Direct perturbation theory of magnetic properties and relativistic corrections for the point nuclear and Gaussian nuclear models

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Starting from the Lévy-Leblond equation, which is the four-component nonrelativistic limit of the Dirac equation, a direct perturbation theory of magnetic properties and relativistic corrections is developed and implemented for point-charge and finite nuclei. The perturbed small components are regularized by projecting them onto an auxiliary small-component basis of Gaussian functions. The relevant operators and matrix elements are derived for the point-nuclear and Gaussian nuclear models. It is demonstrated how the usual paramagnetic spin-orbit, Fermi-contact, and spin-dipole integrals of Ramsey's theory can be evaluated in the same manner as field and field-gradient integrals—that is, as derivatives of potential-energy integrals. A few illustrative calculations are performed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1405009]

I. INTRODUCTION

On various occasions, the Lévy-Leblond equation[1] has served as a zeroth-order equation for a direct perturbation theory (DPT) of relativistic effects.[2,3] Direct perturbation theory follows from introducing a change in the metric into the Dirac(–Coulomb) equation and expanding this equation in powers of $1/c$, where c is the velocity of light ($c = 137.035\,989\,5\, a_0 E_h/\hbar$). In Ref. 4, for example, it is discussed how a four-component framework (and corresponding computer program) can be utilized to perform nonrelativistic calculations in the Lévy-Leblond formalism, and how the Dirac- and Lévy-Leblond equations are both related to the zeroth-order regular approximation (ZORA) (see also Ref. 5).

In this paper, we shall apply a DPT of relativistic corrections to magnetic properties. Although the necessary theory has already been put forward by Kutzelnigg,[6] the required matrix elements have not yet been computed. In the present paper, we propose a general procedure by which these matrix elements can be evaluated—namely, by projecting the perturbed small components onto an appropriate basis of Gaussian functions. Much of the material presented in this paper is contained in Ref. 7.

Four-component relativistic calculations usually employ the Gaussian nuclear model for energy calculations; in such calculations, it is thus desirable to be able to compute nucleus-dependent molecular properties such as electric field-gradients[8] and magnetic terms[9,10] for the Gaussian nuclear model. Accordingly, in this paper, we not only provide formulas for the computation of matrix elements for the point nuclear model but also for the Gaussian nuclear model, presenting simple formulas according to which the relevant integrals may be calculated as derivatives of the potential-energy integrals for Gaussian nuclei. In particular, the integrals of the paramagnetic spin-orbit (PSO), Fermi-contact (FC), and spin-dipole (SD) integrals of Ramsey's theory are obtained in the same manner as the usual electric field (EF) and electric field-gradient (EFG) integrals.

II. DPT OF MAGNETIC AND RELATIVISTIC CORRECTIONS

A. The zeroth-order Lévy-Leblond equation

The zeroth-order starting point for our discussion is the Lévy-Leblond equation

$$D^{00}\Psi^{00} = E^{00} S^{00}\Psi^{00}, \tag{1}$$

$$D^{00} = \begin{pmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & -2 \end{pmatrix}, \quad S^{00} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \Psi^{00} = \begin{pmatrix} \varphi^{00} \\ \chi^{00} \end{pmatrix}. \tag{2}$$

Here V is the nuclear potential, $\mathbf{p}$ is the momentum vector, and the vector $\boldsymbol{\sigma}$ contains the three Pauli spin matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3}$$

The two-component functions φ^{00} and χ^{00} are the ''large'' and ''small'' components, respectively, of the four-component spinor Ψ^{00}. It follows from Eq. (1) that the zeroth-order small component is given by

$$\chi^{00} = \tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\,\varphi^{00}, \tag{4}$$

and substitution of this relationship into Eq. (1) yields the one-electron Schrödinger equation

$$[V + \tfrac{1}{2}(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{p})]\varphi^{00} = (V+T)\varphi^{00} = H\varphi^{00} = E^{00}\varphi^{00}. \tag{5}$$

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The unperturbed large component is expanded in a basis set $\{\xi_k\}$ of ordinary (but two-component) atomic orbitals (AO's)

$$\varphi^{00}=\sum_k c_k^{00}\xi_k, \tag{6}$$

which we shall take to be Gaussian functions.

B. The perturbed Lévy-Leblond equation

We now introduce two perturbations. The first is due to a magnetic field represented by the vector potential $\mathbf{A}$ (we assume that $\mathbf{A}$ satisfies the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A}=0$),

$$D^{01}=\begin{pmatrix} 0 & \boldsymbol{\sigma}\cdot\mathbf{A} \\ \boldsymbol{\sigma}\cdot\mathbf{A} & 0 \end{pmatrix}, \quad S^{01}=0, \tag{7}$$

and the second perturbation introduces relativistic corrections,

$$D^{20}=\begin{pmatrix} 0 & 0 \\ 0 & V \end{pmatrix}, \quad S^{20}=\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{8}$$

The traditional equations of perturbation theory can be derived in the usual manner by expanding the energy and the wave function in powers of the perturbation parameters and collecting equal powers, assuming the intermediate normalization

$$\langle\Psi^{mn}|S^{00}|\Psi^{00}\rangle=\delta_{0m}\delta_{0n}. \tag{9}$$

In keeping with the notation of Kutzelnigg[3,6] the first superscript in Eqs. (7)–(9) refers to the order of c^{-1} in the relativistic perturbation and the second to the order of the magnetic perturbation. The first-order relativistic correction is thus of order c^{-2}.

To first order, we obtain the following coupled equations for the magnetic large and small components φ^{01} and χ^{01}, respectively:

$$(V-E^{00})\varphi^{01}+\boldsymbol{\sigma}\cdot\mathbf{p}\chi^{01}-E^{01}\varphi^{00}+\boldsymbol{\sigma}\cdot\mathbf{A}\chi^{00}=0, \tag{10}$$

$$\chi^{01}=\tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^{01}+\tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{A}\varphi^{00}. \tag{11}$$

Analogously, we obtain for the relativistic perturbation

$$(V-E^{00})\varphi^{20}+\boldsymbol{\sigma}\cdot\mathbf{p}\chi^{20}-E^{20}\varphi^{00}=0, \tag{12}$$

$$\chi^{20}=\tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^{20}+\tfrac{1}{4}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^{00}. \tag{13}$$

At this point, we could proceed by inserting the small-component Eqs. (11) and (13) into the large-component Eqs. (10) and (12), respectively, and by solving the large-component equations as usual by expanding the perturbed large components in a basis of ordinary Gaussian basis functions. Once algebraic approximations to φ^{01} and φ^{20} have been computed, the perturbed small components are then determined from Eqs. (11) and (13).

