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Coupled-Perturbed Scheme for the Calculation of Electronic g-Tensors with Local Hybrid Functionals

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Abstract: A coupled-perturbed Kohn−Sham (CPKS) scheme for calculating second-order magnetic properties has been developed for the case of general occupied-orbital-dependent (OOD) exchange-correlation functionals involving the exact-exchange energy density. The origin of the coupling terms in the functional derivatives of OOD functionals with respect to the orbitals has been thoroughly analyzed, and general expressions for the resulting coupling terms have been obtained. The generalized CPKS scheme thus obtained has been implemented within the MAG-ReSpect code and tested in calculations of electronic g-tensors with local hybrid functionals. Compared to previously tested global hybrids, like B3LYP, thermochemically optimized local hybrids provide only little to moderate improvement for test sets of main-group radicals and paramagnetic transition-metal complexes. Closer analyses point to possible areas in which the fundamentally more flexible local hybrids may be improved for the property at hand.

1. Introduction

Accurate prediction of magnetic resonance (MR) parameters is an important field of modern quantum chemistry. Examples include electronic g-tensors, hyperfine coupling tensors or zero-field splittings in electron paramagnetic resonance (EPR), and chemical shifts or spin-spin coupling constants in nuclear magnetic resonance (NMR). The past 20 years have seen tremendous success of new computational methods based on both post-Hartree−Fock methods (multiconfiguration SCF, many-body perturbation theory, coupled cluster, etc.) and Kohn−Sham (KS) density functional theory (DFT).[1] The advantage of DFT is its often an excellent compromise between the accuracy and the computational efficiency for larger systems. The underlying exchange-correlation (xc) functional is known to be the principal factor determining the accuracy of a DFT calculation. A particular place is occupied by the so-called hybrid xc functionals first introduced by Becke,[2,3] which include a constant, fractional admixture of the exact-exchange (EXX) energy:

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$$E_{xc}^{hybr} = a_0 E_x^{exact}[\{\varphi_k\}_k^{occ}] + \tilde{E}_{xc}^{DFT}[\rho, \nabla\rho, ...], 0 \le a_0 \le 1 \tag{1}$$

where

$$E_x^{exact} = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{j_\sigma, k_\sigma}^{occ} \int \int \frac{\varphi_{j_\sigma}^*(\mathbf{r})\varphi_{k_\sigma}^*(\mathbf{r}')\varphi_{j_\sigma}(\mathbf{r}')\varphi_{k_\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \tag{2}$$

and $\tilde{E}_{xc}^{DFT}[\rho,\nabla\rho, ...]$ is some "conventional" density functional contribution based, for instance, on the local (spin) density approximation (LDA, LSDA),[4−7] the generalized gradient approximation (GGA),[8−12] or the meta-GGA:[13,14]

$$\tilde{E}_{xc}^{DFT} = \int \tilde{\varepsilon}_{xc}^{DFT}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), ...]d\mathbf{r} \tag{3}$$

These *global* hybrid functionals have been very successful for various properties (in particular also for MR parameters[1,15]). However, a number of limitations associated with global hybrids are known. In particular, it is usually not possible to find a unique constant a_0 for the EXX admixture to obtain optimum accuracy for different properties as well as for different systems. For example, accurate prediction of the atomization energies requires relatively modest EXX admixtures of about 0.16−0.30. Larger values are required,

e.g., for reaction barriers.[16] Similar divergences are known for many properties.[15,17−20] For example, GGA functionals without EXX admixture provide accurate main group g-tensors,[21] whereas relatively large EXX admixtures are required for accurate g-tensors of transition-metal complexes.[17,18] There is, thus, clearly a need for improved exchange-correlation functionals not exclusively but also for MR parameters. A new class of functionals that has shown promise for thermochemistry and for reaction barriers (and for nuclear shieldings within an approximate optimized effective potential (OEP) scheme)[22] are so-called local hybrid functionals.[23−32] In contrast to the constant EXX admixture of global hybrids, eq 1, local hybrids include EXX in a position-dependent way, governed by a "local mixing function" (LMF), γ:

$$E_{xc}^{\text{loc-hybr}} = \sum_{\sigma=\alpha,\beta} \int \{\gamma_\sigma(\mathbf{r})\varepsilon_{x,\sigma}^{\text{exact}}(\mathbf{r}) + $$
$$[1 - \gamma_\sigma(\mathbf{r})]\varepsilon_{x,\sigma}^{\text{DFT}}(\mathbf{r})\}d\mathbf{r} + E_c^{\text{DFT}} \quad (4)$$

where $\varepsilon_{x,\sigma}^{\text{exact}}$ is the exact-exchange energy density:

$$\varepsilon_{x,\sigma}^{\text{exact}}(\mathbf{r}) = -\frac{1}{2}\sum_{j_\sigma,k_\sigma}^{\text{occ}} \varphi_{j_\sigma}^*(\mathbf{r})\varphi_{k_\sigma}(\mathbf{r}) \int \frac{\varphi_{k_\sigma}^*(\mathbf{r}')\varphi_{j_\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \quad (5)$$

whose integral over the entire real space is the alpha- or beta-spin E_x^{exact} (cf. eq 2). Note that in this paper we use the symbol "γ" rather than "g" for the LMF (see refs 22, 26−28, 32) to avoid any confusion with the "g-tensor". The performance of local hybrids is determined by the LMF as well as by the choice of density functional exchange and correlation contributions. We have been able to construct simple local hybrids, so far with only one or two semiempirical parameters and mixing only local and exact exchange, which are successful simultaneously for thermochemistry and barriers.[22,26−28,32]

A first self-consistent application to MR parameters employed the localized Hartree−Fock (LHF) approximation[33] to the OEP[34,35] to transform the nonlocal and nonmultiplicative potential of local hybrids into a local and multiplicative potential (localized-local hybrid potentials).[36] This allowed the use of an uncoupled KS perturbation scheme to obtain nuclear shieldings.[22] While the first results were encouraging, comparisons of a similar LHF-based scheme[37] with a basis-set expansion OEP method[38] for global hybrids indicated discrepancies between the results of the two approaches. This is possibly due to inaccuracies of the virtual orbitals obtained with the LHF approximation. Yet, currently, there are still problems with the numerical stability of basis-set OEP expansions and use of the, possibly necessary, very large basis sets limits the efficiency.[39,40]

While the OEP is the correct way to obtain local and multiplicative potentials from orbital-dependent functionals, most self-consistent implementations of global hybrid functionals omit the OEP transformation step and use directly the nonlocal Hartree−Fock-type potential obtained by taking straightforward functional derivatives with respect to the orbitals (FDOs) followed by the substitution:

$$\hat{v}_{xc}(\mathbf{r})\varphi_k(\mathbf{r}) \leftarrow \frac{1}{2}\frac{\delta E_{xc}}{\delta\varphi_k(\mathbf{r})} \quad (6)$$

in the corresponding one-electron Kohn−Sham equations. This is sometimes termed "generalized KS approach".[41,42] In calculations of second-order magnetic properties (as are most MR parameters), the nonlocal exchange potential leads to coupling terms, and coupled-perturbed Kohn−Sham (CPKS) equations have to be solved iteratively.[43−45]

This is well-established for global hybrids but has, so far, not been reported for local hybrids or for other comparably complex occupied-orbital-dependent (OOD) functionals[46,47] (also often termed "hyper-GGA functionals"[24,48,49]). We fill this gap here by reporting a CPKS scheme for a generalized OOD functional. The scheme has been implemented with local hybrid functionals and is tested for electronic g-tensors of main-group radicals and transition-metal complexes.

