁶).

Our alternative route to solving the Dirac-Kohn-Sham equations employs the resolution of identity (RI) approach to reformulate the basic Dirac-Kohn-Sham equations before

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elimination of the small component. Our method is related to Dyllal's unnormalized elimination of the small component (UESC) approach formulated at the Hartree-Fock level.⁸ Due to complicated expressions and integrals arising from exchange contributions (because of the presence of the small component), Dyllal applied his approach to one-electron systems only. We have been able to avoid these difficulties by working within the DKS framework and considering only nonrelativistic local or gradient-corrected functionals which do not contribute to the nondiagonal terms. In this case we can benefit from the fit of the electron density arising from both small and large components, for the calculation of exchange-correlation and Coulomb potentials. Here we report the basic equations and the first implementation of the DKS2-RI method for multielectron systems, using an explicit basis for the large component only. We use an unrestricted noncollinear two-component density functional theory (DFT) approach,⁹ as implemented in our ReSpect code.¹⁰ We will introduce the method in Sec. II and provide computational details in Sec. III. In Sec. IV we provide first one-electron spin-orbit splittings of the mercury atom and subsequently pilot calculations of g -tensors and hyperfine tensors for Cu, Ag, and Au atoms, and for three Hg complexes (HgH, HgF, and HgCN).

II. RESOLUTION OF IDENTITY DIRAC-KOHN-SHAM METHOD

We start with a general formulation of the Dirac-Kohn-Sham method for a nonrelativistic local-density approximation (LDA) or generalized gradient approximation (GGA) functional

$$\begin{pmatrix} \hat{V}_{2\times 2} & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & \hat{V}_{2\times 2} - 2c^2\hat{1}_{2\times 2} \end{pmatrix} \begin{pmatrix} |\varphi_i^L\rangle \\ |\varphi_i^S\rangle \end{pmatrix} = \varepsilon_i \begin{pmatrix} |\varphi_i^L\rangle \\ |\varphi_i^S\rangle \end{pmatrix}, \quad (1)$$

where ε_i is the one-electron energy, φ_i^L and φ_i^S are the large and small components of the four-component molecular orbital φ_i , c is the speed of the light, \mathbf{p} is the momentum operator $\mathbf{p} = -i\nabla$, and $\boldsymbol{\sigma}$ and $\hat{1}_{2\times 2}$ are, respectively, the vector composed of Pauli matrices and the identity matrix,

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

$$\hat{1}_{2\times 2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

We use the notation $\hat{V}_{2\times 2}$ for the noncollinear potential to distinguish it from the collinear potential (which does not contribute to $\alpha\beta$ and $\beta\alpha$ blocks of the two-component Kohn-Sham matrices for both the large and the small components) used in the original DKS2 work,⁶ as well as in most ZORA or related implementations.

Equation (1) may also be written as

$$\hat{V}_{2\times 2}|\varphi_i^L\rangle + c\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi_i^S\rangle = \varepsilon_i|\varphi_i^L\rangle, \quad (2a)$$

$$c\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi_i^L\rangle + (\hat{V}_{2\times 2} - 2c^2\hat{1}_{2\times 2})|\varphi_i^S\rangle = \varepsilon_i|\varphi_i^S\rangle. \quad (2b)$$

Equation (2b) serves as a basis for elimination of the small component since it allows an expression of the small component in terms of the large one,

$$|\varphi_i^S\rangle = c[(2c^2 + \varepsilon_i)\hat{1}_{2\times 2} - \hat{V}_{2\times 2}]^{-1}\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi_i^L\rangle. \quad (3)$$

By substituting Eq. (3) into Eq. (2a) one gets

$$\left[\hat{V}_{2\times 2} + \frac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\hat{R}_{(i)}\boldsymbol{\sigma}\cdot\mathbf{p} \right] |\varphi_i^L\rangle = \varepsilon_i|\varphi_i^L\rangle, \quad (4)$$

where

$$\hat{R}_{(i)} = \left[\left(1 + \frac{1}{2c^2}\varepsilon_i \right) \hat{1}_{2\times 2} - \frac{1}{2c^2}\hat{V}_{2\times 2} \right]^{-1}. \quad (5)$$

This is almost the same expression as was implemented by van Lenthe *et al.*,⁶ except for their use of a collinear potential. We will continue to call the explicit use of Eqs. (4) and (5) the Dirac-Kohn-Sham two-component (DKS2) method. As noted already in the Introduction, Eqs. (4) and (5) lead to a few well-known problems such as the dependence of the Fock matrix on the ε_i and the necessity of evaluating integrals containing operator $\hat{R}_{(i)}$ numerically on a grid (which is a computationally much more demanding task than the usual evaluation of the exchange-correlation potential on a grid in DFT). To reduce the computational effort to an affordable level, substantial additional approximations to $\hat{R}_{(i)}$ were initially suggested by Chang *et al.*¹¹ and were later rediscovered and worked out in detail by van Lenthe *et al.* under the name ZORA:³ among other things the one-electron energy in the denominator [cf. $\hat{R}_{(i)}$, Eq. (5)] is set to zero. Further approximations were made subsequently.¹²