However, concerning point-charge nuclei and large components that are expanded in a basis of Gaussian functions that are regular at these nuclei, the direct use of Eqs. (11) and (13) leads to singularities at the nuclei in the perturbed small components (since the small components contain products of the singular operators V or $\boldsymbol{\sigma}\cdot\mathbf{A}$ with Gaussian basis functions).[3] As we shall see, these singularities are avoided by projecting the small component Eqs. (11) and (13) onto an auxiliary small-component basis $\{\zeta_k\}$. In this manner, the projected perturbed small components are regularized as well, becoming analytic at the nuclei. The same regularized large and small components occur in a formulation of DPT in the framework of stationary perturbation theory (stationary DPT).[3]

C. Projection onto the small-component basis

A unique feature of stationary DPT[3] is that we do not use the perturbed small components as given by Eqs. (11) and (13), but rather their projections $\chi_{\mathcal{P}}^{01}$ and $\chi_{\mathcal{P}}^{20}$ onto the small component basis,

$$\chi_{\mathcal{P}}^{01}=\mathcal{P}\chi^{01}, \tag{14}$$

$$\chi_{\mathcal{P}}^{20}=\mathcal{P}\chi^{20}. \tag{15}$$

Here the projector onto the small-component basis $\{\zeta_k\}$ is defined as

$$\mathcal{P}=\sum_{m,n}|\zeta_m\rangle(\mathbf{S}^{-1})_{mn}\langle\zeta_n|, \tag{16}$$

and $\mathbf{S}^{-1}$ is the inverse of the small-component overlap matrix $\mathbf{S}$ with elements $S_{mn}=\langle\zeta_m|\zeta_n\rangle$. It is important to realize that these projections introduce *approximations* into the theory, depending on our choice of small-component basis $\{\zeta_k\}$. In principle, we could choose the small-component basis in such a manner that the errors due to the approximations become small or even vanish exactly. However, we shall here assume that the projections Eqs. (14) and (15) indeed introduce approximations and instead consider the effect of these approximations, in particular how it leads to a nonexact evaluation of certain integrals by means of the resolution-of-identity (RI) approximation in the small-component basis.

In high-order relativistic DPT, it is common practice to choose the small-component auxiliary basis as $\{\zeta_k\}=\{\boldsymbol{\sigma}\cdot\mathbf{p}\xi_k\}$.[11–13] Then, for each function ξ_k in the large-component basis, there is exactly one function $\zeta_k=\boldsymbol{\sigma}\cdot\mathbf{p}\xi_k$ in the small-component basis. With this auxiliary small-component basis, it follows that

$$\langle\xi_k|\boldsymbol{\sigma}\cdot\mathbf{p}\chi_{\mathcal{P}}^{01}=\langle\xi_k|\boldsymbol{\sigma}\cdot\mathbf{p}\chi^{01}, \tag{17}$$

$$\langle\xi_k|\boldsymbol{\sigma}\cdot\mathbf{p}\chi_{\mathcal{P}}^{20}=\langle\xi_k|\boldsymbol{\sigma}\cdot\mathbf{p}\chi^{20}, \tag{18}$$

as the small-component basis contains the range of the operator $\boldsymbol{\sigma}\cdot\mathbf{p}$ on the domain $\{\xi_k\}$—see, for example, Ref. 14. Thus, for calculations in the Gaussian basis $\{\xi_k\}$, the projection onto $\zeta_k=\boldsymbol{\sigma}\cdot\mathbf{p}\xi_k$ yields approximate first-order perturbed *small* components [Eqs. (11) and (13)] but has no effect on the perturbed *large* components [Eqs. (10) and (12)]. Clearly, the usefulness of this approach depends critically on the flexibility of the generated small-component basis.

Kutzelnigg[6] has pointed out that the small-component auxiliary basis $\{\zeta_k\}=\{\boldsymbol{\sigma}\cdot\mathbf{p}\xi_k\}$ is inadequate for the expansion of χ^{01}, suggesting to include $\{\boldsymbol{\sigma}\cdot\mathbf{A}\xi_k\}$ in the basis. As the auxiliary basis would then contain the range of the operator $\boldsymbol{\sigma}\cdot\mathbf{A}$ as well as the range of $\boldsymbol{\sigma}\cdot\mathbf{p}$, such an approach would lead to a compact representation of the small-

component wave function and give a balanced representation of the electronic system in the presence of relativistic and magnetic perturbations.

Nevertheless, for a practical implementation of relativistic corrections to magnetic properties within the framework of DPT, it is convenient to have a single small-component basis for χ^{20} and χ^{01}. This basis should be chosen as $\{\zeta_k\}\supset\{\boldsymbol{\sigma}\cdot\mathbf{p}\xi_k\}$ to satisfy Eqs. (17) and (18) and be large enough to yield reasonable approximations to χ^{01}. In particular, for the accurate calculation of properties, AO's of symmetries different from those needed for the calculation of the unperturbed energy are sometimes needed. The relative advantages and disadvantages of the two approaches (the use of one or several small-component bases) will not be discussed further here; in the following, we shall instead consider the effect of the RI approximation Eqs. (14) and (15) on the first- and second-order energies.