2. Local Hybrids, Generalized OOD Functionals and Their Potentials

Local hybrids are sometimes considered to be "hyper-GGA" functionals. From an implementation point of view, we prefer to assign them to the general class of OOD functionals (see Introduction):

$$E_{xc}^{\text{OOD}} = \int \varepsilon_{xc}^{\text{OOD}}(\mathbf{r})d\mathbf{r}$$

$$\varepsilon_{xc}^{\text{OOD}} = \varepsilon_{xc}^{\text{OOD}}[\rho_\alpha, |\nabla\rho_\alpha|, \nabla^2\rho_\alpha, \tau_\alpha, \varepsilon_{x,\alpha}^{\text{exact}};$$
$$\rho_\beta, |\nabla\rho_\beta|, \nabla^2\rho_\beta, \tau_\beta, \varepsilon_{x,\beta}^{\text{exact}}; \nabla\rho_\alpha\cdot\nabla\rho_\beta] \quad (7)$$

where

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2}\sum_{k_\sigma}^{\text{occ}} |\nabla\varphi_{k_\sigma}(\mathbf{r})|^2, \qquad \sigma = \alpha,\beta \quad (8)$$

is the noninteracting local kinetic energy density. The extra variable τ_σ leads to additional nonmultiplicative terms in the corresponding FDOs $(-(1/2)\{[\nabla(\partial\varepsilon_{xc}/\partial\tau_\sigma)]\cdot\nabla + (\partial\varepsilon_{xc}/\partial\tau_\sigma)\nabla^2\}\varphi_{k_\sigma})$. However, in contrast to the exact-exchange operator, which is defined by its action on an arbitrary one-particle function $\psi(\mathbf{r})$ as

$$[\hat{v}_x^{\text{exact}}\psi](\mathbf{r}) = -\sum_k^{\text{occ}} \varphi_k(\mathbf{r}) \int \frac{\varphi_k^*(\mathbf{r}')\psi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \quad (9)$$

neither the permutation of spatial variables $(\mathbf{r},\mathbf{r}')$ nor the integration over $\mathbf{r}'$ are involved, and therefore, no additional complications arise for magnetic linear-response properties (see below). In some OOD functionals (eq 7), the exact-exchange energy density appears in a more complicated nonlinear form, for example, as an ingredient of the local mixing function γ (cf. eq 4) in a recent local hybrid.[31] These types of subtle differences between various OOD functionals regarding their ingredients affect not only their FDOs but also potentially the evaluation of the linear response to a magnetic perturbation (see below). This will be taken into account in the following discussion.

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3. Electronic g-Tensors and Generalized CPKS Scheme

The CPKS scheme will now be developed for the particular case of electronic g-tensors when treated with a second-order perturbation theory on top of a nonrelativistic one-component SCF calculation. We will report the g-shift tensor, $\Delta\mathbf{g}$, which is the correction to the isotropic free-electron g-tensor,

$$\mathbf{g} = g_e\mathbf{1} + \Delta\mathbf{g} \qquad (10)$$

where $g_e = 2.002319...$ Cartesian components ($u, v = x, y, z$) of $\Delta\mathbf{g}$ are defined as

$$\Delta g_{uv} = \frac{1}{\mu_B}\frac{\partial^2 E}{\partial B_u \partial S_v}\bigg|_{\mathbf{B}=\mathbf{S}=0} = 2\frac{\partial^2 E}{\partial B_u \partial S_v}\bigg|_{\mathbf{B}=\mathbf{S}=0} \qquad (11)$$

(we employ atomic units based on the SI system with the Bohr magneton $\mu_B = 1/2$), where E is the energy of the molecular system in the magnetic field $\mathbf{B}$, and $\mathbf{S}$ is its effective spin. Therefore, one has to look for terms bilinear in $\mathbf{B}$ and $\mathbf{S}$. Perturbational treatment of spin-orbit coupling with a Breit−Pauli-type Hamiltonian (or related quasirelativistic Hamiltonians) leads to a second-order perturbation scheme to compute $\Delta\mathbf{g}$. Its detailed description can be found elsewhere[21,45,50] (see also refs 43, 44, 51). Here, we restrict ourselves only to the points relevant to derive the CPKS scheme for OOD functionals. At Breit−Pauli level, the g-shift $\Delta\mathbf{g}$ consists of three terms:

$$\Delta\mathbf{g} = \Delta\mathbf{g}_{SO/OZ} + \Delta\mathbf{g}_{RMC} + \Delta\mathbf{g}_{GC} \qquad (12)$$

of which the "paramagnetic" second-order spin-orbit/orbital Zeeman cross term, $\Delta\mathbf{g}_{SO/OZ}$, usually dominates. The remaining terms are due to the relativistic mass correction, $\Delta\mathbf{g}_{RMC}$, and the one-electron part of the gauge correction. These are calculated as "first-order properties" (expectation values, see eqs 7 and 9 in ref 21 for details). We will, in the following, be concerned exclusively with the Cartesian components u, v of the second-order $\Delta\mathbf{g}_{SO/OZ}$. These are evaluated as

$$\Delta g_{SO/OZ,uv} = \frac{\alpha^2}{2}g_e\left[\sum_{k_\alpha}^{occ}\sum_{a_\alpha}^{vac}\frac{\langle\varphi_{k_\alpha}|\hat{H}_{SO,v}|\varphi_{a_\alpha}\rangle\langle\varphi_{a_\alpha}|\hat{f}_{O,u}|\varphi_{k_\alpha}\rangle}{\varepsilon_{k_\alpha} - \varepsilon_{a_\alpha}} - \right.$$
$$\left.\sum_{k_\beta}^{occ}\sum_{a_\beta}^{vac}\frac{\langle\varphi_{k_\beta}|\hat{H}_{SO,v}|\varphi_{a_\beta}\rangle\langle\varphi_{a_\beta}|\hat{f}_{O,u}|\varphi_{k_\beta}\rangle}{\varepsilon_{k_\beta} - \varepsilon_{a_\beta}}\right] \qquad (13)$$

where α is the fine structure constant ($\alpha = 1/137.035999...$), and $\hat{H}_{SO, v}$ denotes the v component of the spatial part of the spin-free spin-orbit (SO) Hamiltonian (cf. eqs 3 and 5 of ref 21).

