Spin in Density-Functional Theory

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The accurate description of open-shell molecules, in particular of transition metal complexes and clusters, is still an important challenge for quantum chemistry. Although density-functional theory (DFT) is widely applied in this area, the sometimes severe limitations of its currently available approximate realizations often preclude its application as a predictive theory. Here, we review the foundations of DFT applied to open-shell systems, both within the nonrelativistic and the relativistic framework. In particular, we provide an in-depth discussion of the exact theory, with a focus on the role of the spin density and possibilities for targeting specific spin states. It turns out that different options exist for setting up Kohn–Sham DFT schemes for open-shell systems, which imply different definitions of the exchange–correlation energy functional and lead to different exact conditions on this functional. Finally, we suggest possible directions for future developments. © 2012 Wiley Periodicals, Inc.

Introduction

Open-shell molecules such as, for example, radicals or transition metal complexes and clusters, feature a measurable magnetic moment that originates from their electronic structure. In fact, the electronic spin gives rise to a magnetic moment that makes such molecular systems functional for various purposes. For instance, organic radicals can be used as spin probes in biomolecules[1] and are of interest as building blocks for molecular spintronics devices,[2,3] single-molecule magnets have the potential to act as molecular qubits for quantum information processing,[4] and open-shell transition metal compounds serve as catalytic centers in (bio-)inorganic chemistry,[5–8] where a change in the spin state can be an essential step in the catalytic cycle.[9]

Consequently, a first-principles theory that is useful for descriptive and analytic purposes and that has the potential to be a predictive tool in theoretical studies on such chemical systems must consider the spin properties of the electronic structure. Although for closed-shell systems, quantum chemical methods—both wavefunction theory for accurate calculations on small molecules[10] and density-functional theory (DFT) for studies on complex chemical systems[11]—offer such predictive tools, the situation is less satisfactory for open-shell systems, in particular for transition metal complexes and clusters.[12]

With wavefunction-based methods, a multireference treatment is in general mandatory for open-shell systems. In particular, the complete active space self-consistent field method, usually in combination with second-order perturbation theory (CASPT2), has been employed to study transition metal complexes (for examples, see Refs. [13–18]). However, the factorial scaling with the size of the active space puts rather severe limits on the size of the active space, which prevents most applications to polynuclear transition metal complexes and clusters. Novel approaches, such as the density matrix renormalization group algorithm[19,20] and its generalizations[21] might make it possible to overcome this limitation, although the molecular sizes that can be studied are clearly much smaller compared to those accessible to DFT methods.

Therefore, DFT is usually the method of choice in theoretical studies of transition-metal catalysis as well as molecular and spectroscopic properties of open-shell molecular systems.[22–25] Despite much success, it has also become clear that for open-shell systems, DFT with the currently available approximate functionals shows a number of shortcomings. In addition to inaccuracies in predicting energies, geometries, and molecular properties (for a case study, see, e.g., Ref. [26] and for overviews, see, e.g., Refs. [11,27,28]), a severe limitation are unsystematic errors in the prediction of the relative energies of different spin states.[29–36] Moreover, the spin density—which serves as an additional fundamental quantity in the spin-DFT formalism commonly employed for open-shell systems—is qualitatively incorrect in some cases.[15,37–39] To make things even worse, the treatment of low-spin states usually requires the use of a broken-symmetry description,[40–43] which provides an unphysical spin density by construction (see, e.g., Refs. [24,44] for a discussion). This precludes the simple prediction of spectroscopic properties depending on the spin density (for schemes to address this difficulty, see e.g., Refs. [45–48]).

Consequently, the development of better approximate DFT methods for open-shell systems is currently still one of the most important and challenging topics in theoretical chemistry.[12,28,49] To make progress is this area, it is important to understand the exact theory underlying DFT for open-shell systems. Although for the closed-shell case, exhaustive

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presentations of this theory exists in several textbooks,[50–53] this is not the case for open-shell systems, which are often only mentioned in passing in these accounts. Here, we attempt to close this gap by reviewing the foundations of DFT for open-shell systems. In our presentation, we will pay particular attention to the role of the spin-density in DFT and to possibilities for targeting different spin states within the exact theory.