D. First-order corrections

For the first-order magnetic and relativistic energies, we obtain

$$E^{01}=\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\chi^{00}\rangle+\langle\chi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{00}\rangle, \tag{19}$$

$$E^{20}=\langle\chi^{00}|V-E^{00}|\chi^{00}\rangle. \tag{20}$$

Obviously, these energies are *not affected* by the projection onto the small-component basis. Using Eq. (4), we find that the first-order energies may be expressed entirely in terms of the zeroth-order large components as

$$E^{01}=\tfrac{1}{2}\langle\varphi^{00}|\{\boldsymbol{\sigma}\cdot\mathbf{A},\boldsymbol{\sigma}\cdot\mathbf{p}\}_+|\varphi^{00}\rangle, \tag{21}$$

$$E^{20}=\tfrac{1}{4}\langle\varphi^{00}|\boldsymbol{\varphi}\cdot\mathbf{p}V\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{00}\rangle-\tfrac{1}{2}E^{00}\langle\varphi^{00}|T|\varphi^{00}\rangle, \tag{22}$$

where we have introduced the anticommutator

$$\{\boldsymbol{\sigma}\cdot\mathbf{A},\boldsymbol{\sigma}\cdot\mathbf{p}\}_+=(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{p})+(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{A}). \tag{23}$$

We shall return to the evaluation of integrals over this and similar operators in Sec. III, when we consider the magnetic perturbation from finite and point-charge nuclei.

E. Second-order corrections

To second order in the magnetic and relativistic perturbations, we obtain

$$E^{02}=\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\chi^{01}_{\mathcal{P}}\rangle+\langle\chi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{01}\rangle, \tag{24}$$

$$E^{40}=\langle\chi^{00}|V-E^{00}|\chi^{20}_{\mathcal{P}}\rangle-E^{20}\langle\chi^{00}|\chi^{00}\rangle, \tag{25}$$

$$E^{21}=2\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\chi^{20}_{\mathcal{P}}\rangle+2\langle\chi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{20}\rangle-E^{01}\langle\chi^{00}|\chi^{00}\rangle \tag{26}$$

$$=2\langle\chi^{00}|V-E^{00}|\chi^{01}_{\mathcal{P}}\rangle-E^{01}\langle\chi^{00}|\chi^{00}\rangle. \tag{27}$$

Thus, the second-order energies *do* depend on the RI approximation, containing the perturbed small-component functions linearly in situations different from Eqs. (17) and (18). In particular, we might worry that the two alternative expressions for the mixed magnetic-relativistic corrections [Eqs. (26) and (27)] are not equivalent in the presence of the projection. To verify their equivalence, we must establish that the Dalgarno–Stewart interchange theorem of double-perturbation theory[15] holds not only for the exact small components χ^{01} and χ^{20} but also for their projected counterparts $\chi^{01}_{\mathcal{P}}$, and $\chi^{20}_{\mathcal{P}}$,

$$\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\chi^{20}_{\mathcal{P}}\rangle+\langle\chi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{20}\rangle=\langle\chi^{00}|V-E^{00}|\chi^{01}_{\mathcal{P}}\rangle. \tag{28}$$

The two sides of Eq. (28) can be rewritten as

$$\begin{aligned}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\chi^{20}_{\mathcal{P}}\rangle&+\langle\chi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{20}\rangle\\&=\tfrac{1}{2}\langle\varphi^{00}|\{\boldsymbol{\sigma}\cdot\mathbf{A},\boldsymbol{\sigma}\cdot\mathbf{p}\}_+|\varphi^{20}\rangle\\&\quad+\tfrac{1}{4}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}\mathcal{P}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{00}\rangle,\end{aligned} \tag{29}$$

$$\begin{aligned}\langle\chi^{00}|V-E^{00}|\chi^{01}_{\mathcal{P}}\rangle&=\tfrac{1}{4}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{p}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{01}\rangle\\&\quad+\tfrac{1}{4}\langle\varphi^{00}|\boldsymbol{\varphi}\cdot\mathbf{p}(V-E^{00})\mathcal{P}\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{00}\rangle.\end{aligned} \tag{30}$$

The second terms on the right-hand sides of Eqs. (29) and (30) are expectation values, with the projector $\mathcal{P}$ acting as an RI between $\boldsymbol{\sigma}\cdot\mathbf{p}(V-E^{00})$ and $\boldsymbol{\sigma}\cdot\mathbf{A}$. The equivalence of these terms is immediately obvious, and it is also easily verified that the first terms on the right-hand sides yield the same energy contribution.

To see more clearly the effect of the projection on the second-order energies, let us rewrite these exclusively in terms of the large components,

$$E^{02}=\tfrac{1}{2}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}\mathcal{P}\boldsymbol{\sigma}\cdot\mathbf{A}|\varphi^{00}\rangle+\tfrac{1}{2}\langle\varphi^{00}|\{\boldsymbol{\varphi}\cdot\mathbf{A},\boldsymbol{\sigma}\cdot\mathbf{p}\}_+|\varphi^{01}\rangle, \tag{31}$$

$$\begin{aligned}E^{40}=&\tfrac{1}{8}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{p}(V-E^{00})\mathcal{P}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{00}\rangle\\&-\tfrac{1}{2}E^{20}\langle\varphi^{00}|T|\varphi^{00}\rangle+\tfrac{1}{4}\langle\varphi^{00}|\boldsymbol{\varphi}\cdot\mathbf{p}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{20}\rangle,\end{aligned} \tag{32}$$

$$\begin{aligned}E^{21}=&\tfrac{1}{2}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}\mathcal{P}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{00}\rangle-\tfrac{1}{2}E^{01}\langle\varphi^{00}|T|\varphi^{00}\rangle\\&+\langle\varphi^{00}|\{\boldsymbol{\sigma}\cdot\mathbf{A},\boldsymbol{\sigma}\cdot\mathbf{p}\}_+|\varphi^{20}\rangle,\end{aligned} \tag{33}$$

$$\begin{aligned}=&\tfrac{1}{2}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{A}\mathcal{P}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{00}\rangle-\tfrac{1}{2}E^{01}\langle\varphi^{00}|T|\varphi^{00}\rangle\\&+\tfrac{1}{2}\langle\varphi^{00}|\boldsymbol{\sigma}\cdot\mathbf{p}(V-E^{00})\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{01}\rangle.\end{aligned} \tag{34}$$

We have here written the second-order energies with the expectation (diamagnetic) term first and the relaxation (paramagnetic) term second. Clearly, the projection affects only the expectation value. For the magnetic second-order energy, for example, the only consequence of the DPT approach is that we are now dealing with the operator $\boldsymbol{\sigma}\cdot\mathbf{A}\mathcal{P}\boldsymbol{\sigma}\cdot\mathbf{A}$ rather than the operator $(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{A})=A^2$ that occurs in the standard nonrelativistic Ramsey formulation. For computations of magnetizabilities, nuclear shieldings, and indirect spin-spin couplings, this means that the diamagnetic terms are evaluated by means of the RI, whereas the paramagnetic terms are unaffected by the projector and thus the same as in the Ramsey theory. In the approach of Kutzelnigg,[6] functions of the form $\{\boldsymbol{\sigma}\cdot\mathbf{A}\xi_k\}$ are included in the auxiliary basis. Since the auxiliary basis then contains the range of the operator $\boldsymbol{\sigma}\cdot\mathbf{A}$, this approach would indeed lead to diamagnetic terms of the form A^2. In passing, we note that expressions for higher-order energies can be found in Ref. 6.