Next,

$$\hat{f}_{O,u} = \hat{l}_{O,u} + i\hat{\omega}_u^1 \qquad (14)$$

where $\hat{l}_{O, u}$ is a spatial component of the orbital Zeeman operator

$$\hat{l}_O = -i(\mathbf{r} - \mathbf{R}_O) \times \nabla \qquad (15)$$

(subscript "O" denotes a common gauge origin at point $\mathbf{R}_O$, see Computational Details below), and $\hat{\omega}_u^1$ is a "response"

operator, which may vanish or persist depending on the exchange-correlation functional employed (see below). As is seen from eq 13, $\Delta\mathbf{g}_{SO/OZ}$ arises from the interplay between two perturbations: spin-orbit coupling and orbital Zeeman operator (both operators are purely imaginary). According to the interchange theorem of double-perturbation theory,[52] one may evaluate a perturbed wave function (a KS determinant in the present case) up to first order in one of the perturbations, followed by computation of matrix elements of the second perturbation with the first-order perturbed and unperturbed wave functions and subtraction of zero-order terms. Translating this into one-electron language in the context of a KS determinant and using conveniently the orbital Zeeman operator (external magnetic field) as the initial perturbation, we rewrite eq 13 as

$$\Delta g_{SO/OZ,uv} = \frac{i\alpha^2}{2}g_e\left[\sum_{k_\alpha}^{occ}\langle\varphi_{k_\alpha}|\hat{H}_{SO,v}|\varphi_{k_\alpha}^{1,u}\rangle - \right.$$
$$\left.\sum_{k_\beta}^{occ}\langle\varphi_{k_\beta}|\hat{H}_{SO,v}|\varphi_{k_\beta}^{1,u}\rangle\right] \qquad (16)$$

where $\varphi_{k_\sigma}^{1,u}$ ($\sigma = \alpha, \beta$) is the first-order correction (linear response) to the occupied orbital φ_{k_σ} (below we omit subscript σ for notational simplicity where it is not crucial; a tilde will always indicate the perturbed quantities):

$$\varphi_k \overset{OZ,u}{\rightarrow} \tilde{\varphi}_k^u; \quad \tilde{\varphi}_k^u = \varphi_k + iB_u\varphi_k^{1,u} + ..., \quad u = x, y, z \qquad (17)$$

$$\varphi_k^{1,u} = -i\sum_a^{vac}\frac{\langle\varphi_a|\hat{f}_{O,u}|\varphi_k\rangle}{\varepsilon_k - \varepsilon_a}\varphi_a \equiv \sum_a^{vac}\beta_{ak}^u\varphi_a \qquad (18)$$

In case of an unperturbed orbital φ_k and a semilocal exchange-correlation potential $\hat{v}_{xc}$ of LSDA, GGA, or meta-GGA type (the latter may be viewed as an OOD functional (eq 7) without dependence on ε_x^{exact}), operator $\hat{\omega}_u^1$ vanishes in eq 14, and $\hat{f}_{O,u} = \hat{l}_{O,u}$. Then, the linear response coefficients β_{ak}^u of eq 18 (cf. eqs 14 and 15) are found straightforwardly in one step as

$$\beta_{ak}^u = \frac{\langle\varphi_a|-[(\mathbf{r} - \mathbf{R}_O)\times\nabla]_u|\varphi_k\rangle}{\varepsilon_k - \varepsilon_a} \qquad (19)$$

If a global hybrid nonlocal operator is employed, then

$$\beta_{ak}^u = \frac{\langle\varphi_a|-[(\mathbf{r} - \mathbf{R}_O)\times\nabla]_u + \hat{\omega}_u^1|\varphi_k\rangle}{\varepsilon_k - \varepsilon_a} \qquad (20)$$

where $\hat{\omega}_u^1 \equiv a_0\hat{v}_{x,u}^{exact, 1}$, and $\hat{v}_{x,u}^{exact, 1}$ is the linear response from the exact-exchange operator (eq 9):

$$[\hat{v}_{x,u}^{exact,1}\psi](\mathbf{r}) =$$
$$-\sum_k^{occ}\int\frac{\{\varphi_k^*(\mathbf{r}')\varphi_k^{1,u}(\mathbf{r}) - [\varphi_k^{1,u}(\mathbf{r}')]^*\varphi_k(\mathbf{r})\}\psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' \qquad (21)$$

When an external magnetic field is switched on, the exact-exchange operator (eq 9) is modified, as it depends on the occupied orbitals. Thus, substituting the complex perturbed orbitals $\tilde{\varphi}_k^u$, eq 17 into eq 9, one obtains

$$[\hat{\tilde{v}}_{x,u}^{exact}\psi](\mathbf{r}) = [\hat{v}_x^{exact}\psi](\mathbf{r}) + iB_u[\hat{v}_{x,u}^{exact,1}\psi](\mathbf{r}) + O(\mathbf{B}^2) \quad (22)$$

(as in eq 9, in eqs 21, 22 $\psi(\mathbf{r})$ is an arbitrary one-particle function). Equation 20 has to be solved iteratively, since its right-hand side depends on the complete set of linear-response coefficients $\{\beta_{bj}^u\}$ ($j = 1, ..., N_{occ}$; $b = 1, ..., N_{vac}$) (cf. eqs 18 and 21).

How is the CPKS scheme modified when passing from a global hybrid (eq 1) to a general OOD (or hyper-GGA) functional (eq 7)? Let us consider the FDOs (eq 6) of such a functional. We assemble them using the partial derivatives of the exchange-correlation energy density, ε_{xc}, with respect to its "ingredients" ρ_σ, $|\nabla\rho_\sigma|$, $\nabla^2\rho_\sigma$, τ_σ, $\varepsilon_{x,\sigma}^{exact}$ ($\sigma = \alpha, \beta$), and $\nabla\rho_\alpha \cdot \nabla\rho_\beta$ (for brevity, we will employ the general designation $\partial\varepsilon_{xc}/\partial\kappa$ for these quantities, where $\kappa = \rho_\alpha$, $|\nabla\rho_\alpha|$, ..., $\varepsilon_{x,\beta}^{exact}$, $\nabla\rho_\alpha \cdot \nabla\rho_\beta$). We will refrain from providing all the lengthy explicit expressions of $\partial\varepsilon_{xc}/\partial\kappa$ (see, e.g., refs 22 and 47 for details) but focus only on their structural features. Some of the ingredients are more critical than others. Obviously, this holds in particular for the exact-exchange energy density, ε_x^{exact}. For global hybrids (eq 1), the situation is particularly simple as none of the derivatives $\partial\varepsilon_{xc}/\partial\kappa$ depend further on ε_x^{exact} itself. Moreover,

$$\frac{\partial\varepsilon_{xc}^{hybr}}{\partial\varepsilon_x^{exact}} = a_0 = const \quad (23)$$

and only the term $a_0 v_x^{exact}\varphi_i$ survives for the corresponding contribution to the FDOs. The CPKS treatment, in this case, is well elaborated (see above).

At first sight, matters appear much more complicated for general OOD functionals (eq 7). The local mixing function γ may depend on any of the ingredients listed above, and $\partial\varepsilon_{xc}/\partial\kappa$ may depend on ε_x^{exact}. Some nonzero contributions from those quantities to the linear response $\hat{\omega}_u^1$, thus, might be expected. It turns out, however, that this is fortunately not the case, since, at the nonrelativistic one-component level, ε_x^{exact} itself yields no response. To show this, we recall that the exact-exchange operator $\hat{v}_x^{exact}$ is defined by eq 9 and rewrite eq 5 as

$$\varepsilon_x^{exact}(\mathbf{r}) = \frac{1}{2}\sum_k^{occ} \varphi_k^*(\mathbf{r})[\hat{v}_x^{exact}\varphi_k](\mathbf{r}) \quad (24)$$

