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Frozen-Density Embedding as a Quasi-Diabatization Tool: Charge-Localized States for Spin-Density Calculations

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Abstract

We present an effective approach for (spin-)density calculations of open-shell molecular complexes that avoid both an overdelocalization of spin densities as often observed in approximate KS-DFT calculations and an overlocalization of spin densities as may occur in fragment approaches with non-suitable fragment choices. The method is based on the frozen-density embedding formalism and makes use of non-orthogonal, spin-/charge-localized Slater determinants, which provide a basis for qualitatively correct descriptions of intersystem spin-density delocalization. The reliability of this method is tested on four complexes featuring different molecular sizes and interactions, and showing different degree of spin-density delocalization, ranging from fully localized to fully delocalized. The resulting spin densities are compared to accurate *ab initio* results. The method is clearly more robust than the corresponding KS-DFT approximations, as it works qualitatively correct in all cases studied.

1 Introduction

The determination of accurate spin densities for radical systems is a challenging task, both for experiment and theory. Experimentally, rather complete spin-density maps can be obtained from polarized neutron diffraction [1–7]. More common is an indirect access to spin densities based on electron paramagnetic resonance (EPR) [8]. In particular, the isotropic part of the EPR hyperfine coupling constants depends on the spin density at atomic nuclei. Spin-density maps have also been constructed based on solid-state paramagnetic nuclear magnetic resonance (NMR) spectroscopy [9]. Also here, the link between spectral information and spin densities is provided through hyperfine coupling constants. Special techniques like electron nuclear double resonance (ENDOR) or photochemically induced dynamic nuclear polarization (photo-CIDNP) magic-angle spinning (MAS) NMR have even been used to analyze the spin-density distribution in dimeric radical cations such as the special pair, which is a dimer of bacteriochlorophyll *a* molecules in photosynthetic reaction centers [10–12].

Quantum chemical calculations of spin densities are very important in this context, as full spin-density maps based on EPR or NMR techniques require additional input and refinement from theory. However, accurate calculations of spin densities or hyperfine couplings are by no means trivial. *Ab initio* electron correlation methods of various types have been applied for this purpose, including complete-active-space self-consistent field (CASSCF) [13], complete-active-space second-order perturbation theory (CASPT2) [14], density-matrix renormalization group (DMRG) algorithm [15, 16], or orbital-optimized second-order Møller–Plesset perturbation theory (OO-MP2) [17]. Density functional theory (DFT) may seem attractive for the calculation of spin densities or spin-density-dependent EPR parameters of larger open-shell systems because of its cost-effectiveness. But the choice of a proper exchange–correlation approximation can be problematic [18–21] and usually requires careful benchmarking [22].

A frequent problem in DFT calculations employing standard approximations is the overdelocalization of spin density due to the self-interaction error (SIE). In fact, it has been suggested to use the term “overdelocalization error” rather than SIE [23]. Possible ways to avoid this error include the use of hybrid functionals with high percentage of exact exchange (or even of Hartree–Fock spin densities [24]) and explicit self-interaction corrections such as the one by Perdew and Zunger [25]. Note, however, that larger amounts of exact exchange typically lead to increasing spin-contamination problems and larger regions with β -spin excess [22, 26–30]. The overdelocalization problem can be particularly severe in intermolecular cases, where a delocalization over several molecules may appear (see, e.g., Ref. [31]). For this class of systems, subsystem DFT (sDFT) and the related frozen-density embedding (FDE) have been shown to lead to localized spin densities [31]. Together with the computational efficiency, this makes sDFT and FDE very attractive for computing EPR parameters of, e.g., solvated radicals [32]. However, this leads to the question if sDFT may actually *underestimate* the delocalization of spin in cases where delocalization over subsystem boundaries is physical. In principle, such a delocalization can be described by sDFT, and weak spin-polarization effects across subsystems have been reported [31]. But a strong delocalization of spin density would first of all require the availability of basis functions at all relevant subsystems in each subsystem calculation. This is usually avoided for efficiency reasons. And since approximate embedding potentials are typically not trustworthy at all in the region of other (“frozen”) subsystems [33], a proper delocalization can hardly be expected. In fact, such approximate potentials can rather be employed to *confine* charge and spin densities, which in turn can be utilized to set up quasi-diabatic electronic states of the embedded molecules [30, 34–36]. In cases where a delocalization is expected, sDFT will typically require to combine all fragments involved into one formal subsystem [31]. This situation is a bit unfortunate, as *a priori* information has to be provided for the choice and setup of subsystems in order to achieve a proper description of the spin density. Particular problems are expected if the degree of

delocalization can change with the geometric arrangement of the subsystems, as has been reported for the “hinge model” for the primary donor in photosystem II (PSII) based on preliminary DFT calculations [37] (for a somewhat related case, see Ref. [38]).

This difficulty can actually pragmatically be solved by also computing the proper couplings between the quasi-diabatic states obtained with full localization, as has been demonstrated in the case of charge-migration and charge-separation processes [30, 34–36]. Especially in the charge-migration cases, charge- and spin-delocalization go hand-in-hand. So far, however, this recipe has only been used to obtain a proper energetics, e.g., for charge transfer integrals or long-range charge-transfer excitation energies. Here, we are going to reconsider these strategies for the purpose of determining accurate spin densities in cases where intermolecular delocalization is relevant. We would like to note that a similar strategy can be followed in the framework of constrained DFT [39], and is dubbed CDFT-CI. However, we are not aware of any applications of that method addressing spin densities. On the conceptual side, a difference between the underlying CDFT and FDE calculations is that the former require the definition of hard constraints, whereas the latter only works with implicit, soft restrictions to localize charge and spin. This can have consequences like an easier mutual polarization of the subsystems in FDE.

In what follows, we introduce the underlying theory of the method for construction of (spin-) densities from quasi-diabatic Slater determinants derived from sDFT. Then, we conduct numerical tests to compare two different approaches for calculating or fitting, respectively, the linear combination coefficients for these diabatic states. Finally, we assess the accuracy of our method comparing the calculated spin-density distributions with accurate reference results from *ab initio* wavefunction methods.

2 Theory

Our motivation stems from the possible delocalization of spin density in photosynthetic systems after initial electron transfer. Hence, we will consider the prototypical case of a radical cation $D^{+\bullet}$ in contact with another system A , for which charge and spin delocalization go hand-in-hand. This has the advantage that the connection of our work to the previously considered cases of charge transfer,

$$D^{+\bullet} + A \leftrightarrow D + A^{+\bullet}, \quad (1)$$

is directly evident. Obviously, generalizations to other cases are straightforward. The description of the electronic structure can be achieved as follows: At first, we construct a basis of determinants representing two charge-localized states, $|D^{+\bullet} + A\rangle$ and $|D + A^{+\bullet}\rangle$. Then, these basis functions are used to calculate elements of overlap and Hamiltonian matrices. Finally, a generalized eigenvalue problem similar to the one from (non-orthogonal) configuration interaction (CI) method will be solved to obtain couplings and excitation energies, as has previously been shown [30,34]. Solving this eigenvalue problem, we also obtain a set of eigenvectors, which will be used to calculate the resulting (spin-) density distribution in the complex. This eigenvector information has not been used in previous FDE work and we will show below that using it requires reconsideration of some of the previously made approximations. Each step of the procedure is described in detail below.