Even though we will not discuss the currently available approximations in detail, we believe that for the future development of better approximations, it is crucial to know which exact theory is to be approximated. This is also a prerequisite for deriving exact conditions on the approximate functionals, for setting up model systems that can be treated exactly, and for obtaining benchmark results from accurate wave-function theory calculations.

This work is organized as follows. First, we introduce spin in the context of nonrelativistic quantum chemistry. This is followed by a discussion of Hohenberg–Kohn (HK) DFT, highlighting the role of the spin density and of spin states for open-shell systems. Next, the treatment of spin in the Kohn–Sham (KS) framework of DFT is reviewed. It turns out that different options exist for deriving KS-DFT for open-shell systems, which are discussed and compared in detail. For completeness, we then discuss DFT within the relativistic framework where spin is no longer a good quantum number. Finally, some possible future directions for DFT applied to open-shell systems are outlined.

Spin in Nonrelativistic Quantum Chemistry

Spin structure of the one-electron wavefunction

The nonrelativistic quantum-mechanical equation of motion for a single electron in an external electrostatic potential $v_{\text{ext}}(\boldsymbol{r})$ is provided by the time-dependent Schrödinger equation (SE), which in Gaussian units reads,

$$\hat{h}\,\psi(\boldsymbol{r},t) = \left[\hat{T} + q_e\,v_{\text{ext}}(\boldsymbol{r})\right]\psi(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t), \quad (1)$$

with the kinetic energy operator $\hat{T} = \frac{\hat{\boldsymbol{p}}^2}{2m_e} = -\frac{\hbar^2}{2m_e}\Delta$, where $\hat{\boldsymbol{p}} = -i\hbar\nabla$ is the momentum operator and m_e and q_e are the mass and the charge of the electron, respectively. Stationary states can then be obtained from the time-independent Schrödinger equation,

$$\hat{h}\,\psi(\boldsymbol{r}) = \left[\hat{T} + q_e\,v_{\text{ext}}(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\,\psi(\boldsymbol{r}). \quad (2)$$

In a nonrelativistic framework, spin is introduced in an *ad hoc* fashion by using a two-component representation for the wavefunction,[54,55] i.e.,

$$\psi(\boldsymbol{r}) = \begin{pmatrix} \psi_\alpha(\boldsymbol{r}) \\ \psi_\beta(\boldsymbol{r}) \end{pmatrix}. \quad (3)$$

For a rigorous introduction of spin in quantum chemistry, it is necessary to start from relativistic quantum mechanics, where spin is naturally included in the Dirac equation. This will be discussed later on in "Spin in Relativistic DFT".

In the nonrelativistic two-component picture, spin-independent operators—such as the one-electron Hamiltonian $\hat{h}$ in Eqs. (1) and (2)—act on both of these components, that is, they are proportional to the 2×2 unit matrix $\mathbf{1}_2$. The two-component structure of the wavefunction is only probed by operators expressed in terms of the Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (4)$$

In particular, the operator corresponding to the electron spin is

$$\hat{\mathbf{s}} = \frac{\hbar}{2}\boldsymbol{\sigma} = \frac{\hbar}{2}\left(\sigma_x, \sigma_y, \sigma_z\right)^T \qquad (5)$$

The three components of this spin operator fulfill the same commutation relations as those of the angular momentum operator $\hat{\mathbf{l}}$, i.e.,

$$[\hat{s}_x, \hat{s}_y] = i\hbar \hat{s}_z, \quad [\hat{s}_y, \hat{s}_z] = i\hbar \hat{s}_x, \quad [\hat{s}_x, \hat{s}_z] = i\hbar \hat{s}_y, \qquad (6)$$

which is the basis for considering spin as an intrinsic angular momentum vector $\hat{\mathbf{s}}$. For the squared magnitude of the electron spin, one obtains the diagonal operator

$$\hat{\mathbf{s}}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \frac{3}{4}\hbar^2 \mathbf{1}_2 \qquad (7)$$

and as for the angular momentum, this operator commutes with each component of the spin (i.e., $[\hat{\mathbf{s}}^2, \hat{s}_\alpha] = 0$ for $\alpha = x, y, z$).