Then, substituting the perturbed orbitals $\tilde{\varphi}_k^u$ (eq 17), as well as $\hat{v}_{x,u}^{exact}$ 22, into eq 24, we have

$$\tilde{\varepsilon}_x^{exact}(\mathbf{r}) = \frac{1}{2}\sum_k^{occ} \tilde{\varphi}_k^*(\mathbf{r})[\hat{\tilde{v}}_x^{exact}\tilde{\varphi}_k](\mathbf{r}) =$$

$$\frac{1}{2}\sum_k^{occ} \varphi_k^*(\mathbf{r})[\hat{v}_x^{exact}\varphi_k](\mathbf{r}) + \frac{i}{2}B\sum_k^{occ}\{\varphi_k^*(\mathbf{r})[\hat{v}_{x,u}^{exact,1}\varphi_k](\mathbf{r}) +$$

$$\varphi_k^*(\mathbf{r})[\hat{v}_x^{exact}\varphi_k^{1,u}](\mathbf{r}) - [\varphi_k^{1,u}(\mathbf{r})]^*[\hat{v}_x^{exact}\varphi_k](\mathbf{r})\} + O(\mathbf{B}^2) \equiv$$

$$\varepsilon_x^{exact}(\mathbf{r}) + iB\varepsilon_{x,u}^{exact,1}(\mathbf{r}) + O(\mathbf{B}^2) \quad (25)$$

where the linear response of the exact-exchange energy density, $\varepsilon_{x,u}^{exact,1}$, can be rewritten as

$$\varepsilon_{x,u}^{exact,1}(\mathbf{r}) = \frac{1}{2}\sum_k^{occ}\sum_j^{occ}\left(\{[\varphi_k^{1,u}(\mathbf{r})]^*\varphi_j(\mathbf{r}) - \right.$$

$$\varphi_k^*(\mathbf{r})\varphi_j^{1,u}(\mathbf{r})\}\int\frac{\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' +$$

$$\left.\varphi_k^*(\mathbf{r})\varphi_j(\mathbf{r})\int\frac{\{[\varphi_j^{1,u}(\mathbf{r}')]^*\varphi_k(\mathbf{r}') - \varphi_j^*(\mathbf{r}')\varphi_k^{1,u}(\mathbf{r}')\}}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}'\right) \quad (26)$$

The double sum on the right-hand side of eq 26 should be invariant with respect to the permutation of indices k and j (both indices run the same set of occupied orbitals). On the other hand, one can easily see that such a permutation leads to $-(\varepsilon_{x,u}^{exact,1})^*$. Therefore,

$$\varepsilon_{x,u}^{exact,1} = -(\varepsilon_{x,u}^{exact,1})^* \quad (27)$$

i.e., $\varepsilon_{x,u}^{exact,1}$ is a purely imaginary quantity. It is well-known that within the nonrelativistic approach, the unperturbed orbitals φ_k can always be chosen real valued without a loss of generality (at least, in the case of orbitally nondegenerate states for which the employed formalism is designed). Then, because of the purely imaginary character of the magnetic (orbital Zeeman) perturbation, the $\varphi_k^{1,u}$ are also real (cf. eqs 17−19). Therefore, $\varepsilon_{x,u}^{exact,1}$ (eq 26) should be real as well since it is composed of real quantities. This in turn contradicts our above observation that the linear response of the exact-exchange energy density is purely imaginary, unless $\varepsilon_{x,u}^{exact,1}$ is zero. Therefore, up to second- and higher-order terms in B, the exact-exchange energy density itself (but not the operator $\hat{v}_x^{exact}$!) and, hence, any analytical functions of ε_x^{exact} are invariant with respect to the presence of the external magnetic field (note that the individual terms $\varphi_k\hat{v}_{x,u}^{exact,1}\varphi_k + \varphi_k\hat{v}_x^{exact}\varphi_k^{1,u} - \varphi_k^{1,u}\hat{v}_x^{exact}\varphi_k$ are not necessarily zero, and only their summation over k gives an overall vanishing result). These arguments for a vanishing $\varepsilon_{x,u}^{exact,1}$ do not hold anymore when passing to two- or four-component relativistic approaches where spin-orbit effects are taken into account variationally, since the unperturbed orbitals cannot be chosen real valued in such a case.

The overall exact-exchange contribution to the FDO (eq 6) of a general OOD functional (eq 7) ($\delta E_{xc}^{OOD}/\delta\varphi_k)_{\varepsilon_x^{exact}}$ is[47]

$$\frac{1}{2}\left(\frac{\delta E_{xc}^{OOD}}{\delta\varphi_k}\right)_{\varepsilon_x^{exact}} = \frac{1}{2}\left[\left(\frac{\partial\varepsilon_{xc}^{OOD}}{\partial\varepsilon_x^{exact}}\right)\hat{v}_x^{exact}\varphi_k + \hat{v}_x^{exact}\left\{\left(\frac{\partial\varepsilon_{xc}^{OOD}}{\partial\varepsilon_x^{exact}}\right)\varphi_k\right\}\right] \quad (28)$$

For global hybrids, the right-hand side of eq 28 reduces simply to $a_0\hat{v}_x^{exact}\varphi_k$ (cf. eq 23). For local hybrids *without* dependence of the LMF γ on ε_x^{exact}:

$$\frac{\partial\varepsilon_{xc}^{Lh}}{\partial\varepsilon_x^{exact}} = \gamma \quad (29)$$

[cf., e.g., eq 14 of ref 22]. For the more general case of local hybrid functionals *with* a dependence of γ on ε_x^{exact}:[31]

$$\frac{\partial\varepsilon_{xc}^{OOD/Lh}}{\partial\varepsilon_x^{exact}} = \gamma + \frac{\partial\gamma}{\partial\varepsilon_x^{exact}}(\varepsilon_x^{exact} - \varepsilon_x^{DFT}) \quad (30)$$

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By writing "OOD/Lh", we emphasize that such a functional may still be structured in the form of eq 4, while a general OOD functional (eq 7) may take any sophisticated form, including some implicitly defined functions. An example is Becke's model for nondynamical correlation (B05).[48]

With the above-mentioned invariance of ε_x^{exact} and with eq 28, the response operator in the general OOD case is obtained as

$$\hat{\omega}_u^1 = \frac{1}{2}\left[\left(\frac{\partial \varepsilon_{xc}^{OOD}}{\partial \varepsilon_x^{exact}}\right)\hat{v}_{x,u}^{exact,1} + \hat{v}_{x,u}^{exact,1}\left(\frac{\partial \varepsilon_{xc}^{OOD}}{\partial \varepsilon_x^{exact}}\right)\right] \qquad (31)$$

while eq 20 itself remains unchanged. It, thus, turns out that implementation of the envisioned generalized CPKS scheme is relatively straightforward: we need to compute the relevant matrix elements of operator (eq 31) instead of $a_0\,\hat{v}_{x,u}^{exact,\,1}$ for global hybrids.

4. Computational Details

The generalized CPKS scheme has been implemented within the MAG-ReSpect code,[53] which uses Gaussian-type orbital basis sets. For evaluating the one- and two-electron spin-orbit integrals entering eq 13 and 16, we have employed the atomic mean-field approximation (AMFI),[54,55] which has proven to combine computational efficiency with high accuracy (see refs 17, 21 and 56 for further details).