III. DPT MATRIX ELEMENTS

A. Nuclear magnetic dipole field

In the present section, we consider the magnetic vector potential and the magnetic induction set up by the dipole moment $\boldsymbol{\mu}_k$ associated with a finite nuclear charge distribution. For a point-charge nucleus at **K**, the vector potential at the position **r** of the electron is given by

$$\mathbf{A}(\mathbf{r},\mathbf{K}) = \frac{\boldsymbol{\mu}_k \times (\mathbf{r}-\mathbf{K})}{|\mathbf{r}-\mathbf{K}|^3}. \tag{35}$$

For a nucleus described by a normalized Gaussian distribution at **K**,

$$G_\eta(R_k) = \left(\frac{\eta}{\pi}\right)^{3/2} e^{-\eta R_k^2}, \tag{36}$$

with

$$R_k = |\mathbf{R}-\mathbf{K}|, \tag{37}$$

the vector potential is obtained by integrating the potential [Eq. (35)] over this distribution:

$$\mathbf{A}_k(\mathbf{r}) = \int \mathbf{A}(\mathbf{r},\mathbf{R}) G_\eta(R_k)\, d\mathbf{R} \tag{38}$$

$$= -\boldsymbol{\mu}_k \times \boldsymbol{\nabla} \int \frac{G_\eta(R_k)}{|\mathbf{r}-\mathbf{R}|}\, d\mathbf{R}, \tag{39}$$

where $\boldsymbol{\nabla}$ is the gradient operator with respect to the coordinates of the electron **r**. The integral in Eq. (39) may be evaluated as

$$\mathcal{V}_k = \int \frac{G_\eta(R_k)}{|\mathbf{r}-\mathbf{R}|}\, d\mathbf{R} = \frac{P(\frac{1}{2}, \eta r_k^2)}{r_k}, \tag{40}$$

where

$$P(a,z) = \frac{1}{\Gamma(a)} \int_0^z t^{a-1} e^{-t} dt \quad (a>0) \tag{41}$$

is the incomplete gamma function and r_k the distance from the electron to nucleus *k*,

$$r_k = |\mathbf{r}-\mathbf{K}|. \tag{42}$$

We may then write the nuclear vector potential and the induction associated with the dipole moment $\boldsymbol{\mu}_k$ as

$$\mathbf{A}_k = \boldsymbol{\mu}_k \times \boldsymbol{\nabla}_k \mathcal{V}_k, \tag{43}$$

$$\mathbf{B}_k = \boldsymbol{\nabla} \times \mathbf{A}_k = (\boldsymbol{\mu}_k \cdot \boldsymbol{\nabla}_k) \boldsymbol{\nabla}_k \mathcal{V}_k - \boldsymbol{\mu}_k \nabla_k^2 \mathcal{V}_k, \tag{44}$$

where $\boldsymbol{\nabla}_k$ is the gradient operator with respect to the position of the nucleus **K**.

The expressions (43) and (44) are general in that they hold for any spherical nuclear distribution, not just the Gaussian distribution—provided, of course, that the integration in Eq. (40) is carried over the appropriate distribution. Moreover, as we shall see shortly, these expressions are in a form that is perfectly suitable for integration over Gaussian orbitals. Still, it is instructive to compare Eqs. (43) and (44) with the corresponding expressions for point charge nuclei. In terms of the incomplete gamma function, we obtain the following expressions for the electrostatic potential, magnetic vector potential, and the magnetic induction of a finite Gaussian-shaped nucleus:

$$\mathbf{A}_k^\eta = P(\tfrac{3}{2}, \eta r_k^2) \frac{\boldsymbol{\mu}_k \times \mathbf{r}_k}{r_k^3}, \tag{45}$$

$$\mathbf{B}_k^\eta = \frac{8\pi}{3} G_\eta(r_k) \boldsymbol{\mu}_k + P(\tfrac{5}{2}, \eta r_k^2) \frac{3(\boldsymbol{\mu}_k \cdot \mathbf{r}_k)\mathbf{r}_k - r_k^2 \boldsymbol{\mu}_k}{r_k^5}. \tag{46}$$

The corresponding expressions for point-charge nuclei are given by

$$\mathbf{A}_k^{\mathrm{pnt}} = \frac{\boldsymbol{\mu}_k \times \mathbf{r}_k}{r_k^3}, \tag{47}$$

$$\mathbf{B}_k^{\mathrm{pnt}} = \frac{8\pi}{3} \delta(\mathbf{r}_k) \boldsymbol{\mu}_k + \frac{3(\boldsymbol{\mu}_k \cdot \mathbf{r}_k)\mathbf{r}_k - r_k^2 \boldsymbol{\mu}_k}{r_k^5}. \tag{48}$$

These expressions may be obtained either by letting η in Eqs. (45) and (46) tend to infinity or by differentiating Eqs. (43) and (44) with $\mathcal{V}_k = 1/r_k$. The expressions for finite nuclei differ from those for point-charge nuclei by the presence of the incomplete gamma functions and the substitution of the Dirac delta function by a Gaussian distribution. As the Gaussian exponent η increases, the incomplete gamma functions tend to unity and the Gaussian distribution becomes the Dirac delta function.