In nonrelativistic quantum mechanics, one postulates that the spin operator $\hat{\mathbf{s}}$ is related to an intrinsic magnetic moment of the electron.[54–57] This spin magnetic moment is described by the operator

$$\hat{\boldsymbol{\mu}}_s = -\frac{2\mu_B}{\hbar}\hat{\mathbf{s}} = -\mu_B\,\boldsymbol{\sigma}, \qquad (8)$$

where $\mu_B = \frac{|q_e|\hbar}{2m_e c}$ is the Bohr magneton, c is the speed of light in vacuum, and the factor two is the electron g-factor when neglecting quantum electrodynamical effects.

Instead of explicitly writing two-component wavefunctions and 2×2 matrix operators, in quantum chemistry it is common to use a different notation, which will turn out to be particularly convenient for handling many-electron systems. Namely, as a shorthand notation, one introduces the orthonormal spin functions $\alpha(s)$ and $\beta(s)$, which depend on a spin variable s.[54,56,58] This spin variable can only assume the values $+\frac{1}{2}$ and $-\frac{1}{2}$, and the spin functions are defined such that

$$\alpha\left(+\tfrac{1}{2}\right) = 1 \quad \text{and} \quad \alpha\left(-\tfrac{1}{2}\right) = 0, \qquad (9)$$
$$\beta\left(+\tfrac{1}{2}\right) = 0 \quad \text{and} \quad \beta\left(-\tfrac{1}{2}\right) = 1. \qquad (10)$$

Then, the wavefunction of Eq. (3) can be expressed as

$$\psi(\mathbf{r}, s) = \psi_\alpha(\mathbf{r})\alpha(s) + \psi_\beta(\mathbf{r})\beta(s), \qquad (11)$$

with the first component given by $\psi(\mathbf{r}, +\frac{1}{2}) = \psi_\alpha(\mathbf{r})$ and the second component given by $\psi(\mathbf{r}, -\frac{1}{2}) = \psi_\beta(\mathbf{r})$. It is important to realize that the spin functions α and β are merely a way of expressing two-component wavefunctions, in which the spin variable s has the role of labeling the different components. Spin-independent operators are then given by a one-component operator acting only on the parts of the wavefunction that depend on the spatial coordinate $\mathbf{r}$, while the spin operators $\hat{s}_x$, $\hat{s}_y$, $\hat{s}_z$, and $\hat{\mathbf{s}}^2$ act only on the parts depending on the spin variable s.

The nonrelativistic one-electron Hamiltonian $\hat{h}$ is spin-independent and hence commutes with all spin operators, in particular $[\hat{h}, \hat{s}_z] = [\hat{h}, \hat{\mathbf{s}}^2] = 0$. Therefore, its eigenfunctions can be chosen as eigenfunctions of $\hat{\mathbf{s}}^2$ and of $\hat{s}_z$. The eigenfunctions of $\hat{s}_z$ are given by $\alpha(s)$ and $\beta(s)$ and the wavefunctions of an electron which are also eigenfunctions of $\hat{s}_z$ are thus of the form

$$\psi(\mathbf{r}, s) = \psi(\mathbf{r})\alpha(s) \quad \text{or} \quad \psi(\mathbf{r}, s) = \psi(\mathbf{r})\beta(s). \qquad (12)$$

For any spatial part of the wavefunction, these two different total wavefunctions are possible, that is, each eigenvalue of the nonrelativistic one-electron Hamiltonian is twofold degenerate. The first is identified with an α- or "spin-up" electron ($s_z = +\hbar/2$), whereas the second one corresponds to a β- or "spin-down" electron ($s_z = -\hbar/2$). Of course, also linear combinations of these two degenerate eigenfunctions are solutions of the Schrödinger equation. Nevertheless, for a single electron any eigenfunction can be expressed as a product of a spatial part and a spin part.