2.1 Density of sDFT-derived determinants

Assuming that the electronic structure can be described in terms of a two-state model, we construct our total electronic wavefunction Ψ as a linear combination of Slater determinants Φ_1 and Φ_2 (note that generalizations to many states are straightforward, but will not be considered in this work),

$$\Psi = a\Phi_1 + b\Phi_2. \quad (2)$$

The functions Φ_1 and Φ_2 represent quasi-diabatic states of the system with spin and charge localized on one particular fragment of the molecular complex. This basis of two localized states is usually appropriate for modeling CT reactions [40–44]. We will construct these states as direct products of monomer wavefunctions (similar to the tensor product localization scheme by Migliore [43, 45]),

$$\Phi_1 \equiv |D^{+\bullet}A\rangle = |D^{+\bullet}\rangle \otimes |A\rangle, \quad (3)$$

$$\Phi_2 \equiv |DA^{+\bullet}\rangle = |D\rangle \otimes |A^{+\bullet}\rangle. \quad (4)$$

Here, $|D^{+\bullet}\rangle$, $|A\rangle$, $|D\rangle$, and $|A^{+\bullet}\rangle$ are Slater determinants composed of Kohn–Sham-like (KS) molecular orbitals (MOs) of the corresponding monomers. The operator $\otimes$ is defined such that matrices of MO coefficients of Φ_1 and Φ_2 take the form

$$\mathbf{C}_{\Phi_1} = \begin{pmatrix} \mathbf{C}_{D^{+\bullet}} & 0 \\ 0 & \mathbf{C}_A \end{pmatrix} \quad (5)$$

and

$$\mathbf{C}_{\Phi_2} = \begin{pmatrix} \mathbf{C}_D & 0 \\ 0 & \mathbf{C}_{A^{+\bullet}} \end{pmatrix}, \quad (6)$$

where we have assumed basis sets localized on monomers. Using KS-like orbitals obtained for monomers in dimer Slater determinants obviously introduces an approximation (for applications, see Refs. [45–47]). In this work, the monomer orbitals $\psi_i^{I,\sigma}(\mathbf{r})$ are obtained from the Kohn–Sham equations with constrained electron density (KSCED),

$$\left[-\frac{\nabla^2}{2} + v_{\text{KS}}^{I,\sigma}(\mathbf{r}) + v_{\text{emb}}^{I,\sigma}(\mathbf{r}) \right] \psi_i^{I,\sigma}(\mathbf{r}) = \epsilon_i^{I,\sigma} \psi_i^{I,\sigma}(\mathbf{r}), \quad (7)$$

where $v_{\text{KS}}^{I,\sigma}(\mathbf{r})$ and $v_{\text{emb}}^{I,\sigma}(\mathbf{r})$ are the KS and embedding one-electron potentials, respectively, I is the subsystem index, and $\sigma = \alpha, \beta$ is a spin label. For detail of this approach, we refer the reader to previous work [30]. Mutual relaxation of fragment densities can be included applying freeze-and-thaw cycles [48]. Because the orbital sets of fragments A and D are not kept orthogonal to each other during the FDE calculations, the resulting determinants

Φ_1 and Φ_2 are composed of non-orthogonal orbitals. Moreover, Φ_1 and Φ_2 are also not necessarily orthogonal (and not normalized). In order to proceed, we have to introduce overlap matrices for the diabatic Slater determinants and will have to deal with matrix elements of operators in a non-orthogonal many-electron basis. General expressions for overlap matrices and matrix elements of one- and two-electron operators for the case of non-orthogonal Slater determinants were first derived by Löwdin [49, 50] (note that normalized Slater determinants were assumed there). An overlap matrix element S_{nm} for Slater determinants Φ_n and Φ_m is given by,

$$S_{nm} = \langle \Phi_n | \Phi_m \rangle = \det(\mathbf{S}^{(nm)}), \quad (8)$$

where the overlap matrix $\mathbf{S}^{(nm)}$ is defined for the sets of MOs $\{\psi_i^{(n)}\}$ and $\{\psi_j^{(m)}\}$ (with matrix elements $S_{ij}^{(nm)} = \langle \psi_i^{(n)} | \psi_j^{(m)} \rangle$) of which the Slater determinants Φ_n and Φ_m are composed. Matrix elements of a one-electron operator $\hat{H}_1$ can be calculated as [50],

$$\langle \Phi_n | \hat{H}_1 | \Phi_m \rangle = \sum_{i=1}^N \langle \Phi_n | \hat{h}_i | \Phi_m \rangle = \sum_{i,j=1}^N \langle \psi_i^{(n)} | \hat{h}_i | \psi_j^{(m)} \rangle D_{ij}^{(nm)}. \quad (9)$$

Here, N is the number of electrons in the dimer and $\mathbf{D}^{(nm)}$ is a signed algebraic complement of the overlap matrix $\mathbf{S}^{(nm)}$. The latter can be rewritten by using the expression for a square inverse matrix,

$$(\mathbf{S}^{(nm)})^{-1} = \frac{1}{\det(\mathbf{S}^{(nm)})} (\mathbf{D}^{(nm)})^T. \quad (10)$$

Taking a transpose of both parts and using the resulting expression for $\mathbf{D}^{(nm)}$, we can write Eq. (9) as

$$\langle \Phi_n | \hat{H}_1 | \Phi_m \rangle = \det(\mathbf{S}^{(nm)}) \sum_{i,j=1}^N \langle \psi_i^{(n)} | \hat{h}_i | \psi_j^{(m)} \rangle (\mathbf{S}^{(nm)})_{ji}^{-1}. \quad (11)$$

Note that the inverse matrix $(\mathbf{S}^{(nm)})^{-1}$ is also transposed here (indices i and j are exchanged). This equation can be used for calculations of the matrix elements $\rho_{(nm)}(\mathbf{r})$ replacing the operator $\hat{H}_1$ by the operator of density $\hat{\rho} = \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r})$. In principle, α - and β -contributions could also be calculated applying the density operator $\hat{\rho}$ to the

α - and β -orbitals separately, as for example has been done in Ref. [30]. In this work, however, we explicitly introduce the operators of α - and β -density,

$$\hat{\rho}^\alpha = \sum_{i=1}^N \left[\frac{1}{2} \hat{\mathbf{1}}_i + \hat{s}_{z,i} \right] \delta(\mathbf{r}_i - \mathbf{r}), \quad (12)$$

$$\hat{\rho}^\beta = \sum_{i=1}^N \left[\frac{1}{2} \hat{\mathbf{1}}_i - \hat{s}_{z,i} \right] \delta(\mathbf{r}_i - \mathbf{r}). \quad (13)$$