A completeness insertion (or resolution of the identity, RI) in the orbital basis set has been employed when evaluating the exact-exchange energy density, eq 5, as described in ref 33 (see also refs 22, 26−28, 32, and 36). To minimize any errors from the RI and from the gauge dependence (see below) and to guarantee the evaluation of the true performance of different functionals, uncontracted basis sets have been used in this work. In the case of main group radicals, we started from H−Ar basis sets due to Jensen,[57−59] which are designed to provide a fast and a controlled convergence toward the basis set limit for spin-spin coupling constants (pcJ-*n* family[58]) and nuclear shielding constants (pcS-*n* family[59]). After a number of trials, we chose the aug-pcS-3 basis sets, composed of (10s6p3d2f) for H, (15s11p5d3f) for B to F (g functions omitted), (18s14p3d2f) for Mg, and (18s15p5d3f) for S (g functions omitted). After some calibration work on the TiF$_3$ complex, we decided to employ Fægri's (16s11p8d) basis sets[60] for the 3d transition metals, supplemented by three f functions.[61] The ligand atoms were treated by uncontracted IGLO-IV basis sets[62] (good compatibility of IGLO and Fægri basis sets has been noted[63] and could be confirmed in our studies). While we have recently constructed specific basis sets for molybdenum EPR parameter calculations[64] for consistency with the calculations on 3d systems, we chose also a Fægri basis for molybdenum (20s14p11d)[60] and augmented it by an even-tempered set of four f exponents (20.31, 5.39, 1.43, and 0.38) based partly on extrapolation from the 3f polarization set for chromium.[61]

We consider here one- and two-parameter local hybrid functionals optimized previously to yield the best atomization energies[26,27] as well as reaction barriers.[32] That is, five

different local hybrids have been evaluated: (i) *Lh*-SVWN with $\gamma_\sigma = 0.48t_\sigma$ (cf. eq 4; "S" stands for Slater−Dirac LSDA exchange[4,5] employed as $\varepsilon_{x,\sigma}^{DFT}$, and "VWN" stands for Vosko−Wilk−Nusair LSDA correlation model V[6] employed as E_c^{DFT}), where

$$t_\sigma = \tau_{W,\sigma}/\tau_\sigma, \qquad \sigma = \alpha, \beta \qquad (32)$$

$$\tau_{W,\sigma} = |\nabla\rho_\sigma|^2/(8\rho_\sigma) \qquad (33)$$

is the von Weizsäcker kinetic energy density, and τ_σ is given by eq 8. This has, so far, been one of the most successful local hybrids for atomization energies and for reaction barriers;[26,28] (ii) *Lh*-SVWN with $\gamma_\sigma = 0.22s_\sigma$, where

$$s_\sigma = |\nabla\rho_\sigma|/[2(3\pi^2)^{1/3}\rho_\sigma^{4/3}] \qquad (34)$$

is the dimensionless density gradient; and (iii) *Lh*-SLYP with $\gamma_\sigma = 0.24s_\sigma$ (here VWN LSDA correlation has been replaced by Lee−Yang−Parr GGA correlation).[11] The last two local hybrids[27] exhibited somewhat inferior atomization energies and reaction barriers compared to the first but provided superior nuclear shielding constants[22] (in that case implemented as localized local hybrid potentials[36] followed by an uncoupled DFT perturbation treatment). Finally, we have evaluated also two local hybrids[32] that include an explicit dependence on spin polarization

$$\zeta = (\rho_\alpha - \rho_\beta)/(\rho_\alpha + \rho_\beta) \qquad (35)$$

These are (iv) *Lh*-SVWN with $g_\sigma = (0.446 \pm 0.0531\,\zeta)t_\sigma$ and (v) *Lh*-SVWN with $\gamma_\sigma = \text{erf}[(0.196 \pm 0.0416\,\zeta)s_\sigma]$ (the plus sign holds for $\sigma = \alpha$, the minus sign holds for $\sigma = \beta$). These two very recent functionals are particularly accurate for atomization energies.[32] According to the order above, we will abbreviate the functionals in the following as "*Lh*-I" to "*Lh*-V" (Tables 1 and 2).

For comparison, we also include results obtained with four global hybrids (B3LYP[3,11] and B3PW91[3,10] with 20% exact exchange and BHLYP[2,11] and BHPW91[1,10] with 50% exact exchange[65]), one GGA (BP86[8,9]) and one LSDA (SVWN[5,6]) functional. These more traditional functionals have previously been evaluated for g-tensor calculations in refs 17, 21, 45, 50, 51, and 66 but with smaller (contracted) basis sets.

Due to the use of the AMFI approximation[54] for the spin-orbit integrals, we used a common gauge origin at the center of mass for the small main group radicals and at the metal nucleus for the transition-metal systems. This choice is well justified for g-tensors (see ref 17 and references therein) and seems to yield negligible gauge errors, in particular, in view of the large uncontracted basis sets used. Indeed, test calculations of the g-tensor for the Fe(CO)$_5^+$ complex (tetragonal pyramid) with the gauge origin shifted to axial carbon and oxygen nuclei give absolute relative deviations of the g-shift components of less than 0.3%.

The molecular structures are DFT-optimized ones employed already in refs 17−19, 50, 21, 66, and 67.

5. Results and Discussion

Table 1 shows the calculated g-shift components for a selection of light main-group radicals compared to experi-

Table 1. Comparison of Calculated and Experimental g-Shift Components for 13 Light Main-Group Radicals (ppm)