Although it is not our main concern here, we note that the nuclear electrostatic potential and the associated EF and EFG operators (arising from nuclear displacements) may be treated in the same manner when point-charge nuclei are replaced by Gaussian distributions. Thus, using the function (40), we may write the general expressions for these operators in the form

$$V_k^\eta = -Z_k \mathcal{V}_k^\eta = -P(\tfrac{1}{2}, \eta r_k^2) \frac{Z_k}{r_k}, \tag{49}$$

$$\mathbf{E}_k^\eta = Z_k \boldsymbol{\nabla}_k \mathcal{V}_k^\eta = -P(\tfrac{3}{2}, \eta r_k^2) Z_k \frac{\mathbf{r}_k}{r_k^3}, \tag{50}$$

$$\mathbf{F}_k^\eta = -Z_k \boldsymbol{\nabla}_k \boldsymbol{\nabla}_k^T \mathcal{V}_k^\eta = \frac{4\pi}{3} Z_k G_\eta(r_k) \mathbf{I}_3 - P(\tfrac{5}{2}, \eta r_k^2) Z_k \frac{3\mathbf{r}_k \mathbf{r}_k^T - r_k^2 \mathbf{I}_3}{r_k^5}, \tag{51}$$

where $\mathbf{I}_3$ is the three-by-three unit matrix. Again, the introduction of finite nuclear distributions is taken care of by the introduction of incomplete gamma functions and the use of a Gaussian distribution rather than a Dirac function for the contact term.

B. Integrals

Having developed convenient expressions for the vector potential and magnetic induction (43) and (44), we shall consider the evaluation of integrals involving these functions. In particular, we are interested in the matrix elements of the operators

$$(\boldsymbol{\sigma} \cdot \mathbf{A}_k)(\boldsymbol{\sigma} \cdot \mathbf{p}) = \mathbf{A}_k \cdot \mathbf{p} + i\, \boldsymbol{\sigma} \cdot \mathbf{A}_k \times \mathbf{p}, \tag{52}$$

$$(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{A}_k)=\mathbf{A}_k\cdot\mathbf{p}+i\,\boldsymbol{\sigma}\cdot\mathbf{p}\times\mathbf{A}_k, \tag{53}$$

$$\tfrac{1}{2}\{\boldsymbol{\sigma}\cdot\mathbf{A}_k,\boldsymbol{\sigma}\cdot\mathbf{p}\}_+=\mathbf{A}_k\cdot\mathbf{p}+\mathbf{B}_k\cdot\mathbf{s}, \tag{54}$$

where we have assumed that the vector potential is divergenceless and introduced the spin of the electron

$$\mathbf{s}=\tfrac{1}{2}\boldsymbol{\sigma}. \tag{55}$$

Let us assume that φ_a and φ_b are two real Gaussians centered at positions $\mathcal{A}$ and $\mathcal{B}$, respectively. Inserting the expressions (43) and (44) in (53)–(54), we obtain

$$\begin{aligned}\langle a|(\boldsymbol{\sigma}\cdot\mathbf{A}_k)(\boldsymbol{\sigma}\cdot\mathbf{p})|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_k\times\boldsymbol{\nabla}_b\langle a|\mathcal{V}_k|b\rangle\\&-(\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_b)(\boldsymbol{\nabla}_k\cdot\boldsymbol{\sigma})\langle a|\mathcal{V}_k|b\rangle\\&+(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})(\boldsymbol{\nabla}_b\cdot\boldsymbol{\nabla}_k)\langle a|\mathcal{V}_k|b\rangle,\end{aligned} \tag{56}$$

$$\begin{aligned}\langle a|(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{A}_k)|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_a\times\boldsymbol{\nabla}_k\langle a|\mathcal{V}_k|b\rangle\\&-(\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_a)(\boldsymbol{\nabla}_k\cdot\boldsymbol{\sigma})\langle a|\mathcal{V}_k|b\rangle\\&+(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})(\boldsymbol{\nabla}_a\cdot\boldsymbol{\nabla}_k)\langle a|\mathcal{V}_k|b\rangle,\end{aligned} \tag{57}$$

$$\begin{aligned}\langle a|(\mathbf{A}_\mathbf{k}\cdot\mathbf{p}+\mathbf{B}_k\cdot\mathbf{s}|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_k\times\boldsymbol{\nabla}_b\langle a|\mathcal{V}_k|b\rangle\\&+\tfrac{1}{2}(\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_k)(\boldsymbol{\nabla}_k\cdot\boldsymbol{\sigma})\langle a|\mathcal{V}_k|b\rangle\\&-\tfrac{1}{2}(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})(\boldsymbol{\nabla}_k\cdot\boldsymbol{\nabla}_k)\langle a|\mathcal{V}_k|b\rangle.\end{aligned} \tag{58}$$

For a more compact representation, we introduce the notation

$$\mathbf{V}_{kab}^{m\times n}=\boldsymbol{\nabla}_m\times\boldsymbol{\nabla}_n\langle a|\mathcal{V}_k|b\rangle, \tag{59}$$

$$\mathbf{V}_{kab}^{mn}=\boldsymbol{\nabla}_m\boldsymbol{\nabla}_n^T\langle a|\mathcal{V}_k|b\rangle. \tag{60}$$

The matrix elements may now be written in the form

$$\langle a|(\boldsymbol{\sigma}\cdot\mathbf{A}_k)(\boldsymbol{\sigma}\cdot\mathbf{p})|b\rangle=i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{k\times b}-\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{bk}-\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{bk})\boldsymbol{\sigma}, \tag{61}$$

$$\langle a|(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{A}_k)|b\rangle=i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{a\times k}-\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{ak}-\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{ak})\boldsymbol{\sigma}, \tag{62}$$

$$\langle a|\mathbf{A}_k\cdot\mathbf{p}+\mathbf{B}_k\cdot\mathbf{s}|b\rangle=i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{k\times b}+\tfrac{1}{2}\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{kk}-\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{kk})\boldsymbol{\sigma}. \tag{63}$$