Here, the operators $\hat{\mathbf{1}}_i$ and $\hat{s}_{z,i}$ acting on an electron i are the unity operator and the z -component of the spin operator $\hat{s}_i$, respectively. Inserting the α -density operator $\hat{\rho}^\alpha$ into Eq. (11), we obtain,

$$\begin{aligned} \rho_{(nm)}^\alpha(\mathbf{r}) &= \det(\mathbf{S}^{(nm)}) \sum_{i,j=1}^N \langle \phi_i^{(n)} | \delta(\mathbf{r}_i - \mathbf{r}) | \phi_j^{(m)} \rangle \langle \sigma_i^{(n)} | \frac{1}{2} \hat{\mathbf{1}}_i + \hat{s}_{z,i} | \sigma_j^{(m)} \rangle (\mathbf{S}^{(nm)})_{ji}^{-1} \\ &= \det(\mathbf{S}^{(nm),\alpha}) \det(\mathbf{S}^{(nm),\beta}) \sum_{i,j=1}^{N_\alpha} \psi_i^{(n),\alpha} \psi_j^{(m),\alpha} (\mathbf{S}^{(nm),\alpha})_{ji}^{-1}, \end{aligned} \quad (14)$$

where the spin-orbital $\psi_i^{(n)}$ has been factorized into its spatial orbital $[\phi_i^{(n)}]$ and spin $[\sigma_i^{(n)}]$ contributions, N_α is the number of α -electrons in the molecular system, and $\psi_i^{(n),\alpha}$ is a spin-orbital with an α -spin function. We order the overlap matrix $\mathbf{S}^{(nm)}$ such that it is in block-diagonal form and can be written as the direct sum of its square-matrix blocks $\mathbf{S}^{(nm),\alpha}$ and $\mathbf{S}^{(nm),\beta}$. In this case, inversion and transposition are applied blockwise,

$$[(\mathbf{S}^{(nm)})^{-1}]^T = [(\mathbf{S}^{(nm),\alpha} \oplus \mathbf{S}^{(nm),\beta})^{-1}]^T = [(\mathbf{S}^{(nm),\alpha})^{-1}]^T \oplus [(\mathbf{S}^{(nm),\beta})^{-1}]^T. \quad (15)$$

The determinant of the total overlap matrix $\det(\mathbf{S}^{(nm)})$ is then equal to the product of the determinants $\det(\mathbf{S}^{(nm),\alpha})$ and $\det(\mathbf{S}^{(nm),\beta})$. A similar expression can be obtained for the operator $\hat{\rho}^\beta$. Hence, the total density $\rho_{(nm)}^{\text{tot}}(\mathbf{r})$ and spin density $\rho_{(nm)}^{\alpha-\beta}(\mathbf{r})$ from the linear combination of the determinants Φ_n and Φ_m are calculated as the sum and difference, respectively, of the α and β densities defined in Eq. (14),

$$\rho_{(nm)}^{\text{tot}}(\mathbf{r}) = \rho_{(nm)}^\alpha(\mathbf{r}) + \rho_{(nm)}^\beta(\mathbf{r}), \quad (16)$$

$$\rho_{(nm)}^{\alpha-\beta}(\mathbf{r}) = \rho_{(nm)}^\alpha(\mathbf{r}) - \rho_{(nm)}^\beta(\mathbf{r}). \quad (17)$$

We now return to Eq. (2) to derive an expression for spin density of the total wavefunction Ψ . For that purpose, we have to calculate the expectation values of the α - and β -density operators $\hat{\rho}^\alpha$ and $\hat{\rho}^\beta$ and normalize them dividing by the norm of the total wavefunction $\langle\Psi|\Psi\rangle$. Thus, for σ -spin component we have,

$$\begin{aligned}\rho^\sigma(\mathbf{r}) &= \frac{\langle\Psi|\hat{\rho}^\sigma|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{a^2\langle\Phi_1|\hat{\rho}^\sigma|\Phi_1\rangle + 2ab\langle\Phi_1|\hat{\rho}^\sigma|\Phi_2\rangle + b^2\langle\Phi_2|\hat{\rho}^\sigma|\Phi_2\rangle}{a^2\langle\Phi_1|\Phi_1\rangle + 2ab\langle\Phi_1|\Phi_2\rangle + b^2\langle\Phi_2|\Phi_2\rangle} \\ &= \frac{a^2\rho_{(11)}^\sigma(\mathbf{r}) + 2ab\rho_{(12)}^\sigma(\mathbf{r}) + b^2\rho_{(22)}^\sigma(\mathbf{r})}{a^2\det(\mathbf{S}^{(11)}) + 2ab\det(\mathbf{S}^{(12)}) + b^2\det(\mathbf{S}^{(22)})}. \quad (18)\end{aligned}$$

Here, matrix element $\langle\Phi_1|\hat{\rho}^\sigma|\Phi_2\rangle$ is equal to $\langle\Phi_2|\hat{\rho}^\sigma|\Phi_1\rangle$ for real orbitals, as can be easily shown. Similar to Eqs. (16) and (17), the normalized total and spin densities are calculated as the sum and difference, respectively, of the σ -density components,

$$\rho^{\text{tot}}(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}), \quad (19)$$

$$\rho^{\alpha-\beta}(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}). \quad (20)$$

Although the above-described model is, in principle, an extension of the electron-transfer FDE (FDE-ET) method introduced previously (see Refs. [30, 34–36]), the possibility to calculate the total electronic density, which is not affected by the overdelocalization issue, makes this approach more general. Note also that similar techniques of constructing quasi-diabatic states were applied to describe S_N2 reactions [51] and proton-transfer processes [52] within the framework of the empirical valence bond (EVB) approach [53]. For these reasons, we suggest the new acronym “FDE-diab” for this class of methods based on the idea of quasi-diabatic states.

The resulting densities calculated with FDE-diab, in general, differ from ones obtained for subsystems with FDE. In particular, the (diagonal) densities $\rho_{(nn)}^{\text{tot}}(\mathbf{r})$ obtained in Eq. (16) are different from the densities that yield the lowest total electronic energy in the preceding FDE calculations. Because of this, one might argue that the densities obtained directly from FDE should be used. However, this would introduce an inconsistency with

the transition densities used for the off-diagonal elements. Using the density from a combined Slater determinant of (non-orthogonal) subsystem orbitals introduces another (slight) approximation, but ensures technical consistency in the setup of the Hamiltonian matrix. Hence, we use the formal mathematical expressions derived above without further approximations introduced. We will show in the following that densities calculated with FDE-diab can be of a better quality than those from FDE and allow one to avoid the spin-density overdelocalization problem of KS-DFT. These results are also encouraging for further calculations of energies and properties using the FDE-diab densities.