We have followed a different route to get around the complicated dependences on the potential and one-electron energies [see Eq. (5)]. Instead of using Eq. (3), we take a step back and apply the RI approximation directly to Eq. (1). Thus, we introduce a completeness relation for the basis of the large component [Eq. (6)], as well as the corresponding relation for the formal basis (see below) of the small component [Eq. (7)],

$$\hat{1} = |\chi_\mu\rangle\mathbf{S}_{\mu\nu}^{-1}\langle\chi_\nu| \quad (6)$$

$$\hat{1} = |\boldsymbol{\sigma}\cdot\mathbf{p}\chi_\mu\rangle\bar{\mathbf{S}}_{\mu\nu}^{-1}\langle\boldsymbol{\sigma}\cdot\mathbf{p}\chi_\nu|, \quad (7)$$

where χ_ν is an atomic orbital and

$$\mathbf{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \quad (8)$$

and

$$\bar{\mathbf{S}}_{\mu\nu} = \langle\boldsymbol{\sigma}\cdot\mathbf{p}\chi_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}\chi_\nu\rangle \quad (9)$$

are overlap matrices for the large and small components. Actually, the overlap matrix for the small component is twice the nonrelativistic kinetic-energy contribution to the Fock matrix,

$$\mathbf{T}_{\mu\nu} = \left\langle \chi_\mu \left| \frac{p^2}{2} \right| \chi_\nu \right\rangle = \frac{1}{2}\bar{\mathbf{S}}_{\mu\nu} \quad (10)$$

Practically, we work with the formal basis for the small component: $\boldsymbol{\sigma} \cdot \mathbf{p} \chi_\nu$. This parallels the idea of Dyall,⁸ who expressed the small component through the ‘‘pseudolarge’’ component $\Phi_i^L: \varphi_i^S = (1/2c) \boldsymbol{\sigma} \cdot \mathbf{p} \Phi_i^L$. This allows us to avoid an introduction of an additional kinetically balanced basis set for the small component explicitly. Since we use RI for the small component in the kinetically balanced basis set, we do not need to project the small component onto the basis for the large component. That would be a drastic approximation setting up an extremely high demand on the basis set used.

Now, after multiplying Eq. (2b) from the left side by $\langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu |$ and using the RI, we can express the small component via the large one as

$$\langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu | \varphi_i^S \rangle = \frac{1}{c} \mathbf{T}_{\mu\alpha} (\boldsymbol{\Omega}_{(i)}^{-1})_{\alpha\beta} \mathbf{T}_{\beta\nu} \mathbf{S}_{\nu\gamma}^{-1} \langle \chi_\gamma | \varphi_i^L \rangle, \quad (11)$$

with $\boldsymbol{\Omega}_{(i)}$ and \mathbf{W} given by

$$\boldsymbol{\Omega}_{(i)} = \left(1 + \frac{1}{2c^2} \boldsymbol{\varepsilon}_i \right) \mathbf{T} - \frac{1}{4c^2} \mathbf{W} \quad (12)$$

and

$$\mathbf{W}_{\mu\nu} = \langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu | \hat{V}_{2 \times 2} | \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\nu \rangle. \quad (13)$$

A close look at Eqs. (11)–(13) shows that we have reached our goal: the evaluation of complicated integrals on a grid is replaced by analytical computations of much simpler integrals (only the exchange-correlation potential is evaluated numerically in the usual manner) and by multiplications and inversions of matrices. Since the inversion of a matrix usually is not a time-consuming step, this matrix formulation of the elimination of the small component has solved most problems of the original DKS2 method.

Now we may write the equation for the MO coefficients of the large component only as

$$(\mathbf{V} + \mathbf{T} \boldsymbol{\Omega}_{(i)}^{-1} \mathbf{T}) \mathbf{C}_{(i)} = \boldsymbol{\varepsilon}_i \mathbf{S} \mathbf{C}_{(i)} \quad (14)$$

where

$$|\varphi_i^L \rangle = \mathbf{C}_{\mu i} |\chi_\mu \rangle.$$

We will keep index i even in the matrix notation in order to stress that we obtain these coefficients from the i -dependent Fock matrix. Equation (14) is the basic equation of the resolution of identity Dirac-Kohn-Sham (DKS2-RI) method. We note here that all operators in Eq. (14) are Hermitian. The additional computational effort in comparison with a nonrelativistic noncollinear Kohn-Sham (i.e., two-component DFT) approach is minor and consists only of the inversion of the Fock matrix and of $\boldsymbol{\Omega}_{(i)}$ for all occupied molecular orbitals. Since the inversion of a matrix is fast (where necessary linear scaling techniques may be employed), the method may be made almost as fast as a nonrelativistic noncollinear two-component DFT approach.