Finally, it is customary to divide the last contributions into two parts, one of which is traceless. We then obtain

$$\begin{aligned}\langle a|(\boldsymbol{\sigma}\cdot\mathbf{A}_k)(\boldsymbol{\sigma}\cdot\mathbf{p})|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{k\times b}+\tfrac{2}{3}\mathrm{Tr}\mathbf{V}_{kab}^{bk}(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})\\&-\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{bk}-\tfrac{1}{3}\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{bk})\boldsymbol{\sigma},\end{aligned} \tag{64}$$

$$\begin{aligned}\langle a|(\boldsymbol{\sigma}\cdot\mathbf{p})(\boldsymbol{\sigma}\cdot\mathbf{A}_k)|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{a\times k}+\tfrac{2}{3}\mathrm{Tr}\mathbf{V}_{kab}^{ak}(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})\\&-\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{ak}-\tfrac{1}{3}\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{ak})\boldsymbol{\sigma},\end{aligned} \tag{65}$$

$$\begin{aligned}\langle a|\mathbf{A}_k\cdot\mathbf{p}+\mathbf{B}_k\cdot\mathbf{s}|b\rangle=&\,i\,\boldsymbol{\mu}_k\cdot\mathbf{V}_{kab}^{k\times b}-\tfrac{1}{3}\mathrm{Tr}\mathbf{V}_{kab}^{kk}(\boldsymbol{\mu}_k\cdot\boldsymbol{\sigma})\\&+\tfrac{1}{2}\boldsymbol{\mu}_k^T(\mathbf{V}_{kab}^{kk}-\tfrac{1}{3}\mathbf{I}_3\mathrm{Tr}\mathbf{V}_{kab}^{kk})\boldsymbol{\sigma}.\end{aligned} \tag{66}$$

In these expressions, the first term is the imaginary singlet PSO contribution, the second term is the real triplet FC contribution, and the last term is the real triplet SD contribution.

We have seen that the orbital contributions to PSO, FC, and SD operators may be calculated from the second derivatives of the matrix element $\langle a|\mathcal{V}_k|b\rangle$. Because of translational invariance, we need never calculate explicitly more than the derivatives with respect to two of the three centers. We also note that

$$\mathbf{V}_{kab}^{a\times b}=-\mathbf{V}_{kab}^{a\times k}=-\mathbf{V}_{kab}^{k\times b}, \tag{67}$$

in agreement with the fact that the PSO contribution is the same for all three operators (assuming that the vector potential is divergenceless). In the case of a point-charge dipole, the Hermitian operator Eq. (66) reduces to the usual expression

$$\begin{aligned}\langle a|\mathbf{A}_k\cdot\mathbf{p}+\mathbf{B}_k\cdot\mathbf{s}|b\rangle=&\left\langle a\left|\frac{\mathbf{r}_k\times\mathbf{p}}{r_k^3}\right|b\right\rangle\cdot\boldsymbol{\mu}_k\\&+\frac{8\pi}{3}\langle a|\,\delta(\mathbf{r}_k)|b\rangle\boldsymbol{\mu}_k\cdot\mathbf{s}\\&+\boldsymbol{\mu}_k^T\left\langle a\left|\frac{3\mathbf{r}_k\mathbf{r}_k^T-r_k^2\mathbf{I}_3}{r_k^5}\right|b\right\rangle\mathbf{s},\end{aligned} \tag{68}$$

containing the standard PSO, FC, and SD operators for point-charge nuclei.

C. Summary

We have demonstrated that the integrals over the first-order magnetic perturbations may be calculated quite straightforwardly as derivatives of the potential integral. To make clear the close relationship of these integrals to the field and field-gradient integrals, we here list the expressions for the EF, EFG, PSO, FC, and SD integrals:

$$\langle a|H_{\mathrm{EF}}|b\rangle=Z_k\boldsymbol{\nabla}_k\langle a|\mathcal{V}_k|b\rangle, \tag{69}$$

$$\langle a|H_{\mathrm{EFG}}|b\rangle=-Z_k\boldsymbol{\nabla}_k\boldsymbol{\nabla}_k^T\langle a|\mathcal{V}_k|b\rangle, \tag{70}$$

$$\langle a|H_{\mathrm{PSO}}|b\rangle=i\,\boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_k\times\boldsymbol{\nabla}_b\langle a|\mathcal{V}_k|b\rangle, \tag{71}$$

$$\langle a|H_{\mathrm{FC}}|b\rangle=-\tfrac{2}{3}\boldsymbol{\mu}_k\cdot\mathbf{s}\nabla_k^2\langle a|\mathcal{V}_k|b\rangle, \tag{72}$$

$$\langle a|H_{\mathrm{SD}}|b\rangle=\boldsymbol{\mu}^T(\boldsymbol{\nabla}_k\boldsymbol{\nabla}_k^T-\tfrac{1}{3}\mathbf{I}_3\nabla_k^2)\langle a|\mathcal{V}_k|b\rangle\mathbf{s}, \tag{73}$$

where the basic operator $\mathcal{V}_k$ is given in Eq. (40).

IV. ILLUSTRATIVE CALCULATIONS

A. Ground-state hydrogen atom

We have performed calculations on the H atom ground state in basis sets of *s*-type Gaussians developed by Morgan.[16] The exponents η_k^N of an Ns Morgan set are given by

$$\eta_k^N=ck^{-\delta}\exp[\,\alpha(N^\beta-k^\beta)\,],\quad k=1,2,...,N, \tag{74}$$

with $c=0.35$, $\delta=0.71$, $\alpha=2.74$, and $\beta=\frac{1}{2}(\sqrt{5}-1)$. The computed perturbation energies through second order obtained with these sets are displayed in Table I. The nucleus has been treated as a point charge and magnetic point dipole.

For accurate computations of the FC term, tight Gaussians—that is, functions with high exponents—are required. Therefore, we have performed a few calculations with Morgan sets to which tight Gaussians have been added. The exponents of the extra functions have been chosen as ten times the largest exponent of the Morgan set, hundred times

TABLE I. Perturbation energies (in a.u.) through sixth order for the H atom ground state. E^{20} and E^{40} are relativistic DPT energies, $E^{01}=(4\pi/3)\langle\delta(r)\rangle$ is the FC term, and E^{21} is the lowest-order relativistic DPT correction to the FC term.