		pure DFT			global hybrids			local hybrids					expt.[g]
		SVWN	BP86	B3PW91	B3LYP	BHPW91	BHLYP	Lh-I[a,f]	Lh-II[b,f]	Lh-III[c,f]	Lh-IV[d,f]	Lh-V[e,f]	
H_2O^+	Δg_{11}	-184	-186	-185	-185	-183	-183	-187	-181	-178	-186	-183	200
	Δg_{22}	4607	3784	3819	3974	3724	3920	3925	3998	4095	3955	4013	4800
	Δg_{33}	16308	10621	11466	12434	11886	13260	12654	13329	14260	12742	13174	18800
CO^+	$\Delta g_{\parallel}$	-100	-102	-97	-102	-86	-95	-94	-94	-93	-94	-92	
	$\Delta g_{\perp}$	-2488	-2399	-2453	-2486	-2547	-2556	-2407	-2506	-2501	-2406	-2476	-2400
CO_2^-	Δg_{11}	430	344	758	684	1075	1004	775	744	586	760	835	880
	Δg_{22}	-5075	-4948	-5280	-5155	-5586	-5464	-5119	-5333	-5199	-5112	-5286	-5070
	Δg_{33}	-679	-690	-695	-704	-732	-729	-717	-772	-798	-710	-713	-710
O_3^-	Δg_{11}	-330	-355	-438	-434	-609	-609	-496	-444	-442	-481	-430	1300
	Δg_{22}	16154	14931	17737	17963	21200	21622	17058	18462	18263	16923	18122	16400
	Δg_{33}	8973	8543	10664	10814	13726	14045	10282	10792	10742	10163	10548	10000
HCO	Δg_{11}	2379	2226	2297	2331	2321	2381	2232	2310	2305	2238	2304	1500
	Δg_{22}	-159	-166	-174	-144	-192	-138	-209	-192	-169	-204	-189	0
	Δg_{33}	-9377	-7726	-7838	-7820	-7752	-7694	-7675	-8296	-8449	-7709	-8380	-7500
H_2CO^+	Δg_{11}	5473	5059	5326	5406	5476	5612	5339	5519	5520	5337	5500	4600
	Δg_{22}	73	92	156	143	782	937	182	184	211	185	179	200
	Δg_{33}	-1551	-966	-293	-231	282	252	-173	-288	-450	-278	-462	-800
C_3H_5	Δg_{11}	-42	-48	-44	-42	-40	-39	-46	-49	-48	-44	-44	0
	Δg_{22}	524	355	386	434	416	473	457	505	526	458	503	400
	Δg_{33}	602	513	500	505	466	475	483	529	557	490	535	800
NO_2	Δg_{11}	-540	-547	-578	-577	-669	-656	-600	-610	-627	-594	-603	-300
	Δg_{22}	3284	3223	3563	3543	3928	3930	3416	3610	3493	3398	3566	3900
	Δg_{33}	-12022	-11021	-11593	-11600	-12005	-12017	-11146	-11889	-11756	-11148	-11873	-11300
NF_2	Δg_{11}	-566	-572	-643	-621	-743	-707	-720	-712	-695	-705	-689	-100
	Δg_{22}	4370	4028	3958	4060	3616	3771	3746	3805	3805	3795	3869	2800
	Δg_{33}	7220	6438	6555	6770	6298	6633	6417	6570	6602	6470	6644	6200
CN	$\Delta g_{\parallel}$	-104	-104	-103	-106	-95	-101	-103	-103	-103	-102	-102	
	$\Delta g_{\perp}$	-1878	-1782	-1915	-1967	-2042	-2216	-1929	-2005	-2015	-1915	-1980	-2000
MgF	$\Delta g_{\parallel}$	15	14	16	9	18	9	16	17	14	16	38	-300
	$\Delta g_{\perp}$	-1804	-1728	-1625	-1606	-1477	-1484	-1550	-1616	-1622	-1567	-1766	-1300
BO	$\Delta g_{\parallel}$	-40	-42	-38	-44	-34	-42	-36	-35	-36	-36	-31	
	$\Delta g_{\perp}$	-1794	-1749	-1739	-1720	-1744	-1693	-1681	-1792	-1764	-1684	-1765	-1700
BS	$\Delta g_{\parallel}$	-57	-60	-59	-61	-59	-62	-59	-58	-58	-58	-57	
	$\Delta g_{\perp}$	-9725	-8997	-8967	-8988	-8899	-8810	-8892	-9180	-9124	-8921	-9164	-8900
MAE[h,i]		602 (537)	711 (453)	653 (422)	640 (443)	904 (697)	901 (741)	554 (361)	656 (490)	611 (476)	543 (353)	638 (466)	
MaxSE[j,i]		-2492 (-1877)	-8179 (-1655)	-7334 (-1738)	-6366 (-1734)	-6914 (-4800)	-5540 (-5222)	-6146 (-1796)	-5471 (2062)	-4540 (1863)	-6058 (-1781)	-5626 (-1730)	
					linear regression analysis for comparison between theory and experiment[k,j]								
slope (A)		0.989 (1.037)	0.836 (0.949)	0.916 (1.048)	0.938 (1.057)	0.999 (1.162)	1.031 (1.178)	0.914 (1.017)	0.968 (1.079)	0.979 (1.073)	0.913 (1.014)	0.960 (1.070)	
intercept (B)		-263 (-212)	-304 (-184)	-170 (-30)	-124 (3)	-13 (160)	66 (221)	-145 (-35)	-164 (-46)	-154 (-54)	-150 (-43)	-178 (-61)	
RC		0.991 (0.992)	0.974 (0.994)	0.972 (0.995)	0.977 (0.995)	0.960 (0.988)	0.966 (0.988)	0.981 (0.995)	0.981 (0.995)	0.985 (0.995)	0.982 (0.995)	0.981 (0.995)	
SD		834 (705)	1235 (576)	1394 (562)	1292 (577)	1842 (968)	1728 (1005)	1135 (542)	1215 (570)	1067 (562)	1110 (533)	1204 (554)	

^{a} Lh-SVWN, $\gamma = 0.48t$. ^{b} Lh-SVWN, $\gamma = 0.22s$. ^{c} Lh-SLYP, $\gamma = 0.24s$. ^{d} Lh-SVWN, $\gamma = (0.446 \pm 0.0531\ \zeta)t$. ^{e} Lh-SVWN, $\gamma = \text{erf}[(0.196 \pm 0.0416\ \zeta)s]$. ^{f} For notational simplicity, the spin labels $\sigma = \alpha, \beta$ have been omitted. ^{g} See refs 50 and 70 for the detailed references to experimental data. ^{h} Mean absolute error. ^{i} Data in parentheses correspond to omission of Δg_{33} for H_2O^+. ^{j} Maximal (signed) error. ^{k} $\Delta g(\text{calc.}) = A\ \Delta g(\text{expt.}) + B$, with $\Delta g(\text{expt.})$ and B in ppm; the standard deviation (SD) is $[\sum_{j=1}^{n}(\Delta g_j - \Delta\bar{g})^2/(n-1)]^{1/2}$. Perfect agreement with experiment corresponds to $A = 1$, $B = 0$, SD $= 0$, and regression coefficient (RC) $= 1$.

Coupled-Perturbed Scheme

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Table 2. Comparison of Calculated and Experimental g-Shift Components for 12 Transition-Metal Compounds (ppt)