Notably, even though we work now with MO coefficients for the large component only, the small component is implicitly present: we use it for the calculation of the density, the potentials, and for normalization. Since we have to normalize a four-component solution vector, both small and large components contribute to the normalization condition

$$1 = \langle \varphi_i^L | \varphi_i^L \rangle + \langle \varphi_i^S | \varphi_i^S \rangle = \mathbf{C}_{(i)}^\dagger \mathbf{S} \mathbf{C}_{(i)} + \frac{1}{2c^2} \mathbf{C}_{(i)}^\dagger \mathbf{T} \boldsymbol{\Omega}_{(i)}^{-1} \mathbf{T} \boldsymbol{\Omega}_{(i)}^{-1} \mathbf{T} \mathbf{C}_{(i)}. \quad (15)$$

This normalization also does not require any time-consuming efforts. It is worth noting that, while we obtain the MO coefficients for the large component from different Fock-type matrices (due to their dependence on one-electron energies of occupied MOs), the resulting full MOs (built from both the large and the small component) are still orthogonal in the limit of the complete basis set (that is, the only restrictions relate to the quality of the RI). The orthogonality is fulfilled since our formulation of the problem corresponds to the original formulation through the Dirac equation. This makes the DKS2-RI approach fundamentally different from the Wood-Boring method which neglects contributions of the small component to the total density and spin densities (resulting in the loss of orthogonality conditions).¹³

The Dirac-Kohn-Sham total energy may be written as (here and in the following, summation over i is assumed)

$$E_{\text{tot}} = \left(\langle \varphi_i^L | \langle \varphi_i^S | \right) \begin{pmatrix} \hat{E}_{2 \times 2} & c \boldsymbol{\sigma} \cdot \mathbf{p} \\ c \boldsymbol{\sigma} \cdot \mathbf{p} & \hat{E}_{2 \times 2} - 2c^2 \hat{1}_{2 \times 2} \end{pmatrix} \begin{pmatrix} |\varphi_i^L \rangle \\ |\varphi_i^S \rangle \end{pmatrix}, \quad (16)$$

where $\hat{E}_{2 \times 2}$ is an energy operator which is closely related to the $\hat{V}_{2 \times 2}$ potential but differs from it in the usual way (by a coefficient of 0.5 in front of the Coulomb electron-electron interaction and by a different exchange-correlation part). At this point, we can use the RI again in form of Eqs. (6) and (7) to obtain an expression for the total energy in terms of MO coefficients,

$$E_{\text{tot}} = \mathbf{C}_{(i)}^\dagger \mathbf{E} \mathbf{C}_{(i)} + \mathbf{C}_{(i)}^\dagger \mathbf{T} \boldsymbol{\Omega}_{(i)}^{-1} \mathbf{T} \mathbf{C}_{(i)} + \mathbf{C}_{(i)}^\dagger \mathbf{T} \boldsymbol{\Omega}_{(i)}^{-1} \left(\frac{1}{4c^2} (\bar{\mathbf{E}} - \mathbf{W}) + \frac{1}{2c^2} \boldsymbol{\varepsilon}_i \mathbf{T} \right) \boldsymbol{\Omega}_{(i)}^{-1} \mathbf{T} \mathbf{C}_{(i)}, \quad (17)$$

where

$$\mathbf{E}_{\mu\nu} = \langle \chi_\mu | \hat{E}_{2 \times 2} | \chi_\nu \rangle, \quad (18)$$

$$\bar{\mathbf{E}}_{\mu\nu} = \langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu | \hat{E}_{2 \times 2} | \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\nu \rangle \quad (19)$$

The strategy of the DKS2-RI method is as follows: the nonrelativistic kinetic energy [see Eq. (10)], nuclear potential- and overlap [see Eq. (8)] are evaluated only once in the beginning of the self-consistent-field (SCF) procedure, and it is sufficient to calculate the remaining integrals required only once per iteration. All integrals except for the exchange-correlation terms may be evaluated analytically. We use fitting of both the total density and the spin density (x , y , and z components) to reduce the computational effort (this requires some additional integrals at every SCF iteration, but they can also be evaluated analytically).

What are the advantages and disadvantages of the DKS2-RI method in comparison with the existing methods, in particular, with the DKS2 method of van Lenthe, *et al.*⁶

and with the methods suggested by Dyllal?⁸ The DKS2 approach is extremely time consuming due to the need to re-evaluate numerically the Fock matrix for each occupied MO [due to a complicated dependence of the Fock matrix on the ε_i —cf. Eq. (5)]. In the DKS2-RI method this problem is avoided by using the RI and by rewriting the DKS equations in a matrix form before elimination of the small component. We still need to recalculate the new Fock matrix for each occupied MO but only with the small extra cost of a matrix inversion and of a few matrix multiplications. In both approaches, the Fock matrix has to be inverted for each occupied MO. But this step is not a computational bottleneck. A main advantage of the DKS2-RI method is that all integrals except for the exchange-correlation potential can be calculated analytically. This allows the use of a much smaller integration grid than needed for the DKS2 method.

Our approach is very close to Dyllal's UESC method, which was formulated at the Hartree-Fock level⁸ and applied only to one-electron systems. This was probably due to the tremendous effort required to implement and evaluate four-index exchange integrals arising from the small component. In the absence of exact-exchange admixture these problems do not appear. Further computation efficiency in our DKS2-RI implementation is gained by fitting together electron density (and components of the spin density) arising from both the large and small components. Thus the evaluation of Coulomb and exchange-correlation potentials does not introduce any additional problems. Another method suggested by Dyllal, the normalized elimination of the small component^{8(b)} (NESC) may also be formulated at the DKS level. NESC is particularly interesting, as it allows the use of only one Fock matrix to find all MOs. However, the price is that one has to recalculate the overlap matrix (which involves parts of the small component) and to invert the matrix of MO coefficients at every SCF iteration. It is likely that a NESC-based DFT method and DKS2-RI will exhibit a similar computational effort. Since both methods should have their own advantages, we plan a NESC-DKS implementation too.