2.2 Generalized eigenvalue problem

The last ingredients for calculations of spin densities are sets of a and b coefficients [see Eqs. (2) and (18)]. Two fundamentally different approaches could be applied to find them. If the reference spin density was known, these coefficients could, in principle, be calculated using a fitting procedure. Minimizing the deviation between the reference results and the model density, one could obtain the optimal values of a and b for predefined matrix elements $\rho_{(nm)}^\sigma(\mathbf{r})$. A second approach is based on energetic criteria rather than the density. In this case, one should solve the generalized eigenvalue problem:

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c}, \quad (21)$$

where $\mathbf{S}$ is the overlap matrix, $\mathbf{H}$ is a matrix of the molecular Hamiltonian, and $\mathbf{c}$ is a vector of the coefficients a and b . The resulting coefficients (according to the variational principle) would represent values providing the lowest energy for the total wavefunction density. Although, this density is not the optimal one, the method has an important advantage, as it does not require the reference. In the following, we focus our attention on the second approach.

In case of our two-state model, Hamiltonian and overlap matrices are 2×2 matrices,

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} \quad (22)$$

and

$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{12} & S_{22} \end{pmatrix}. \quad (23)$$

The elements of the overlap matrix S_{nm} were introduced previously in Eq. (8). Elements H_{nm} could, in principle, be calculated using an approach similar to Eq. (9) after deriving matrix elements of two-electron operators in the basis of our diabatic-state determinants. An alternative that has successfully been used in the context of FDE-diab calculations before is to calculate these elements from the corresponding scaled (transition) densities [39, 54],

$$H_{nm} = \langle \Phi_n | \hat{H} | \Phi_m \rangle \approx E \left[\frac{\rho_{nm}^{\text{tot}}(\mathbf{r})}{S_{nm}} \right] S_{nm}. \quad (24)$$

Note that computing off-diagonal elements in this way is an approximation, that is pragmatically motivated to get consistent DFT-type results for all elements of the Hamiltonian matrix. For further details, we refer the reader to Ref. [34]. Eigenvalues and eigenvectors can then be obtained from the determinant,

$$\det(\mathbf{H} - E\mathbf{S}) = \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0, \quad (25)$$

and Eq. (21). The eigenvector components a and b corresponding to the lowest eigenvalue give us access to the spin density. This approach will be denoted as FDE-diab/eig in the following. For the case of fitted coefficients, the abbreviation FDE-diab/fit is used.

In practical calculations, an additional simplification is often introduced. Thus, if we assume the elements S_{11} and S_{22} as being equal to one, simple analytical expressions for ΔE and the corresponding couplings can be obtained (see for example Ref. [34]). Although this condition is not satisfied in general ($S_{11} \neq S_{22} \neq 1$), the problem is usually

avoided by dividing S_{12} by the value of $\sqrt{S_{11}S_{22}}$. Then, assuming that $S_{11} = S_{22}$ and omitting the term S_{nn} at the right-hand side of Eq. (24) for diagonal elements, we write

$$\det(\mathbf{H} - E\mathbf{S}) = \begin{vmatrix} H'_{11} - E & H_{12} - ES'_{12} \\ H_{12} - ES'_{12} & H'_{22} - E \end{vmatrix} = 0. \quad (26)$$

Usually both approaches for solving the eigenvalue problem lead to very similar results. In the following, we do not introduce an approximation and use Eqs. (24) and (25).

We should note that the FDE-diab method, being directly applied to multiple fragments/states, is computationally more expensive than standard KS-DFT. However, different techniques can be thought of to make it more efficient for larger molecular systems. For example, the so-called disjoint approximation for computing transition densities drastically decreases the computational cost of FDE-ET [34] and could similarly also be incorporated into FDE-diab. Also, automatic selection algorithms for choosing only relevant states (based on the values of electronic couplings) to be included into the Hamiltonian matrix could be developed. With such techniques used, FDE-diab can be more efficient than conventional KS-DFT for large systems.

3 Computational details

In this pilot study, we apply the FDE-diab approach to the following systems (see Fig. 1): i) a $\text{Be}^+ \cdots \text{H}_2$ electrostatic complex, ii) a $[\text{CH}_3\text{Cl} \cdots \text{CH}_3\text{F}]^{+\bullet}$ radical cation, iii) a guanine–thymine ($\text{GT}^{+\bullet}$) base-pair radical cation, and iv) a toluene dimer $[(\text{Tol})_2]^{+\bullet}$ radical cation. Cartesian coordinates for the $\text{Be}^+ \cdots \text{H}_2$ equilibrium structure and the structure of the GT pair were taken without further geometry optimization from Ref. [55] and the SI of Ref. [56], respectively. The structure of neutral $(\text{Tol})_2$ was optimized using ADF [57] with the B3LYP [58–60] XC functional and the TZP basis set from the ADF basis-set library. The D3 dispersion correction with Becke–Johnson damping [61] was applied. During

structure optimization, the $\mathcal{C}_{2h}$ point group symmetry was imposed. The same strategy was used for the separate monomers of $[\text{CH}_3\text{Cl}\cdots\text{CH}_3\text{F}]$. Then, the optimized molecules were placed at a distance of 3.0 Å between the Cl and C atom of CH_3F . The molecular point group $\mathcal{C}_{3v}$ was lowered to $\mathcal{C}_1$ by rotation around the C–Cl $\cdots$ C–F axis by about 20 degrees.

Figure 1: Molecular geometry of a) the $\text{Be}^+\cdots\text{H}_2$ complex, b) $[\text{CH}_3\text{Cl}\cdots\text{CH}_3\text{F}]^{+\bullet}$, c) the $\text{GT}^{+\bullet}$ pair, and d) the $(\text{Tol})_2$ dimer.

Reference single-point calculations of spin densities were carried out with unrestricted open-shell KS-DFT and with wavefunction theory-based (WFT) approaches such as full configuration interaction (FCI), CASSCF [62, 63], restricted active space self-consistent field (RASSCF) [64], and a variant of OO-MP2 including the resolution-of-the-identity approximation (OO-RI-MP2) [65]. In case of DFT methods, several XC functionals were tested. PW91 [66] was applied as a member of the generalized-gradient-approximation