		pure DFT		global hybrids				local hybrids					
		SVWN	BP86	B3PW91	B3LYP	BHPW91	BHLYP	Lh-I[a]	Lh-II[b]	Lh-III[c]	Lh-IV[d]	Lh-V[e]	expt.
$Co(CO)_4$	$\Delta g_{\parallel}$	3.51	4.08	12.3	12.7	65.5	69.7	8.1	8.16	8.74	7.78	7.56	3.6[f]
	$\Delta g_{\perp}$	96.8	80.5	108.6	112.9	148.5	157.2	116.1	115.2	121.4	115.0	112.0	127.6[f]
$CrOF_4^-$	$\Delta g_{\parallel}$	−22.5	−18.5	−24.6	−24.4	−35.7	−35.3	−25.4	−25.6	−25.8	−25.1	−25.3	−43.3[g]
	$\Delta g_{\perp}$	−31.5	−25.2	−30.5	−30.0	−54.1	−54.3	−31.3	−32.5	−32.5	−31.0	−32.2	−34.3[g]
$CrOCl_4^-$	$\Delta g_{\parallel}$	21.2	18.9	14.6	16.3	−0.82	1.15	15.1	15.3	14.9	15.8	16.5	10[h]
	$\Delta g_{\perp}$	−22.5	−19.3	−27.1	−26.7	−56.5	−56.8	−27.2	−28.0	−28.0	−26.6	−27.2	−25[h]
$Cu(NO_3)_2$	Δg_{zz}	125.8	121.3	184.7	182.7	326.7	319.6	176.0	179.9	183.8	171.4	172.0	246.6[i]
	Δg_{xx}	28.2	28.6	46.5	46.3	84.5	84.1	43.1	43.1	44.3	41.7	40.8	49.9[i]
	Δg_{yy}	30.8	30.7	46.8	46.7	86.8	86.1	43.5	43.5	44.9	42.3	41.6	49.9[i]
$Cu(acac)_2$	Δg_{zz}	125.1	120.1	182.8	181.1	304.1	297.7	172.3	177.6	181.8	168.2	170.1	285.2[j]
	Δg_{xx}	30.5	30.5	47.2	46.9	77.9	76.9	43.1	43.8	45.1	42.0	41.8	48.7[j]
	Δg_{yy}	35.3	34.8	51.7	51.5	79.9	79.2	47.6	48.5	49.7	46.6	46.6	48.7[j]
$Fe(CO)_5^+$	$\Delta g_{\parallel}$	−1.03	−1.42	−3.48	−3.56	−10.1	−9.4	−2.1	−2.31	−2.51	−2.05	−2.26	−1.4[k]
	$\Delta g_{\perp}$	61.8	51.4	66.6	68.8	86.2	90.1	73.0	71.8	74.9	72.3	69.4	78.4[k]
$Mn(CO)_5$	$\Delta g_{\parallel}$	−1.05	−1.30	−2.55	−2.69	−6.78	−6.72	−1.93	−1.97	−2.14	−1.87	−1.89	−2.3[l]
	$\Delta g_{\perp}$	27.3	23.7	28.4	29.3	32.8	33.9	31.0	30.2	31.6	30.8	28.9	35.7[l]
MnO_3	$\Delta g_{\parallel}$	3.65	2.63	−1.71	−1.27	−17.9	−18.3	−0.3	−0.19	−0.71	0.025	0.19	1.3[m]
	$\Delta g_{\perp}$	−0.78	2.54	1.78	3.96	−213.7	−233.0	3.3	3.17	2.12	3.76	3.40	6.1[m]
$MoOF_4^-$	$\Delta g_{\parallel}$	−77.6	−70.5	−82.8	−85.0	−99.5	−102.4	−86.4	−84.7	−84.6	−85.7	−84.3	−107.7[n]
	$\Delta g_{\perp}$	−66.9	−58.6	−63.2	−63.7	−69.4	−69.8	−66.1	−66.9	−66.4	−66.0	−66.9	−76.9[n]
$MoOCl_4^-$	$\Delta g_{\parallel}$	7.10	5.97	−3.95	−3.46	−21.8	−21.5	−2.86	−1.48	−1.29	−2.03	−0.47	−37.3[n]
	$\Delta g_{\perp}$	−51.3	−46.5	−51.8	−52.2	−59.7	−60.1	−53.1	−53.5	−53.0	−52.8	−53.3	−56.1[n]
$Ni(CO)_3H$	$\Delta g_{\parallel}$	1.39	1.72	4.96	5.34	14.6	15.4	2.93	2.86	3.08	2.82	2.54	1.9[o]
	$\Delta g_{\perp}$	41.6	42.4	72.6	74.1	168.3	173.5	61.3	65.3	66.2	58.8	60.1	65.1[o]
TiF_3	$\Delta g_{\parallel}$	−1.26	−1.33	−1.44	−1.28	−1.43	−1.23	−1.66	−1.59	−1.51	−1.61	−1.60	−3.7[p]
	$\Delta g_{\perp}$	−53.5	−37.2	−51.1	−49.4	−76.2	−70.9	−60.9	−58.3	−57.6	−60.2	−59.1	−123.7[p]
MAE[q]		24.7	27.9	16.3	16.2	32.6	33.6	15.5	15.2	14.5	16.2	16.6	
MaxSE[q,r]		−160.1	−165.1	−102.4	−104.1	−219.8	−239.1	−112.9	−107.6	−103.4	−117.0	−115.1	
				linear regression analysis for comparison between theory and experiment[s]									
slope (A)		0.539	0.491	0.702	0.701	1.14	1.13	0.692	0.701	0.714	0.678	0.678	
intercept (B)		0.6	2.0	5.4	5.8	4.9	4.9	3.8	4.2	4.8	3.6	3.4	
RC		0.956	0.965	0.981	0.979	0.887	0.872	0.980	0.981	0.980	0.979	0.980	
SD		14.7	12.5	13.0	13.7	55.3	59.3	13.0	13.0	13.5	13.1	12.8	

[a] Lh-SVWN, $\gamma = 0.48t$. [b] Lh-SVWN, $\gamma = 0.22s$. [c] Lh-SLYP, $\gamma = 0.24s$. [d] Lh-SVWN, $\gamma = (0.446 \pm 0.0531 \zeta)t$. [e] Lh-SVWN, $\gamma = \mathrm{erf}[(0.196 \pm 0.0416 \zeta)s]$. [f] ref 71 (EPR in Kr matrix). [g] ref 72 (EPR in aqueous $KCrOF_4$−HF solutions). [h] refs 73 (EPR of Cr-surface impregnated rutile (TiO_2) subjected to the exposure of SO_2, Cl_2, and HCl), and 74 (EPR in CH_2Cl_2 solution). [i] ref 75 (EPR in Ne matrix). [j] ref 76 (EPR of radicals trapped in $CHCl_3$ glass). [k] ref 77 (EPR in $Co(CO)_6$ host crystal). [l] ref 78 (EPR in C_6D_6 matrix). [m] ref 79 (EPR in Ne matrix). [n] ref 80 (single crystal EPR). [o] ref 81 (EPR in Kr matrix). [p] ref 82 (EPR in Ar matrix). [q] See footnotes h and j in Table 1. [r] Except for BHPW91 and BHLYP, where the largest error is observed for the $\Delta g_{\perp}$ component of MnO_3 (due to strongly spin-contaminated solutions), for all other functionals, the largest outlier is the Δg_{zz} component of $Cu(acac)_2$. [s] See footnote k to Table 1 (data in ppt).

ment. It has been demonstrated previously[21] that standard GGA or global hybrid functionals tend to reproduce the spread of these main-group g-tensors well, with a slight overestimate of the absolute value in most cases. A notable exception is the Δg_{33} component of the H_2O^+ radical, which is significantly underestimated by standard functionals. This has been traced back previously to a near-degeneracy situation.[17] We do, therefore, not expect much room for improvement with local hybrid functionals, in particular, as the experimental error bars often exceed 500 ppm (0.5 ppt or 0.0005), and the agreement between theory and experiment of ca. 500−1000 ppm should be considered as satisfactory.[45]

Looking at the mean absolute errors (MAEs) and results of linear regression analyses, we do indeed confirm the previously found[17] relatively small overall sensitivity of the results to the functional. Even LSDA, which is poor for thermochemistry, kinetics, and other properties, performs well here. We, therefore, use the local hybrid data in Table 1 mainly to validate the generalized CPKS implementation. Indeed, the performance of the five local hybrids Lh-I to Lh-V is overall similar to that of standard global hybrids like B3PW91 or B3LYP. Looking more closely, we see that, upon consideration of all molecules and components, the s-LMF functionals provide a somewhat larger and, thus, an

improved slope than those of the *t*-LMF-based local hybrids and the standard global hybrids. This changes upon exclusion of the Δg_{33} component of H_2O^+. Now all slopes (except for BP86) are larger than 1, and the *t*-LMFs give the slightly better slopes than the *s*-LMFs. The global hybrids BHLYP and BHPW91 with 50% exact exchange give even larger slopes. MAEs and standard deviations (SD) of all local hybrids are comparable to B3PW91, B3LYP, or BP86 and are lower than those of BHLYP or BHPW91 (the 50% EXX admixture of the latter two functionals leads to some spin contamination, which may be responsible for the larger scatter of the data).[17]

Looking at the special case of H_2O^+ (see above), performance of the local hybrids is also similar to that of the global hybrids. The slightly larger Δg_{33} component with *Lh*-III may reflect the use of the LYP correlation functional (see also BHLYP results). For this radical, the LSDA, in form of the SVWN functional, has been shown previously to perform particularly well, most likely due to fortuitous error cancellation regarding the near-degeneracy of the Kohn–Sham eigenvalues.[17] Apart from H_2O^+, the largest deviations from experiment (cf. maximal signed errors (MaxSEs) in Table 1) are observed almost always for either Δg_{11} (negative) or Δg_{22} (positive) components of the O_3^- radical anion (the only exception is SVWN, which shows the largest error for the Δg_{33} component of HCO).