N[a]	E^{00}	E^{20}	E^{40}	E^{01}	E^{21}
10	−0.499 998 68	−0.124 961 85	−0.062 293 51	1.316 526 55	1.883 761 48
20	−0.500 000 00	−0.124 999 91	−0.062 499 26	1.332 528 47	1.992 012 72
30	−0.500 000 00	−0.125 000 00	−0.062 499 99	1.333 266 26	1.999 167 88
40	−0.500 000 00	−0.125 000 00	−0.062 500 00	1.333 325 76	1.999 889 55
50	−0.500 000 00	−0.125 000 00	−0.062 500 00	1.333 332 29	1.999 982 69
9+1	−0.499 997 18	−0.124 982 27	−0.062 399 69	1.325 710 24	1.940 217 08
18+2	−0.500 000 00	−0.124 999 96	−0.062 499 65	1.333 179 30	1.998 165 70
27+3	−0.500 000 00	−0.125 000 00	−0.062 500 00	1.333 327 62	1.999 910 82
36+4	−0.500 000 00	−0.125 000 00	−0.062 500 00	1.333 332 96	1.999 992 98
45+5	−0.500 000 00	−0.125 000 00	−0.062 500 00	1.333 333 29	1.999 999 16
∞[b]	$-\frac{1}{2}$	$-\frac{1}{8}$	$-\frac{1}{16}$	$\frac{4}{3}$	2

[a]Number of *s*-type Gaussians in the Morgan basis (Ref. 16). The $K+L$ basis sets have been constructed by augmenting the K*s* Morgan sets by L tight functions with exponents $10^M\times\eta_1^K$ $(M=1,2,...,L)$.
[b]Exact values.

that exponent, and so on. With these tight functions added, the numerical results for E^{01} and E^{21} converge more rapidly to the exact values that with Morgan sets of the same size, as expected.

Moreover, we have computed the FC term E^{01} of the H atom as a function of the size of the nucleus (Fig. 1). The expectation value of $G_\eta(r)$ of the ground-state wave function $\varphi^{00}=1/\sqrt{\pi}e^{-r}$ is easily evaluated as

$$\frac{4\pi}{3}\langle G_\eta(r)\rangle=\frac{4}{3}\left[\left(\frac{2}{\eta}+1\right)\mathrm{erfc}\left(\frac{1}{\sqrt{\eta}}\right)\exp\left(\frac{1}{\eta}\right)-\frac{2}{\sqrt{\pi\eta}}\right]. \tag{75}$$

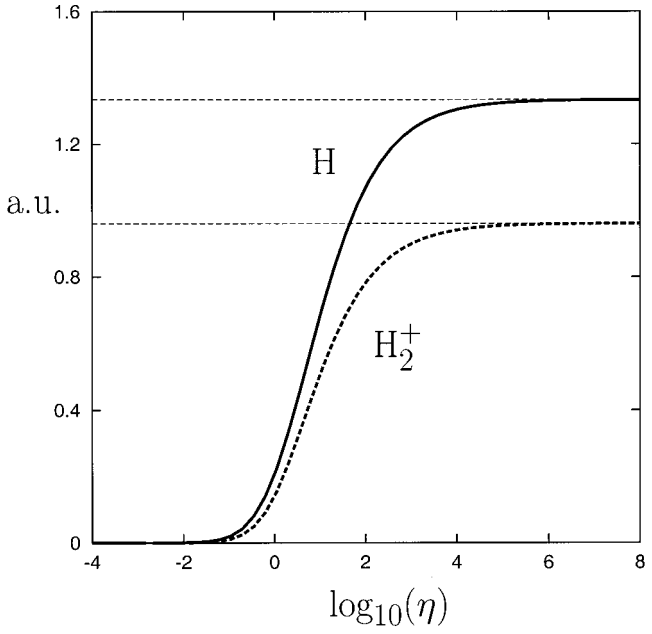

FIG. 1. Hyperfine interaction (E^{10} in a.u.) of the H atom (solid line) and the H_2^+ molecule with $R_{H-H}=2.0\ a_0$ (dashed line) as a function of the exponent η of the Gaussian-shaped nucleus. Exact values are plotted for H, while the curve for H_2^+ has been determined numerically using the $26s13p7d3f1g$ basis. Asymptotic values for $\eta\to\infty$ are shown as thin dashed lines.

The Gaussian distribution of the magnetic dipole reduces E^{01}, but the effect becomes noticeable only for Gaussian exponents η smaller than about 10^5. For $\eta=10^5$, the reduction of E^{01} is almost 1%.

B. H_2^+ molecule ion

Calculations on the H_2^+ ground state have been performed at an internuclear separation $R_{H-H}=2.0\ a_0$ with a basis set of the form $26s13p7d3f1g$. This set has been derived as follows: We have added three diffuse *s*-type Gaussians with exponents 0.007 15, 0.0129, and 0.0232 to the $(20+3)s$ Morgan basis (cf. Sec. IV A). The 13*p*, 7*d*, 3*f*, and 1*g* sets have been chosen to contain the exponents 1–13, 4–10, 6–8, and 7, respectively, of the 20*s* Morgan basis, which has been ordered with increasing exponents from 1 to 20.

Table II shows—in comparison with the results of Ref. 11—the perturbation energies up to third order in the relativistic perturbation (E^{60}) and up to first order in the magnetic perturbation (FC term, E^{01}). In our $26s13p7d3f1g$ basis, the agreement with the results of Ref. 11 is satisfactory. In this basis, we have computed the FC term (on only one of the two nuclei) as a function of the exponent η of the Gaussian nuclear model (Fig. 1).

TABLE II. Perturbation energies (in a.u.) for the H_2^+ ground state with $R_{H-H}=2.0\ a_0$.

Energy	This work[a]	Ref. 11
E^{00}	−1.102 634 18	−1.102 634 213
E^{20}	−0.138 332 4	−0.138 332 985
E^{40}	−0.041 714	−0.041 727 8
E^{60}	−0.028 276	−0.028 32
E^{01}	0.961 227	

[a]A basis set of the type $26s13p7d3f1g$ has been used, cf. Sec. IV B.