(GGA) family of functionals. Functionals with different amount of exact exchange, such as hybrid B3LYP and BHandHLYP, the meta-hybrid M06-HF [67, 68], and a version of B3LYP with Yukawa-type range-separation (CAMY-B3LYP) [69] were tested. FCI, CASSCF, and RASSCF calculations were carried out with MOLCAS 8.1 [70]. In case of FCI, Dunning’s polarized triple- ζ correlation-consistent cc-pVTZ [71] basis set was used, while for CASSCF and RASSCF its double- ζ variant cc-pVDZ was applied. In case of CASSCF calculations for $[\text{CH}_3\text{F}\cdots\text{CH}_3\text{Cl}]^{+\bullet}$, $\text{GT}^{+\bullet}$, and $(\text{Tol})_2^{+\bullet}$, we correlated 11 electrons in 12 orbitals [CASSCF(11,12)]. The choice of the active space size in RASSCF calculations [applied to $\text{GT}^{+\bullet}$ and $(\text{Tol})_2^{+\bullet}$] is similar to the one from Ref. [22]. Only 4 MOs around the HOMO–LUMO gap are included into the RAS2 space. The active space size is increased due to larger number of orbitals in RAS1 and RAS2. The maximum number of electrons in RAS3 as well as number of holes in RAS1 are set to 2. Notations by Sauri *et al.* [72] are used throughout the paper. There, $\text{RASSCF}(n,l,m;i,j,k)$ is used to denote the number of electrons n in the active space, number of holes l and electrons m in the RAS1 and RAS3 subspaces, respectively. The indices i , j , and k stand for the number of orbitals in RAS1, RAS2, and RAS3, respectively. According to this notation, RASSCF calculations applied in this work could be denoted as $\text{RASSCF}(n,2,2;i,4,i)$ with i equal to 11 in case of $(\text{Tol})_2^{+\bullet}$ and 13 for $\text{GT}^{+\bullet}$. Guess orbitals for CASSCF/RASSCF calculations were generated using restricted Hartree–Fock (RHF) applied to the corresponding closed-shell systems. OO-RI-MP2 calculations are carried out with ORCA [73] using a cc-pVTZ basis set.

The FDE-diab calculations employed a development version of ADF using a locally modified scripting framework of PYADF [74]. To calculate spin densities, we applied the following procedure: First, two localized charge/spin states of the complexes, $D^{+\bullet} + A$ and $D + A^{+\bullet}$, were calculated with FDE to generate MOs of the diabatic states. FDE-MOs were calculated with the LDA, BP86 [75, 76], and PW91 [66, 77] XC functionals with the corresponding conjoint [78] kinetic-energy functionals (Thomas–Fermi [79, 80],

LLP91 [78], and PW91k [81], respectively) and the TZP basis set from the ADF library. Then, occupied MOs were evaluated at grid points of uniform and Becke [82,83] (for accurate integration) grids. For that, a modified version of the DENSF program from the ADF suite was used. The ADF implementation of the FDE-diab method (see Refs. [30, 34]) was applied to calculate the elements of overlap and Hamiltonian matrices according to Eqs. (8) and (24). The coefficients a and b were obtained by solving the generalized eigenvalue problem as described in Sec. 2.2. Finally, the values of the normalized spin density were calculated on grid points from the corresponding MOs. Calculations of reference spin-density values on grid points were performed with MULTIWFN program [84] to compare these results with those from FCI, CASSCF, and RASSCF.

In addition to spin-density isoplots, a quantitative measure for the spin-density delocalization was introduced. For that purpose, an in-house code was used to generate accurate atom-centered Becke grids [82,83] (of “Grid 4” quality), which define “atomic basins” for each studied molecular structure. Subsequently, an integration of the spin-density distributions and negative spin densities over atoms was conducted (for application of this Becke population analysis scheme, see Ref. [22]). The error of the numerical integration was lower than $5.0 \times 10^{-4} e$ in all cases, where e is the elementary charge.

4 Results

To calculate final spin-density distributions and assess the applicability of the FDE-diab method, we address a number of issues. First of all, we perform a numerical integration of the resulting spin density using accurate atom-centered grids to ensure integration to the right number of electrons present. Then, we assess the accuracy of different approximations applied in calculations of MOs (XC energy functionals and kinetic energy functionals), which are used in Slater determinants construction. For that, comparisons

with accurate reference spin-density distributions are carried out. Because the coefficients a and b [see Eq. (2)] can be obtained either from a density fit or by solving the eigenvalue problem in Eq. (21), we present results of both approaches. Finally, we present test applications of FDE-diab/eig for a number of model systems featuring different molecular sizes as well as different types of intermolecular interactions.

4.1 Reference spin densities

For our numerical tests, we consider a simple example of the electrostatic complex of the beryllium cation Be^+ (^2S) with a hydrogen molecule H_2 . This compound was studied in very detail in a number of previous works including theoretical [55, 85–87] as well as experimental [88] investigations. Thus, it is well known that the complex is formed due to weak ($D_e \approx 3200 \text{ cm}^{-1}$) long-range electrostatic and induction interactions leading to a T-shaped molecular structure ($\mathcal{C}_{2v}$ symmetry). The ground 2A_1 electronic state features an avoided crossing with the first excited state at a distance of $R \approx 1.2 \text{ \AA}$ between Be^+ and the H_2 center-of-mass [55]. These states are well separated at larger bond distances (already for the equilibrium structure, with $R_e = 1.776 \text{ \AA}$), thus allowing a single-reference treatment of the ground electronic state. Due to a small molecular system size, accurate *ab initio* approaches can be applied for this complex. As was shown in our previous work, reliable calculations of spin densities do not require very large basis sets to be used [22]: The deviations between spin-density distributions calculated with cc-pVDZ and cc-pVTZ basis sets were one order of magnitude smaller than the ones introduced by approximate XC functionals. Hence, already triple- ζ basis sets are an appropriate choice for calculations of reference spin densities.

Results of spin-density calculations for the $\text{Be}^+ \cdots \text{H}_2$ complex are presented in Fig. 2. Here, we use FCI/cc-pVTZ results as a reference. As one can see, all calculations lead to very similar distributions. The spin density is mostly localized at the Be^+ cation with a

smaller contribution at H_2 . In case of KS-DFT calculations, we do not observe significant overdelocalization and all tested functionals perform well. Only a slightly larger amount of positive spin density at H_2 is predicted by KS-DFT than by FCI. The delocalization of spin density is somewhat larger for the M06-HF functional, which indicates that self-interaction is not a decisive factor in this case.

Figure 2: Spin-density isosurface plots (isovalue: ± 0.01 a.u.) for the $\text{Be}^+ \cdots \text{H}_2$ electrostatic complex. Blue and red color represent positive and negative spin polarization.

Isosurface plots, however, only provide limited information about the quality of different methods. To gain a better understanding of the results, we present values of the spin density at the line connecting the Be^+ nucleus with the center-of-mass of H_2 . The resulting curves are depicted in Fig. 3. The different behavior of FCI and KS-DFT methods at the Be^+ ion ($R = 0.0$ Å) [Fig. 3a)] is caused by the fact that the ADF package used for the latter employs Slater-type basis functions, which better reproduce the cusp-region. By contrast, the FCI calculations are carried out with Gaussian basis sets. In this re-

gion, spin polarization is positive. All KS-DFT calculations overestimate the value of the spin density in comparison to FCI. Increasing the amount of exact exchange, we obtain larger values of spin density. The best agreement with FCI is found for the case of the PW91 functional, while the largest deviation is produced by the M06-HF approximation. The values obtained with B3LYP and CAMY-B3LYP almost coincide. At larger distances [Fig. 3b)], negative spin polarization appears. As has been discussed previously (see Refs. [22, 26–30]), a larger amount of exact exchange typically leads to larger spin contamination, which goes hand-in-hand with increasing negative spin-density contributions. This can also be seen in our calculations (particularly at distances of about 0.4 Å). Increasing the amount of exact exchange in the sequence PW91 (0%), B3LYP (25%), M06-HF (100%), we also increase the areas below zero corresponding to negative spin density. However, results obtained with BHandHLYP (50%) do not show the same trend and the use of this functional leads to the largest negative spin polarization (also at the distance of about 1.2 Å). At these distances, the best agreement with FCI is found for the case of CAMY-B3LYP.