A rather different situation than for these main-group radicals holds for the transition-metal complexes (Table 2). Here, the dependence on EXX admixture is much more pronounced. As shown previously,[17] the semilocal functionals (SVWN and BP86) exhibit reasonable correlation with experiment but with a severe systematic underestimation of the linear regression slope. Global hybrids with a moderate EXX admixture (B3PW91 and B3LYP) improve matters but still recover only ca. 70% of the slope. The "half and half" functionals BHPW91 and BHLYP finally overestimate the slope somewhat and exhibit unacceptably large scattering of the results (cf. MAEs and SDs). This is related to significant spin contamination in many cases (much more so than in the main-group radicals), as has been analyzed in detail previously.[17,19,68]

The five local hybrids tested perform essentially as good as B3PW91 and B3LYP. This holds not only for the overall statistics of the results but also for most individual systems. A very slight reduction of the slope is found when introducing spin polarization into the LMF (*Lh*-IV and *Lh*-V). This may reflect the overall somewhat reduced average EXX admixture.[32]

Looking at individual complexes, we note TiF$_3$ as a case with particularly large underestimate of the $\Delta g_\perp$ component (Table 2). Here, even a larger than 50% EXX admixture would still improve the agreement with experiment (spin contamination is not a problem for this molecule). For this example, all five local hybrids provide results intermediate between the hybrids with 20% and 50% exact exchange. Similar behavior pertains, e.g., to Co(CO)$_4$ and Ni(CO)$_3$H, where, however, the local hybrid results are already in favorable agreement with experiment (in the latter case, the standard global hybrids overshoot already). In contrast, for

the two copper complexes, Cu(NO$_3$)$_2$ and Cu(acac)$_2$, the local hybrids give slightly lower g-shifts than B3LYP or B3PW91 and, thus, also slightly worse agreement with experiment.

A possible explanation for the fact that the local hybrids exhibit larger g-shifts than B3LYP or B3PW91 for the early 3d complex TiF$_3$ but reduced g-shifts for the later metal centers Ni and Cu (for the intermediate Co, the g-shifts are very similar) relates to a previously discussed behavior[27,36] of the *average* exact exchange admixtures of the simple one- or two-parameter local hybrids discussed here. This trend may be monitored by density-averaged LMF values:

$$\bar{\gamma}_\sigma = \int \gamma_\sigma(\mathbf{r})\rho_\sigma(\mathbf{r})d\mathbf{r} / \int \rho_\sigma(\mathbf{r})d\mathbf{r} =$$
$$(1/N_\sigma)\int \gamma_\sigma(\mathbf{r})\rho_\sigma(\mathbf{r})d\mathbf{r}, \qquad \sigma = \alpha, \beta \quad (36)$$

or, in a simplified spin-averaged way, by

$$\bar{\gamma} = \frac{N_\alpha\bar{\gamma}_\alpha + N_\beta\bar{\gamma}_\beta}{N_\alpha + N_\beta} \quad (37)$$

It has been found that these average EXX admixtures tend to decrease as one moves to higher nuclear charges both for isolated atoms and for molecules made from these atoms.[27,36] For the free 3d atoms, $\bar{\gamma}$ gradually decreases from 0.229 (Ti) to 0.186 (Cu). The overall range for the complexes is less pronounced (they exhibit all values between 0.21 and 0.25) due to the contributions from the ligand spheres. However, as the g-shift is dominated by the spin-orbit contributions of the metal center and localized ligand-field-type excitations in all of these systems, the observed decrease of $\bar{\gamma}$ (which derives mainly from core and semicore regions of the atoms) is certainly most relevant and explains some of the observed trends. The future development of local hybrids will benefit from an improved understanding of the predominant density regions affecting certain properties.

The lowest atomic $\bar{\gamma}$ value (0.167) is found for the 4d element Mo. However, for the two Mo complexes in the test series, the local hybrids provide, again, g-shift results close to the B3LYP and B3PW91 data. They underestimate the absolute value of the (negative) experimental $\Delta g_\perp$ components slightly and of the $\Delta g_\parallel$ components more strongly. However, in these cases, one has to keep in mind that for 4d complexes, higher-order spin-orbit effects, which have been neglected in the present work, become already notable. In axially symmetric Mo complexes, they have been shown in our previous work to render particularly the $\Delta g_\parallel$ component more negative.[64,69] For example, at B3PW91 level, $\Delta g_\parallel$ in MoOCl$_4^-$ is lowered by about 11 ppt and $\Delta g_\perp$ by about 4 ppt when going from a perturbational treatment of spin-orbit coupling to a two-component variational Douglas–Kroll–Hess calculation of the g-shift tensors.[64] Taking into account similar corrections for higher-order spin-orbit effects in 4d systems, performance of the standard global hybrids and the local hybrids for the two Mo complexes is somewhat better than suggested by the data in Table 2, in particular for the parallel component.

The present local-hybrid results for g-tensors of transition-metal complexes suggest that for the systems and the particular property at hand, the (average or local) EXX

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admixture at the metal center itself is most crucial for the performance. Overall, the five local hybrids studied perform as good but not notably better than standard global hybrids B3LYP or B3PW91. Probably, the one- or two-parameter LMFs studied, which were optimized exclusively for thermochemistry and for reaction barriers, provide too low exact exchange near the transition-metal center to improve the agreement compared to global hybrids with ca. 20% exact-exchange admixture throughout the system. This provides clues toward the construction of improved LMFs, a line we intend to follow in the future.

6. Conclusions and Outlook

A generalized coupled-perturbed Kohn−Sham (CPKS) scheme for the calculation of second-order magnetic properties has been derived and implemented for occupied orbital-dependent (OOD) functionals depending on the exact-exchange energy density. Within a nonrelativistic one-component approach, the coupling terms in the CPKS scheme arise exclusively from variation of the exact-exchange energy density itself with respect to the orbitals, cf. eq 31. These terms involve the nonlocal exchange operator. Other occurrences of the exact-exchange energy density in functional derivatives of the OOD functionals, with respect to the orbitals, do not contribute to the coupling terms. This allows a relatively straightforward implementation of the CPKS equations for OOD ("hyper-GGA") functionals and for magnetic properties.

The generalized CPKS scheme has been implemented and tested for electronic g-tensors with local hybrid functionals. Overall, the five local hybrids tested exhibit similar performance for the g-shift tensors of main-group radicals and transition-metal complexes as the standard global hybrids, like B3LYP. In case of the transition-metal complexes, in particular, closer analysis of the results suggests that with the local mixing functions (LMFs) tested, the larger flexibility of local over global hybrids has not yet been exploited sufficiently. This pertains mostly to the EXX admixture around the transition-metal center. This result may not be surprising given: (i) the use of only one or two semiempirical parameters in the LMFs studied so far; and (ii) the optimization of these parameters only for main group thermochemistry and reaction barriers. Indeed, these simple local hybrids outperform standard global hybrids already notably in these areas. Improved performance for g-tensors and, of course, for various other magnetic or electric properties will depend on the construction of more flexible LMFs and on their optimization for the various critical regions within an atom, molecule, or solid.

Finally, comparison between a direct use of nonlocal exact-exchange potentials and a transformation to local and multiplicative potentials within an OEP framework will be of interest. This will require the implementation of more accurate OEP-based schemes than used in our previous evaluation of localized local hybrid potentials for nuclear shieldings.[22]

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