A related approach was recently suggested and implemented by Filatov^{5(b)} who used the RI approximation at the infinite-order regular approximation (IORA) level. We think that the present DKS2-RI method has a number of advantages, in particular, (a) it converges to the exact DKS result with increasing the basis set, whereas IORA does not; (b) DKS2-RI exhibits no problems with so-called “picture-change effects” in property calculations (see discussion in Sec. III); and (c) the present DKS2-RI implementation includes spin polarization at the noncollinear DFT level, providing an attractive basis for the calculations of electron paramagnetic resonance (EPR) properties where spin polarization plays a crucial role (see below).

III. CALCULATION OF g -TENSOR AND HYPERFINE TENSOR WITH THE DKS2-RI METHOD

Before delving into the derivation of the equations for g tensor and hyperfine tensor at the DKS2-RI level, we outline briefly the general procedure followed. We start with the expression for the total energy in the presence of a magnetic

field within the four-component Dirac-Kohn-Sham framework. This allows us to apply perturbation theory and the Hellmann-Feynman theorem without further complications. Then, after formulating the expressions for the g -tensor and hyperfine structure tensors, we will again use the matrix representation and resolution of identity to formulate the final equations via MOs for the large component only. It is thus clear that for these first-order properties the RI is only used as a technical tool to simplify the equations. Notably, we always stay within the Dirac four-component picture for the operators and therefore no problems arise associated with picture-change effects that are intrinsic to methods such as DKH or ZORA.

The total energy in the presence of a magnetic field in the four-component DKS method can be obtained from Eq. (16) by the principle of minimal coupling as

$$E(J_v, \mathbf{A}) = (\langle \varphi_{i(J_v, \mathbf{A})}^L | \langle \varphi_{i(J_v, \mathbf{A})}^S |) \times \begin{pmatrix} \hat{E}_{2 \times 2}(J_v) & c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} & \hat{E}_{2 \times 2}(J_v) - 2c^2 \hat{1}_{2 \times 2} \end{pmatrix} \times \begin{pmatrix} | \varphi_{i(J_v, \mathbf{A})}^L \rangle \\ | \varphi_{i(J_v, \mathbf{A})}^S \rangle \end{pmatrix}, \quad (20)$$

where $\boldsymbol{\pi} = \mathbf{p} + (\mathbf{A}/c)$, $\varphi_{i(J_v, \mathbf{A})}$ is the four-component i th MO in the presence of a magnetic field characterized by a vector potential \mathbf{A} , and v is the direction of the total magnetization vector J .

Below, we will use the following definitions of g -tensor and hyperfine structure (HFS) tensor (for a detailed discussion of the definitions and related issues, see Refs. 9 and 14–16 and work cited therein):

$$g_{uv} = \frac{2c}{\langle \tilde{S}_v \rangle} \left(\frac{\partial \langle \varphi_{i(J_v, 0)} | \hat{E}_{(J_v, B_u)} | \varphi_{i(J_v, 0)} \rangle}{\partial B_u} \right)_{B_u=0}, \quad (21)$$

$$A_{uv}^M = \frac{1}{\langle \tilde{S}_v \rangle} \left(\frac{\partial \langle \varphi_{i(J_v, 0)} | \hat{E}_{(J_v, I_u^M)} | \varphi_{i(J_v, 0)} \rangle}{\partial I_u^M} \right)_{I_u^M=0}, \quad (22)$$

where B_u and I_u^M are the external magnetic field and magnetic moment of nucleus M , $\langle \tilde{S}_v \rangle$ is an effective spin used to characterize the system under study, and the summation over occupied MOs is assumed. Index 0 means that the corresponding MOs are independent of the vector potential (due to an external magnetic field or nuclear magnetic moment). Below we will use the notation $\hat{E}_{(J_v, \mathbf{A})}$ for the four-component energy operator in the presence of a magnetic field [see Eq. (20)], that is either $\hat{E}_{(J_v, B_u)}$ or $\hat{E}_{(J_v, I_u^M)}$. All expressions are now already written in terms of unperturbed MOs, and we may therefore use all the machinery developed in the previous section (that is, we may switch from the four-component to the two-component approach).