Finally, the average spin-density quality of different methods can be assessed in terms of a Becke population analysis. Integrated spin populations are presented in Tab. I. In agreement with the previous discussion, the largest degree of localization is found for the case of FCI, while KS-DFT leads to slightly delocalized (by about 2–5%) densities. The best averaged performance was obtained with the hybrid B3LYP, CAMY-B3LYP, and BHandHLYP functionals. PW91 and M06-HF show somewhat worse performance in comparison with other KS-DFT approximations (by 1% and 3%, respectively) in terms of spin-density delocalization. The amount of negative contribution to the spin density is smaller than 0.5% and depends on the exact exchange. The smallest negative contribution is calculated with PW91, while the largest is obtained using M06-HF.

Table I: Spin populations obtained by integration of the spin-density distributions over fragments (second column) and by separate integration of the negative and positive spin densities over entire complex (third column). Results are presented for $\text{Be}^+\cdots\text{H}_2$. All values are given in e .

Method	$\text{Be}^+\cdots\text{H}_2$	
	Be/ H_2	pos./neg.
FCI	0.79/0.21	1.003/ -0.003
PW91	0.76/0.24	1.002/ -0.002
B3LYP	0.77/0.23	1.003/ -0.003
CAMY-B3LYP	0.77/0.23	1.003/ -0.003
BHandHLYP	0.77/0.23	1.004/ -0.004
M06-HF	0.74/0.26	1.004/ -0.004

Figure 3: Spin-density values at the line connecting the Be^+ cation and the H_2 center-of-mass. The Be^+ ion is placed at the center of the Cartesian coordinate system, while the distance to the H_2 center-of-mass is measured along the Z -axis. Results are presented for a) the region close to the Be nucleus and b) the intermolecular region. The dashed grey horizontal line represents zero spin density.

4.2 Spin density from FDE-diab

Before proceeding to the actual calculations of the spin density, we ensure that the resulting distribution obtained with Eq. (20) is correctly normalized. For that purpose, we conduct a numerical integration of the spin density using atom-centered Becke grids (“verygood” quality in ADF). The deviation from the exact number of excess α -electrons was less than 1.0×10^{-8} . Thus, the spin density integrates to the right number. In the following, we always normalize densities analytically and numerical integration is applied in Becke population analysis only.

We now calculate the spin-density distribution of the $\text{Be}^+ \cdots \text{H}_2$ complex with FDE-diab. As described above, two different techniques can be used to find a and b coefficients. If reference results are available, these coefficients can be obtained by a fitting procedure minimizing deviations from the reference at each point of the grid or in some specific region (FDE-diab/fit). In this work, we present an example of such calculation using the FCI results as the reference. Values of the spin density on the line between Be^+ and center-of-mass of H_2 (as defined before) are used for the fit. Matrix elements of the density operator are calculated using the FDE(3)-diab/PW91/PW91k approximation. Here, the integer in parentheses stands for the number of freeze-and-thaw cycles applied. Increasing this number beyond 3 does not lead to significant changes in the spin-density distribution and indicates the convergence of our results. As a quality criterion for the fit, we calculate the root-mean-square deviation of the resulting spin-density values from FCI. Calculated spin densities are presented in Fig. 4, while the coefficients a and b are listed in Tab. II. The second approach for calculations of spin densities assumes that one should solve an eigenvalue problem (FDE-diab/eig). As a result, energies of two electronic states (eigenvalues) and two sets of a and b coefficients (defining eigenvectors) are found. To compare these results with FDE-diab/fit, we solve the eigenvalue problem described in Eq. (25) without any further approximations introduced. Results for the first (lowest-

energy) eigenvalue are presented in Tab. II and Fig. 4. As one can see from the values of a^2 , $2ab$, and b^2 , the calculated spin density is dominated by $\rho_{(11)}^{\alpha-\beta}(\mathbf{r})$ and the transition density term $\rho_{(12)}^{\alpha-\beta}(\mathbf{r})$. Both of them contribute to the resulting distribution with the highest weights and define the spin density to be localized mostly at the Be^+ cation. FDE-diab/fit leads to slightly more localized spin densities than FDE-diab/eig. The localization ratios from spin population analysis are 0.73/0.27 and 0.72/0.28 for FDE-diab/fit and FDE-diab/eig, respectively. Despite these minor differences, both approaches produce very similar spin densities and qualitatively reproduce the reference results. However, the amount of positive spin density at H_2 is overestimated in both cases and results from FDE-diab are worse by about 2–5% than all tested KS-DFT approximations (see Fig. 2 and Tab. I). But this has to be attributed to the good performance of KS-DFT approximations in this case, rather than to a bad performance of FDE-diab.

Figure 4: Spin-density isosurface plots (isovalue: ± 0.01 a.u.) for the $\text{Be}^+ \cdots \text{H}_2$ electrostatic complex. The PW91 and PW91k approximations were applied for XC and nonadditive kinetic energy, respectively. Blue color represents positive spin polarization.

We also studied the dependence of our results on the XC and kinetic-energy functionals used. For that purpose, calculations with the LDA/TF and BP86/LLP91 approximations were conducted. Results for a and b coefficients are collected in Tab. II, while the spin density on the line connecting the Be^+ cation and the H_2 center-of-mass are shown in

Table II: Linear combination coefficients obtained with the FDE-diab/fit and FDE-diab/eig approaches. Results for the lowest eigenvalue are presented. The absolute error of the fit is below 1.0×10^{-6} . The eigenvectors are normalized such that the condition $a^2 + b^2 = 1$ is fulfilled.

Approximation	a	b	a^2	$2ab$	b^2
FDE-diab/LDA/TF/eig	-0.996501	-0.083583	0.993014	0.166581	0.006986
FDE-diab/BP86/LLP91/eig	-0.996812	-0.079792	0.993633	0.159075	0.006367
FDE-diab/PW91/PW91k/eig	-0.996576	-0.082679	0.993164	0.164792	0.006836
FDE-diab/PW91/PW91k/fit	-0.998213	-0.059749	0.996430	0.119284	0.003570

Fig. 5. The dependence found was minor in all cases. Becke population analysis shows that 72% of spin density is localized at Be^+ independently of the kinetic-energy functional used.