Spin structure of the many-electron wavefunction

Within the two-component picture introduced in the previous section, the one-electron Hilbert space $^1\mathcal{H}$ is spanned by all admissible one-electron wavefunctions (which have two components related to the spin of the electron). For an N-electron system, the wavefunction is an element of the corresponding N-electron Hilbert space $^N\mathcal{H}$, which is the tensor product space of the Hilbert spaces of each electron, i.e.,

$$^N\mathcal{H} = {}^1\mathcal{H}(1) \otimes {}^1\mathcal{H}(2) \otimes \ldots \otimes {}^1\mathcal{H}(N), \qquad (13)$$

where the number given in parentheses designates the corresponding electron. As the one-particle wavefunctions have two components, the N-electron wavefunctions have 2^N-components and operators have the dimension $2^N \times 2^N$. For a more detailed discussion of the tensor structure of the many-electron wavefunction, see for example, Refs. [19–21] and chapter 8.4 in Ref. [57].

As an alternative to explicitly handling many-component wavefunctions, it is again convenient to introduce spin coordinates s_i that can be used to distinguish the different components.[56,59,60] Then, the N-electron wavefunction depends on N spin coordinates in addition to the N spatial coordinates,

$$\Psi = \Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_N, s_N) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \qquad (14)$$

where $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ denotes the combination of spatial and spin coordinates. Each spin coordinate can assume the values $-1/2$ and $+1/2$. Each possible combination of values for these spin variables corresponds to one component of the many-electron wavefunction. In total, 2^N different combinations of values are possible, that are thus used to label the 2^N components of the many-electron wavefunction.

The nonrelativistic Hamiltonian describing N electrons in an external electrostatic potential $v_{ext}(\boldsymbol{r})$ is (in Gaussian units) given by,

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_e}\Delta_i + q_e\, v_{ext}(\boldsymbol{r}_i)\right] + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{q_e^2}{r_{ij}}, \quad (15)$$

where the Laplace operator Δ_i acts on the coordinate of the ith electron and $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the distance between electrons i and j. This Hamiltonian does not contain any spin-dependent terms and only acts on the spatial coordinates.

The operator of the total spin $\hat{\boldsymbol{S}}$ of a many-electron system is obtained[58,56] by summing the spins of the individual electrons $\hat{\boldsymbol{S}} = \sum_{1=1}^{N}\hat{\boldsymbol{s}}(s_i)$. In particular, one has for the z-component of the total spin operator,

$$\hat{S}_z = \sum_{i=1}^{N}\hat{s}_z(s_i), \quad (16)$$

and for the square of the total spin

$$\hat{\boldsymbol{S}}^2 = \sum_{i=1}^{N}\sum_{j=1}^{N}\hat{\boldsymbol{s}}(s_i)\cdot\hat{\boldsymbol{s}}(s_j) = \frac{3}{4}N\hbar^2 + 2\sum_{i=1}^{N}\sum_{j=i+1}^{N}\hat{\boldsymbol{s}}(s_i)\cdot\hat{\boldsymbol{s}}(s_j), \quad (17)$$

where the first term emerges because any many-electron wavefunction is an eigenfunction of $\hat{\boldsymbol{s}}^2(s_i)$ with eigenvalue $(3/4)\hbar^2$ (i.e., electrons are spin-1/2 particles). Note that $\hat{\boldsymbol{S}}^2$ couples different electrons, that is, it is a two-electron operator.[61]

Both $\hat{\boldsymbol{S}}^2$ and $\hat{S}_z$ commute with the Hamiltonian of Eq. (15) and with each other, i.e.,

$$[\hat{H},\hat{\boldsymbol{S}}^2] = [\hat{H},\hat{S}_z] = [\hat{\boldsymbol{S}}^2,\hat{S}_z] = 0. \quad (18)$$