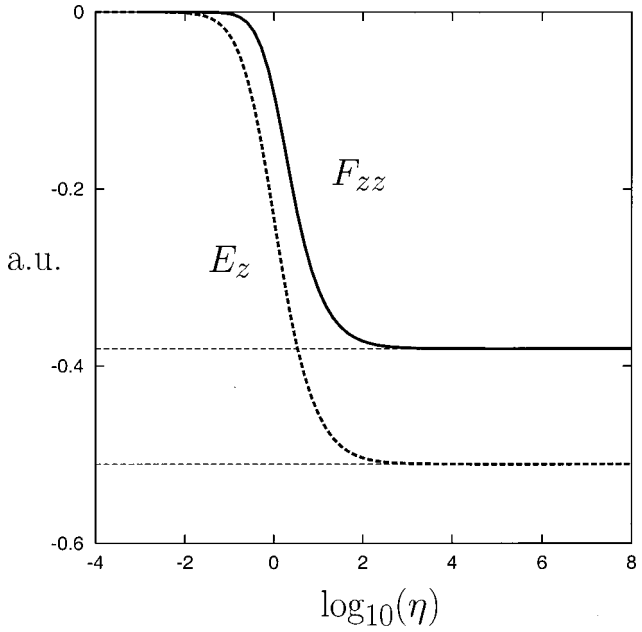

FIG. 2. Electronic contribution to the electric field vector component E_z (dashed line) and electric field-gradient tensor component F_{zz} (solid line) at one of the two nuclei of the H_2 molecule ($R_{H-H}=1.4\ a_0$) as a function of the exponent η of the Gaussian-shaped nucleus, as obtained from full CI calculations with the cc-pVTZ basis set. Asymptotic values for $\eta\to\infty$ are shown as thin dashed lines.

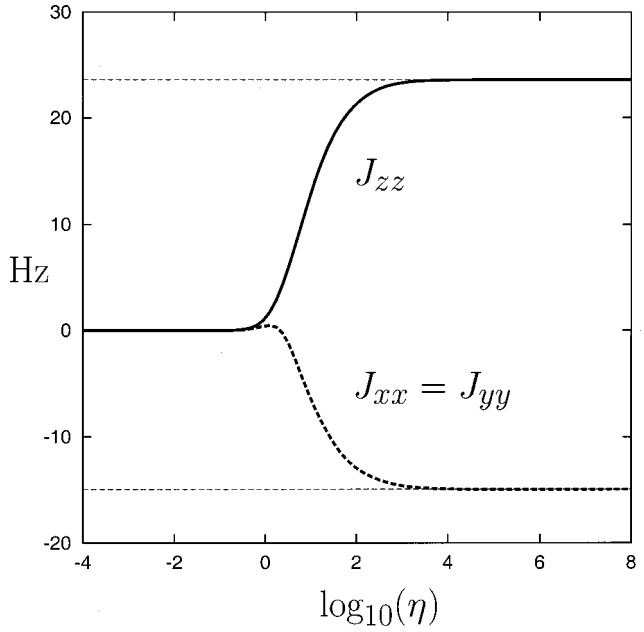

FIG. 3. DSO contributions (dashed line: $J_{xx}=J_{yy}$, solid line: J_{zz}) to the indirect spin–spin coupling constant of the H_2 molecule ($R_{H-H}=1.4\ a_0$) as a function of the exponent η of the Gaussian-shaped nucleus, as obtained from Hartree–Fock calculations with the cc-pVTZ large-component and corresponding UKB $2s6p2d1f$ small-component basis sets. Asymptotic values for $\eta\to\infty$ are shown as thin dashed lines.

C. H_2 molecule

The computation of EF's and EFG's for Gaussian-shaped nuclei is illustrated with calculations on the H_2 molecule at an internuclear distance of 1.4 a_0. The results obtained in the standard cc-pVTZ basis are depicted in Fig. 2, showing that only very large nuclear sizes (i.e., for $\eta<5$) will give rise to values for the properties of interest that deviate noticeably from the results obtained with the point nuclear model. For point-shaped nuclei ($\eta\to\infty$), $E_z=-0.5104$ a.u. and $F_{zz}=-0.3802$ a.u. at the level of full configuration interaction (CI) in the cc-pVTZ basis.

We have also computed the diamagnetic spin-orbit (DSO) contribution to the indirect spin-spin coupling constant in H_2 at $R=1.4\ a_0$ at the Hartree–Fock level in the cc-pVTZ basis (Fig. 3). This contribution corresponds to the first term in Eq. (31). Without the projector $\mathcal{P}$, the DSO tensor components amount to $J_{xx}=J_{yy}=-14.894$ Hz and $J_{zz}=23.793$ Hz, yielding a total isotropic DSO contribution of $J_{\mathrm{DSO}}=\frac{1}{3}\mathrm{Tr}(\mathbf{J})=-1.998$ Hz. When we introduce the projector $\mathcal{P}$ on an auxiliary small-component basis of the type $2s6p2d1f$, we obtain $J_{xx}=J_{yy}=-14.969$ Hz, $J_{zz}=23.597$ Hz, and $J_{\mathrm{DSO}}=-2.114$ Hz. The auxiliary basis was obtained by taking the first derivatives with respect to x, y, and z of the primitive functions ($5s2p1d$) of the cc-pVTZ basis. This choice corresponds to unrestricted kinetic balance (UKB); see also Ref. 9.

The effect of the projector $\mathcal{P}$ on the DSO tensor components amounts to a few tenths of a Hz (ca. 1%). Similar effects have been observed in Ref. 9 for the DSO contributions to the spin-spin coupling constants in H_2O, where it was also found that a small-component basis in terms of a restricted kinetic balance (RKB) appeared to be insufficient. However, more computations with auxiliary basis sets are required to obtain full insight into the basis-set requirements for the RI approximation in Eq. (31).

V. CONCLUSIONS

Matrix elements that occur in a DPT of magnetic properties and relativistic corrections can be computed by projecting the perturbed small components onto an appropriate small-component auxiliary basis set. The relevant matrix elements can be simply evaluated for the Gaussian nuclear model, commonly used in relativistic calculations on molecules containing heavy elements. The Gaussian integrals involving the PSO, FC, and SD operators are closely related to those of the EF and EFG operators, and may be evaluated as derivatives of the potential integrals.

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