Finally, because it was reported in Ref. [31] that FDE can describe the spin-polarization effects between two subsystems, we estimated its influence on the resulting spin densities by carrying out calculations for the closed-shell fragments in the FDE computations (Be in $|\text{Be}^+ \cdots \text{H}_2^+\rangle$ and H_2 in $|\text{Be}^+ \cdots \text{H}_2\rangle$) in restricted and unrestricted fashion [see Figs. 5a) and 5b), respectively]. The difference between these two approaches can be easily seen in the range of distances between about 0.4 and 1.4 Å. Restricted FDE calculations lead to larger deviations from the reference at shorter distances producing more localized spin densities and overestimating the positive spin polarization. At the same time, unrestricted calculations overestimate negative spin polarization closer to the H_2 center-of-mass. Also, the spin density contribution at H_2 is larger in this case. The errors are very similar in magnitude but differ in sign. For the particular case of the $\text{Be}^+ \cdots \text{H}_2$ electrostatic complex, restricted calculations lead to slightly better agreement with the reference FCI calculations, but results are still worse than from standard KS-DFT. Spin population

Figure 5: Spin-density values at the line connecting the Be^+ cation and the H_2 center-of-mass. The Be^+ ion is placed at the center of the Cartesian coordinate system, while the distance to the H_2 center-of-mass is measured along the Z -axis. Results are presented for the case of a) restricted FDE-diab/eig and b) unrestricted FDE-diab/eig treatment of the closed-shell fragments Be and H_2 .

analyses conducted for cases of restricted and unrestricted calculations lead to the same spin density localization of 72% with only small deviations below 1%. We re-iterate, however, that results from FDE-diab are qualitatively correct and deviations from the reference FCI results (according to spin population values) are only about 7%. Moreover, KS-DFT calculations show surprisingly good agreement with FCI for this example of the $\text{Be}^+ \cdots \text{H}_2$ complex (with errors about 2–5%). Hence, we now turn our attention to systems where KS-DFT spin densities are expected to severely suffer from overdelocalization.

4.3 Applications of FDE-diab

For all presented examples in this chapter, we apply the FDE(3)-diab/eig scheme with the PW91 XC and PW91k kinetic energy functional. The restricted and unrestricted treatments of the closed-shell fragments lead to very similar results for the spin density. Hence, the latter was applied for all presented results. Analytical normalization factors were used to avoid numerical integration over grid points. Setting the number of freeze-and-thaw cycles to 3 was found to be sufficient for the FDE calculations.

As our first example, we consider the $[\text{CH}_3\text{F}\cdots\text{CH}_3\text{Cl}]$ complex. According to experimental data, the difference between the ionization energies of CH_3Cl and CH_3F is about 1.2–1.7 eV (11.22–11.30 and 12.45–13.05 eV, respectively) [89]. Hence, removal of an electron should lead to the localization of the charge at CH_3Cl . Similar localization is expected for the spin-density distribution. The reference CASSCF(11,12) and OO-RI-MP2 calculations support this assumption. They lead to completely localized spin-density distributions (see Fig. 6 and Tab. III). Very similar spin densities are found when hybrid functionals with high percentages of exact exchange (BHandHLYP with 50% and M06-HF with 100%) are used. Also, FDE-diab leads to localized spin densities. The remaining functionals applied suffer from severe overdelocalization. The use of the PW91 functional leads to only 46% of spin density localized at CH_3F , thus producing an error of 54% with respect to the reference CASSCF results. Hybrid B3LYP and CAMY-B3LYP perform better with 79% and 94% of spin density localized at the CH_3F fragment. Thus, for this molecular system FDE-diab/PW91/PW91k outperforms GGA and hybrid functionals with small to medium amounts of exact exchange (less than $\sim 60\%$). The amount of negative spin density reaches 4% for BHandHLYP and below in other cases.

Our second example is a π -stacked GT base pair. The charge distribution of the corresponding radical cation $\text{GT}^{+\bullet}$ was investigated in several studies (for examples, see Refs. [31, 56]). Because guanine is the easier oxidized compound, the charge and spin-

Figure 6: Spin-density isosurface plots (isovalue: ± 0.001 a.u.) for the $[\text{CH}_3\text{F}\cdots\text{CH}_3\text{Cl}]^{+\bullet}$ complex. Blue and red color represent positive and negative spin polarization.

density distribution are mostly localized at the guanine moiety. *Ab initio* calculations conducted with CASSCF in Ref. [31] reproduce these results. In the same work, it was demonstrated that GGA functionals predict delocalization of spin-density distribution over both molecules of the base pair. This effect can be considerably decreased applying hybrid functionals. However, only M06-HF with 100% of exact-exchange leads to an almost complete localization of the spin density at the guanine molecule. This behavior of KS-DFT approximations was explained by the SIE, which leads to unphysical

Table III: Spin populations obtained by integration of the spin-density distributions over fragments and by separate integration of the negative and positive spin densities over entire complex. Results are presented for the $[\text{CH}_3\text{Cl}\cdots\text{CH}_3\text{F}]^{+\bullet}$, $\text{GT}^{+\bullet}$, and $(\text{Tol})_2^{+\bullet}$ radical cations. All values are given in e .

Method	$[\text{CH}_3\text{Cl}\cdots\text{CH}_3\text{F}]^{+\bullet}$		$\text{GT}^{+\bullet}$		$(\text{Tol})_2^{+\bullet}$	
	$\text{CH}_3\text{Cl}/\text{CH}_3\text{F}$	pos./neg.	G/T	pos./neg.	Tol / Tol	pos./neg.
RASSCF	—	—	0.98/0.02	1.05/−0.05	0.97/0.03	1.02/−0.02
CASSCF	1.00/0.00	1.02/−0.02	0.98/0.02	1.11/−0.11	0.50/0.50	1.05/−0.05
PW91	0.46/0.54	1.02/−0.02	0.72/0.28	1.08/−0.08	0.50/0.50	1.05/−0.05
B3LYP	0.79/0.21	1.03/−0.03	0.82/0.18	1.14/−0.14	0.50/0.50	1.08/−0.08
CAMY-B3LYP	0.94/0.06	1.03/−0.03	0.94/0.06	1.18/−0.18	0.50/0.50	1.12/−0.12
BHandHLYP	1.00/0.00	1.04/−0.04	0.98/0.02	1.31/−0.31	0.50/0.50	1.19/−0.19
M06-HF	1.00/0.00	1.02/−0.02	0.98/0.02	1.23/−0.23	0.50/0.50	1.16/−0.16
FDE-diab	1.00/0.00	1.02/−0.02	0.98/0.02	1.08/−0.08	0.50/0.50	1.05/−0.05