Therefore, the eigenfunctions Ψ of the Hamiltonian can always be chosen as eigenfunctions of $\hat{S}_z$ and $\hat{S}^2$ with,

$$\hat{\boldsymbol{S}}^2\Psi = S(S+1)\hbar^2\,\Psi \quad (19)$$

$$\hat{S}_z\Psi = M_S\hbar\,\Psi \quad \text{with} \quad M_S = -S,\ldots,+S. \quad (20)$$

In general, eigenfunctions of the Hamiltonian belonging to different eigenvalues of $\hat{\boldsymbol{S}}^2$ have different energies, while for each energy eigenvalue there are always $2S + 1$ degenerate eigenfunctions differing in M_S. As all three components of $\hat{\boldsymbol{S}}$ commute with the Hamiltonian, any choice of the quantization axis is possible and will lead to identical results.

Finally, the spin structure of the many-electron wavefunction[59] is also determined by the Pauli principle.[62,63] It requires that the wavefunction is antisymmetric (i.e., it has to change sign upon exchange of two electrons). This can be expressed with the permutation operator,

$$\hat{\mathcal{P}}_{ij}\Psi(\ldots,\boldsymbol{r}_i,s_i,\ldots,\boldsymbol{r}_j,s_j,\ldots) = \Psi(\ldots,\boldsymbol{r}_j,s_j,\ldots,\boldsymbol{r}_i,s_i,\ldots), \quad (21)$$

as $\hat{\mathcal{P}}_{ij}\Psi = -\Psi$. Here, $\hat{\mathcal{P}}_{ij}$ exchanges both the spatial and the spin coordinates of electrons i and j. To express this requirement in a different form, one can introduce the antisymmetrizer $\hat{\mathcal{A}}$ defined as

$$\hat{\mathcal{A}} = \frac{1}{\sqrt{N!}}\sum_{p=1}^{N!}(-1)^p\,\hat{\mathcal{P}}_p, \quad (22)$$

where the permutation operators $\hat{\mathcal{P}}_p$ are ordered such that even numbers p are assigned to those that are generated by an even number of pair permutations, and odd numbers denote those generated by an odd number of pair permutations. Then, the requirement that the wavefunction is antisymmetric with respect to any pair permutation is equivalent to requiring $\hat{\mathcal{A}}\Psi = \sqrt{N!}\,\Psi$ that is, Ψ has to be an eigenfunction of $\hat{\mathcal{A}}$.

As this Hamiltonian does not contain terms that couple the spatial and the spin coordinates, one could naively expect that—as in the one-electron case—the many-electron wavefunction can always be written as a product of a part depending on the spatial coordinates and of a part depending on the spin coordinates. However, for systems with more than two electrons this is in general not the case. The antisymmetrizer $\hat{\mathcal{A}}$ then contains a sum of permutation operators each acting on both spatial and spin coordinates. Hence, it couples spin and spatial coordinates so that its eigenfunctions cannot be expressed as a product of a spatial and a spin part. Thus, the structure of the many-electron wavefunction with respect to the exchange of spatial coordinates is dependent on the spin structure.[64–66] This is the most important consequence of the presence of spin in a nonrelativistic theory.

Spin structure of the electron density and spin density

The (total) electron density $\rho(\boldsymbol{r})$ describes the probability density for finding any electron of a many-electron system at position $\boldsymbol{r}$. It can be calculated from the wavefunction as

$$\rho(\boldsymbol{r}) = N\int|\Psi(\boldsymbol{r},s_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)|^2\,ds_1d\boldsymbol{x}_2\cdots d\boldsymbol{x}_N, \quad (23)$$

that is, by integrating the squared absolute value of the wavefunction over all but one spatial coordinate. By writing out the integration over the corresponding spin variable explicitly,