$$\begin{aligned} & \langle \varphi_{i(J_v,0)} | \hat{E}_{(J_v,\mathbf{A})} | \varphi_{i(J_v,0)} \rangle \\ &= E(J_v,0) + \frac{1}{2c} \mathbf{C}_{(i,J_v)}^\dagger \mathbf{\Gamma}^\dagger \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{T} \mathbf{C}_{(i,J_v)} \\ &+ \frac{1}{2c} \mathbf{C}_{(i,J_v)}^\dagger \mathbf{T} \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{\Gamma} \mathbf{C}_{(i,J_v)} + \Theta(A^2), \end{aligned} \quad (23)$$

where

$$\mathbf{\Gamma}_{\mu\nu} = \langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu | \boldsymbol{\sigma} \cdot \mathbf{A} | \chi_\nu \rangle, \quad (24)$$

$$E(J_v,0) = \mathbf{C}_{(i,J_v)}^\dagger \mathbf{E}(J_v) \mathbf{C}_{(i,J_v)} + \mathbf{C}_{(i,J_v)}^\dagger \mathbf{T} \mathbf{Q}_{(i,J_v)} \mathbf{T} \mathbf{C}_{(i,J_v)}, \quad (25)$$

$$\begin{aligned} \mathbf{Q}_{(i,J_v)} &= \mathbf{\Omega}_{(i,J_v)}^{-1} + \frac{1}{2c^2} \mathbf{\Omega}_{(i,J_v)}^{-1} \\ &\times \left\{ \frac{1}{2} [\bar{\mathbf{E}}(J_v) - \mathbf{W}(J_v)] + \varepsilon_i \mathbf{T} \right\} \mathbf{\Omega}_{(i,J_v)}^{-1}, \end{aligned} \quad (26)$$

with the vector potential \mathbf{A} either due to the external magnetic field

$$\mathbf{A} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}_G), \quad \mathbf{r}_G = \mathbf{r} - \mathbf{r}_0 \quad (27)$$

or the magnetic moment of nucleus M

$$\mathbf{A} = \frac{\boldsymbol{\mu}^M \times \mathbf{r}_M}{r_M^3}, \quad \boldsymbol{\mu}^M = g^M \beta_N \mathbf{I}^M. \quad (28)$$

Here \mathbf{r}_0 is an arbitrary fixed gauge origin, $\boldsymbol{\mu}^M$ is a magnetic point dipole, describing the magnetic moment of the M th nucleus, β_N is the nuclear magneton, m_e and m_p are the electron and proton masses, respectively, $g^M = g_{\text{nuc}}(m_e/m_p)$, and g_{nuc} is a nuclear g -value. Thus the final expressions for g -tensor g_{uv} and HFS A_{uv}^M are

$$\begin{aligned} g_{uv} &= \frac{1}{\langle \tilde{S}_v \rangle} (\mathbf{C}_{(i,J_v)}^\dagger \mathbf{\Lambda}_{B(u)}^\dagger \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{T} \mathbf{C}_{(i,J_v)} \\ &+ \mathbf{C}_{(i,J_v)}^\dagger \mathbf{T} \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{\Lambda}_{B(u)} \mathbf{C}_{(i,J_v)}), \end{aligned} \quad (29)$$

$$\begin{aligned} A_{uv}^M &= \frac{1}{2c \langle \tilde{S}_v \rangle} (\mathbf{C}_{(i,J_v)}^\dagger \mathbf{\Lambda}_{I^M(u)}^\dagger \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{T} \mathbf{C}_{(i,J_v)} \\ &+ \mathbf{C}_{(i,J_v)}^\dagger \mathbf{T} \mathbf{\Omega}_{(i,J_v)}^{-1} \mathbf{\Lambda}_{I^M(u)} \mathbf{C}_{(i,J_v)}), \end{aligned} \quad (30)$$

where

$$(\mathbf{\Lambda}_{B(u)})_{\mu\nu} = \frac{\partial \mathbf{\Gamma}_{\mu\nu}(B_u)}{\partial B_u} = \frac{1}{2} \langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu | (\mathbf{r}_G \times \boldsymbol{\sigma})_u | \chi_\nu \rangle, \quad (31)$$

$$\begin{aligned} (\mathbf{\Lambda}_{I^M(u)})_{\mu\nu} &= \frac{\partial \mathbf{\Gamma}_{\mu\nu}(I_u^M)}{\partial I_u^M} \\ &= g^M \beta_N \left\langle \boldsymbol{\sigma} \cdot \mathbf{p} \chi_\mu \left| \frac{(\mathbf{r}_M \times \boldsymbol{\sigma})_u}{r_M^3} \right| \chi_\nu \right\rangle. \end{aligned} \quad (32)$$

A detailed derivation of Eqs. (20)–(32) will be presented elsewhere.¹⁷ Note that in our calculations all gauge correction terms are included automatically. The calculation of all expressions is straightforward and fast as one may expect

from the calculation of a first-order property (it takes only a fraction of the SCF computation time). The implementation of this approach (based on the resolution of identity) for the calculation of magnetic properties is currently under way. As the large and small components are obtained from DKS2-RI (see Sec. II), all integrals necessary for the calculation of HFS and g -tensors may also be obtained from them by numerical integration. This option has been used in the present work.