delocalization. Our CASSCF(11,12) calculations are in a good agreement with the ones in Ref. [31] (see Fig. 7 and Tab. III) and predict that 98% of spin density is localized at guanine. OO-RI-MP2 calculations predict that some small amount of spin density is actually localized on the thymine molecule. This might be a consequence of dynamic correlation, which is partially included in the MP2 calculation, while it is not taken into account in CASSCF calculations (with small active space sizes). It was also shown in our previous work [22] that it is difficult to converge the spin-density distribution with respect to the active space size of CASSCF/RASSCF and DMRG calculations (especially in case of asymmetrical structures). Thus, correlation of 11 electrons on 12 orbitals cannot guarantee convergence of the resulting spin densities. However, further increase of the active space size with RASSCF up to RASSCF(29,2,2;13,4,13) did not produce a larger amount

of spin density at the thymine molecule. The results obtained with KS-DFT are similar to the ones reported in Ref. [31]. The functionals tested here lead to larger spin-density delocalization than both CASSCF and OO-RI-MP2, except for BHandHLYP and M06-HF. Results from CAMY-B3LYP are somewhat worse with slightly delocalized spin densities (94% of localization). PW91 and B3LYP show 72% and 82% of localization, respectively. The degree of localization found in case of FDE-diab is very similar to the results from CASSCF and RASSCF. The amount of negative spin density is growing in a sequence of PW91, B3LYP, CAMY-B3LYP, BHandHLYP and reaching 31%. A somewhat lower value of 23% was calculated with M06-HF. It should be noted that FDE-diab reproduces the spin density localization found with CASSCF and RASSCF with the amount of negative spin density also being very similar as in the reference results (with a deviation of 3%).

Our final example is the symmetric dimer $(\text{Tol})_2$, consisting of the two π -stacked toluene molecules. Both molecules have the same ionization energy of about 8.8–9.0 eV [89] and are not separated to very large distance from each other. Thus, the spin density should be symmetrically delocalized over both molecules. As one can see from Fig. 8 and Tab. III, all calculations are in a good agreement with our expectations except RASSCF(25,2,2;11,4,11). In the latter case, the spin density is almost completely localized on one molecule (97%). By contrast, CASSCF(11,12) featuring the larger RAS2 MO space produces correct results. This clearly indicates that $(\text{Tol})_2^{+\bullet}$ cannot be described with only 4 MOs incorporated to the RAS2 space. All KS-DFT calculations lead to qualitatively correct spin-density distributions, similar to the ones from CASSCF(11,12) and OO-RI-MP2, since in this case a full delocalization is actually the correct result. The only difference is the amount of negative spin density, which correlates with the amount of exact exchange used. It grows in the sequence of PW91, B3LYP, CAMY-B3LYP, BHandHLYP from 5 to 19 %. The only exception in this row is M06-HF, which produces a smaller amount of the negative spin density than BHandHLYP. The latter, however, is still large compared to the other functionals. Again, this is consistent with previously

Figure 7: Spin-density isosurface plots (isovalue: ± 0.001 a.u.) for the $\text{GT}^{+\bullet}$ base pair. Blue and red color represent positive and negative spin polarization.

reported observations [22, 26–30] (see also Sec. 4.1). FDE-diab reproduces qualitatively correct distributions with results very similar to OO-RI-MP2.

Figure 8: Spin-density isosurface plots (isovalue: ± 0.001 a.u.) for the $(\text{Tol})_2^{+\bullet}$ dimer. Blue and red color represent positive and negative spin polarization.

5 Future perspectives

The results presented in the previous chapters are encouraging for further applications of FDE-diab following our initial motivation, i.e., in calculations on the photosynthetic reaction center of PSII. These calculations might shed some light on the anomalous spin-density distributions measured for the chlorophyll *a* molecule in the photo-CIDNP NMR experiments [37, 90] as well as on the nature of the primary electron donor and origin of its high RedOx potential. However, already the simplest hinge model [37] is a more complicated case for the spin-density calculations than all examples considered in this work. Moreover, description of the reaction center will also require a consideration of the surrounding protein and different protonation states of amino acids. Although such calculations are possible with FDE, where (at least the nearby part of) the protein environment is considered explicitly, it might be problematic for the two-states model. It is not always clear which two subsystems should be defined for the construction of Slater determinants in FDE-diab. In approximate calculations, these subsystems can, in principle, be determined as the ones with the largest electronic couplings. However, if the spin-density is strongly delocalized over multiple molecular fragments, this approximate approach may lead to qualitatively wrong results. The issue can be solved by generalization of FDE-diab to N electronic states. Such a generalization is trivial from the theoretical point of view, but requires an efficient implementation of FDE-diab, where expensive operations on grid points are avoided. Developments along those lines are planned for our future work.

We should also note here that FDE-diab is not restricted to the cases described by Eq. (1), but can be applied to a broader range of open-shell molecular systems featuring non-covalent interactions. For anionic radical systems, however, the dependence on the basis set size can be more pronounced. Another point to be discussed is the dependence of the spin-density distributions on the initial sets of MOs. It has been demonstrated above that FDE calculations with different XC and kinetic-energy functionals lead to very similar

results. However, using the FDE method is not the only possibility for the construction of spin/charge-localized states. Different methods (as for example constrained DFT [46]) can be applied for these purposes. To address these issues, benchmark calculations for larger sets of test systems should be conducted.

6 Conclusions

In this work, for the first time the model of two spin-(and charge-)localized states was applied for calculations of spin-density distributions. A similar methodology has only been used before to find energies and couplings for the corresponding charge-transfer reactions [30, 34–36], where a basis of two quasi-diabatic states has been found to be sufficient for accurate calculations, and for the calculation of free energy profiles of S_N2 [51] and proton-transfer reactions [52]. We have shown that this model can also be applied to obtain qualitatively correct spin densities. We reconsidered the underlying theory of this method and constructed the α - and β -densities as the expectation values of the total wavefunction. This gave us an access to further calculations of the total- and spin-density distributions. Using the FDE methodology for calculations of initial MOs allowed us to avoid the overdelocalization problem characteristical for non-hybrid KS-DFT approximations. Spin densities were calculated for a set of complexes featuring different molecular sizes as well as different types of intermolecular interactions. Subsequently, they were compared to accurate *ab initio* results. The FDE-diab method with GGA XC functionals outperformed all standard non-hybrid DFT functionals and functionals with small or moderate amount of exact exchange (less than about 60%) in all cases where considerable overdelocalization of the spin densities occurred in the KS case. Moreover, for the case of the $GT^{+\bullet}$ base pair it also produces better results than M06-HF, which otherwise leads to good spin densities. We would also like to note that curing the delocalization problem through exact-exchange admixture usually makes the spin-contamination problem

worse [22, 26–30], and is computationally less efficient than the use of (semi-) local functionals. The latter is easily possible with FDE-diab. Being based on FDE, the FDE-diab methodology has the same limitations such as inability to cut through covalent bonds and to describe strong interactions (unless special projection [91, 92] or potential reconstruction techniques [93–96] are used). At the same time, it is a very efficient subsystem method, which can easily be extended to the case of N molecular systems and applied to calculations of total electronic densities. The latter can, in principle, provide an access to calculations of EPR parameters unaffected by intermolecular charge overdelocalization effects.

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