IV. COMPUTATIONAL DETAILS

The structures of the Hg complexes have been taken from Ref. 18. All calculations were performed at the DFT level, using the ReSpect (Ref. 10) program (including the property module MAG-ReSpect). In this initial study we will exclusively use the local Vosko-Wilk-Nusair exchange-correlation functional¹⁹ (referred to as LDA below). The basis set used for RI was identical to the orbital basis set. For heavy elements (Cu, Ag, Au, and Hg) we used basis sets due to Faegri²⁰ in a fully uncontracted fashion augmented with a set of additional s , p , and d diffuse functions (and f functions for Au and Hg), obtained by dividing the smallest exponent with the same angular momentum of a given basis by a factor of 3. For light nuclei (H, C, N, and F) we used the fully uncontracted IGLO-III basis of Kutzelnigg *et al.*²¹ For fitting of the total electron density and the components of spin density, even-tempered uncontracted auxiliary basis sets were used (6s/2p/2d for H; 11s/7p/7d for C, N, and F; 18s/12p/12d/9f/9g for Cu; 22s/15p/15d/12f/12g for Ag; and 24s/17p/17d/14f/14g for Au and Hg). Special attention was paid to the accuracy of numerical integration. The grid for numerical integration contained 256 points of radial quadrature for heavy atoms and 64 for light ones. For the angular part, we used 86 points in atomic calculations and 110 points otherwise.

As a reference point for comparison, we have also implemented the computationally very demanding DKS2 method without DKS2-RI approximation, following straightforwardly Eqs. (4) and (5). Note that the method differs from the original one⁶ by the use of the noncollinear potential $\hat{V}_{2 \times 2}$.

V. RESULTS AND DISCUSSION

Before going to HFS and g -tensor results, we discuss briefly the one-electron spin-orbit splittings of the Hg atom (i.e., differences between one-electron spinor energies, see Table I). The SO splittings calculated with the DKS2-RI method are very close to the results obtained with the exact DKS2 implementation. The remaining difference may be attributed to the use of RI as well as to the effects of numerical integrations (DKS2 is much more sensitive to the quality of the grid than the DKS2-RI method). The results of these two approaches are in very good agreement also with the four-component results of Engel *et al.*,²² keeping in mind the differences in basis sets and exchange-correlation functionals (exchange-only LDA, i.e., X_{α} , in Ref. 22). DKH calculations give reasonable results for the higher MOs (with the exception of the results of Mayer *et al.*²³ which behave nonmono-

TABLE I. One-electron spin-orbit splittings of the Hg atom. All values in a.u. HF stands for Hartree-Fock results.

Method	DKH (this work)	DKH (this work)	DKH (this work)	DKH (Ref. 23)	DKS2 (this work)	DKS2-RI (this work)	Dirac-4 (Ref. 22)
Basis	Tsuchiya <i>et al.</i> ^a	Tsuchiya <i>et al.</i> ^a	Faegri ^a		Faegri ^a	Faegri ^a	
Functional	HF	LDA	LDA	LDA	LDA	LDA	LDA exc.-only ^b
$2p_{1/2} \rightarrow 2p_{3/2}$	76.12	75.26	74.99	72.65	70.69	71.22	71.49
$3p_{1/2} \rightarrow 3p_{3/2}$	17.15	16.73	16.64	16.11	15.62	15.76	15.83
$3d_{3/2} \rightarrow 3d_{5/2}$	3.38	3.31	3.33	3.86	3.39	3.39	3.39
$4p_{1/2} \rightarrow 4p_{3/2}$	4.20	4.06	4.03	3.90	3.78	3.81	3.83
$4d_{3/2} \rightarrow 4d_{5/2}$	0.74	0.70	0.70	0.82	0.71	0.71	0.71
$4f_{5/2} \rightarrow 4f_{7/2}$	0.16	0.14	0.15	0.23	0.15	0.15	0.15
$5p_{1/2} \rightarrow 5p_{3/2}$	0.74	0.72	0.72	0.69	0.67	0.68	0.68
$5d_{3/2} \rightarrow 5d_{5/2}$	0.074	0.066	0.067	0.0079	0.067	0.068	0.067

^aBasis sets due to Tsuchiya *et al.* (Ref. 26) or Faegri (Ref. 20).^bExchange-only LDA calculations (Ref. 22) (essentially these are X_α results).

tonically, probably due to additional approximations involved) but deviate significantly for the deepest orbitals. Overall the results show that DKS2-RI reproduces essentially the results of the exact DKS2 approach, while DKH gives a noticeable overestimation of the splitting for the lowest MO. These results give us confidence in the DKS2-RI method.

The isotropic hyperfine couplings of the group 11 atoms are often used for benchmark studies. Tables II and III provide the isotropic HFS and g -values for Cu, Ag, and Au with DKH (see Ref. 24 for more details on the theory) and DKS2-RI methods, compared to the available ZORA (Ref. 25) results and experimental data. For Cu, all the methods give very similar results. This was expected since relativistic effects play only a relatively small role for the $3d$ element. All calculations overestimate the experimental value. This is probably due to the use of LDA. Other computational details (e.g., basis-set limitations and point nucleus approximation) are not expected to explain the discrepancy.

For Ag, DKH and DKS2-RI give very similar results, whereas the ZORA results from Ref. 25 are slightly different. Again, all theoretical absolute values are somewhat too large, probably again due to the use of LDA (here basis-set and finite-nucleus effects may also contribute already to computational errors). The DKS2-RI result for Au is in perfect agreement with the experiment. Unfortunately, this is probably due to error compensation: the use of a larger basis set (as judged from previous DKH results²⁴ with the basis set²⁶ of Tsuchiya *et al.*) might increase the HFS value by about 10%–15%, whereas some pilot calculations suggest that the use of a finite-nucleus model would decrease them by about the same amount. Again, the effect of the LDA has to be kept in mind.

TABLE II. Isotropic HFCs (in MHz) of group 11 atoms.

Atom	ZORA (ADF) ^a	DKH (ReSpect) ^{b,c}	DKS2-RI (ReSpect) ^b	Exp. ^a
Cu	6750	6725	6737	5867
Ag	−1909	−1984	−1967	±1713
Au	3134	3367	2986	3053

^aZORA results (DFT LDA, STO basis sets and restricted two-component calculations) and experimental data were taken from Ref. 25.^bLDA and Faegri basis sets (see text for details).^cUnrestricted one-component calculations.

The results for atomic g -values (Table III) are less informative, as deviations from the free-electron value are very small for these atoms with $d^{10}s^1$ configuration, except for Au. It is interesting to note that the DKH and DKS2-RI approaches give a positive deviation from the free-electron g -value (in agreement with the experimental data), whereas the ZORA value is slightly below g_e . The most probable reason for the deviation is that two-component ZORA approach was implemented and used in the calculations of HFS and g -tensors in a restricted fashion (this is suggested by preliminary results using our unrestricted two-component ZORA implementation).²⁷

Table IV presents isotropic and anisotropic HFS data for HgX complexes, obtained with one-component ZORA and DKH and two-component ZORA and DKS2-RI methods. Note that in contrast to the other results the two-component ZORA calculations were done in a spin-restricted fashion.¹⁸ Furthermore, the ZORA calculations were done with the BP86 GGA functional and STO basis sets, whereas our DKH and DKS2-RI results were obtained with LDA functional and GTO basis sets.

The DKH results are generally above ZORA for A_{iso} for reasons discussed before.²⁴ The DKS2-RI results are somewhat closer to the ZORA data (keeping in mind that the appreciable differences between one- and two-component ZORA result for HgF and HgH) and thus closer to the experiment than the one-component DKH for HgH and HgCN but somewhat further for HgF. The inclusion of spin polarization is of particular importance for HgH (as suggested by an analysis of the data presented in Ref. 18): the inclusion of spin polarization in one-component calculations decreases the isotropic value by about 250 Hz, thus dramatically improving the agreement with the experiment. In the case of

TABLE III. g -values of group 11 atoms.

Atom	ZORA (ADF) ^a	DKH (ReSpect) ^b	DKS2-RI (ReSpect) ^b	Exp. ^a
Cu	2.002 29	2.002 29	2.002 33	2.0025
Ag	2.002 29	2.002 29	2.002 37	2.0022
Au	2.002 27	2.003 13	2.003 23	2.0042

^aZORA results (DFT BP86, STO basis sets and restricted two-component calculations) and experimental data were taken from Ref. 25.^bLDA and Faegri basis sets (see text for details).

TABLE IV. ^{199}Hg HFCs tensors (in MHz) for some Hg complexes.

Complex	Method	A_{iso}	A_{aniso}^a
HgH	ZORA-1c (ADF) ^{b,c}	7 004	638
	DKH-1c (ReSpect) ^{c,f}	7 984	712
	ZORA-2c (ADF) ^{b,d}	9 018	2268
	DKS2-RI	6 357	2176
	Expt. ^e	7 002	1182
HgF	ZORA-1c (ADF) ^{b,c}	18 195	330
	DKH-1c (ReSpect) ^{c,f}	21 212	347
	ZORA-2c (ADF) ^{b,d}	19 819	782
	DKS2-RI	19 292	603
	Expt. ^e	22 127	742
HgCN	ZORA-1c (ADF) ^{b,c}	15 202	511
	DKH-1c (ReSpect) ^{c,f}	17 438	555
	ZORA-2c (ADF) ^{b,d}	15 905	1506
	DKS2-RI	14 993	1429
	Expt. ^e	15 850	1380

^a $A_{\text{aniso}} = A_{\parallel} - A_{\perp}$.^bZORA results (DFT BP86 and STO basis sets) and experimental data were taken from Ref. 18.^cUnrestricted one-component calculations.^dRestricted two-component calculations.^eReference 18.^fLDA, basis sets: Faegri basis on Hg and IGLO-II on light atoms (see text for details).

A_{aniso} , the most noticeable differences between methods pertain to one-component versus two-component approaches. The latter provide about twice larger values than the former, suggesting an appreciable importance of spin-orbit (SO) coupling. For HgF and HgCN, the two-component data are thus closer to the experiment, whereas they are too large for HgH.

For g -tensors of the same systems (Table V), DKS2-RI appears to perform somewhat better than spin-restricted two-component ZORA (this might arise from the approximations made in the ZORA SO operators, or from spin polarization, which is known to affect g -tensors^{9,16}). The differences between DKS2-RI and DKH data are very small. This is not surprising, as g -tensor is not very sensitive to the core area

TABLE V. g -tensors for some small Hg complexes.

Complex	Method	g_{\parallel}	g_{\perp}
HgH	ZORA (ADF) ^a	1.9723	1.7505
	DKH ^{b,c}	1.9804	1.7972
	DKS2-RI	1.9811	1.7950
	Expt. ^d	1.976(2)	1.8280
HgF	ZORA (ADF) ^a	1.9883	1.9362
	DKH ^{b,c}	1.9895	1.9487
	DKS2-RI	1.9892	1.9521
	Expt. ^d	1.993(1)	1.961(1)
HgCN	ZORA (ADF) ^a	1.9839	1.8651
	DKH ^{b,c}	1.9845	1.8732
	DKS2-RI	1.9853	1.8823
	Expt. ^d	...	1.8789

^aZORA results (DFT BP86, STO basis sets, and restricted two-component calculations) and experimental data were taken from Ref. 18.^bLDA, basis sets: Faegri basis on Hg and IGLO-II on light atoms (see text for details).^cUnrestricted two-component calculations (present work).^dReference 18.

where DKS2-RI and DKH differ most. This gives us additional confidence in our recent DKH results.⁹

VI. CONCLUSIONS

A method for the solution of the Dirac-Kohn-Sham equations in a two-component fashion using a basis for the large component only has been developed and implemented and was applied to g -tensor and hyperfine tensor calculations of a few atoms and molecules of heavy elements. The approach, termed DKS2-RI, is closely related to Dyall's UESC method. However, in contrast to the latter, which was formulated at the Hartree-Fock level and applied to one-electron systems only, DKS2-RI takes full advantage of the local or gradient-corrected exchange-correlation potentials and has been applied here to the multielectron case. The DKS2-RI results should converge to those of exact DKS with an increase of basis set since the error associated with the use of RI vanishes. DKS2-RI is an attractive alternative to currently existing approximate two-component methods (such as Douglas-Kroll-Hess, ZORA, or others) for relativistic calculations of the structure and properties of molecules. In spite of the formal two-component framework of DKS2-RI, no picture-change problems arise in the property calculations.

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¹M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).²B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986).³E. van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **99**, 4597 (1993).⁴C. van Wüllen, in *Relativistic Quantum Chemistry*, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2004), Vol. 2; D. Sundholm, *ibid.* (2002), I, pp. 758–792.⁵K. G. Dyall and E. van Lenthe, *J. Chem. Phys.* **111**, 1366 (1999); M. Filatov, *Chem. Phys. Lett.* **365**, 222 (2002).⁶E. van Lenthe, E. J. Baerends, and J. G. Snijders, *Chem. Phys. Lett.* **236**, 235 (1995).⁷C. van Wüllen, *J. Chem. Phys.* **109**, 392 (1998).⁸K. G. Dyall, *J. Chem. Phys.* **100**, 2118 (1994); **106**, 9618 (1997).⁹I. Malkin, O. L. Malkina, V. G. Malkin, and M. Kaupp, *J. Chem. Phys.* **123**, 244103 (2005).¹⁰V. G. Malkin, O. L. Malkina, R. Reviakine *et al.*, *ReSpect program, version 2.1*, 2005.¹¹C. Chang, M. Pelissier, and P. Durand, *Phys. Scr.* **34**, 394 (1986).

- ¹²G. Hong, L. Li, and M. Dolg, *Int. J. Quantum Chem.* **80**, 201 (2000).
- ¹³J. H. Wood and A. M. Boring, *Phys. Rev. B* **18**, 2701 (1978).
- ¹⁴*Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004).
- ¹⁵M. L. Munzarová, *Calculation of NMR and EPR Parameters: Theory and Applications (Ref. 14)*, Chap. 29, pp. 471–490; B. Engels, *Calculation of NMR and EPR Parameters: Theory and Applications (Ref. 14)*, Chap. 30, pp. 491–500.
- ¹⁶S. Patchkovskii and G. Schreckenbach, *Calculation of NMR and EPR Parameters: Theory and Applications (Ref. 14)*, Chap. 32, pp. 513–540.
- ¹⁷M. Repisky, S. Komorovský, E. Malkin, I. Malkin, O. Malkin, V. Malkin, and M. Kaupp (unpublished).
- ¹⁸P. Belanzoni, E. van Lenthe, and E. J. Baerends, *J. Chem. Phys.* **114**, 4421 (2001).
- ¹⁹S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ²⁰K. Faegri and J. Almlöf, *J. Comput. Chem.* **7**, 396 (1986).
- ²¹W. Kutzelnigg, U. Fleischer, and M. Schindler, in *NMR-Basic Principles and Progress*, edited by P. Diehl, E. Fluck, H. Günther, R. Kosfeld, and J. Seelig (Springer, Heidelberg, 1990), Vol. 23, p. 165ff.
- ²²E. Engel, S. Keller, and R. M. Dreizler, *Phys. Rev. A* **53**, 1367 (1996).
- ²³M. Mayer, S. Krüger, and N. Rösch, *J. Chem. Phys.* **115**, 4411 (2001).
- ²⁴I. Malkin, O. L. Malkina, V. G. Malkin, and M. Kaupp, *Chem. Phys. Lett.* **396**, 268 (2004).
- ²⁵E. van Lenthe, A. van Avoird, and P. E. S. Wormer, *J. Chem. Phys.* **108**, 4783 (1998).
- ²⁶T. Tsuchiya, M. Abe, T. Nakajima, and K. Hirao, *J. Chem. Phys.* **115**, 4463 (2001).
- ²⁷M. Repisky, S. Komorovský, O. L. Malkina, and V. G. Malkin (unpublished).