$$\rho(\boldsymbol{r}) = N\int\left|\Psi\left(\boldsymbol{r},+\tfrac{1}{2},\boldsymbol{r}_2,s_2,\ldots,\boldsymbol{r}_N,s_N\right)\right|^2\,d^3r_2ds_2\ldots d^3r_Nds_N \quad (24)$$

$$+ N\int\left|\Psi\left(\boldsymbol{r},-\tfrac{1}{2},\boldsymbol{r}_2,s_2,\ldots,\boldsymbol{r}_N,s_N\right)\right|^2\,d^3r_2ds_2\ldots d^3r_Nds_N \quad (25)$$

$$= \rho_\alpha(\boldsymbol{r}) + \rho_\beta(\boldsymbol{r}), \quad (26)$$

one notices that it is a sum of components $\rho_\alpha(\boldsymbol{r})$ and $\rho_\beta(\boldsymbol{r})$ that can be interpreted as the probability densities of finding an α- or a β-spin electron.[60,56] Their integrals,

$$N_\alpha = \int\rho_\alpha(\boldsymbol{r})\,d^3r \quad \text{and} \quad N_\beta = \int\rho_\beta(\boldsymbol{r})\,d^3r, \quad (27)$$

give the number of α- and β-electrons.

It is then natural to define the spin density, which gives the excess of α-electrons at a given point, as

$$Q(\boldsymbol{r}) = N \int \Psi^*(\boldsymbol{r}, s_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\, \sigma_z(s_1) \Psi(\boldsymbol{r}, s_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$$
$$\times\, \mathrm{d}s_1 \mathrm{d}\boldsymbol{x}_2 \cdots \mathrm{d}\boldsymbol{x}_N = \rho_\alpha(\boldsymbol{r}) - \rho_\beta(\boldsymbol{r}). \tag{28}$$

Here, the Pauli matrix $\sigma_z(s_1)$ operates on the first spin coordinate only. Just as the electron density, which is probed by X-ray diffraction experiments, the spin density is an observable. The spin density $Q(\boldsymbol{R}_I)$ at the position of a nucleus I is accessible from electron paramagnetic resonance experiments, where it determines the nuclear hyperfine coupling constants.[56,67,68] Similarly, the spin density at a nucleus can give rise to shifts in paramagnetic nuclear magnetic resonance.[68–71] Full spatially resolved spin densities can be determined in neutron scattering experiments.[72–77]

The expectation value of a multiplicative one-electron operator such as $\hat{V} = \sum_{i=1}^{N} v(\boldsymbol{r}_i)$ can be calculated directly from the electron density,

$$\langle \hat{V} \rangle = \langle \Psi | \hat{V} | \Psi \rangle = \int \rho(\boldsymbol{r}) v(\boldsymbol{r})\, \mathrm{d}^3 r, \tag{29}$$

that is, the full wavefunction is not needed. Similarly, expectation values of spin-dependent operators expressed only in terms of σ_z can be obtained from the spin density. In particular, the expectation value of $\hat{S}_z$ is given by

$$\langle \hat{S}_z \rangle = \frac{\hbar}{2} \int Q(\boldsymbol{r})\, \mathrm{d}^3 r, \tag{30}$$

and for eigenfunctions of $\hat{S}_z$, one has

$$M_S = \frac{1}{2} \int Q(\boldsymbol{r})\, \mathrm{d}^3 r = \frac{1}{2}(N_\alpha - N_\beta). \tag{31}$$

The contribution of the electron spin magnetic moments to the interaction of a molecule with an inhomogeneous external magnetic field $\boldsymbol{B}_{\mathrm{ext}}(\boldsymbol{r})$, the so-called spin Zeeman interaction, is determined by the operator[56]

$$\hat{H}_Z = \sum_{i=1}^{N} \boldsymbol{B}_{\mathrm{ext}}(\boldsymbol{r}_i) \cdot \hat{\boldsymbol{\mu}}_s(s_i) = -\mu_B \sum_{i=1}^{N} \boldsymbol{B}_{\mathrm{ext}}(\boldsymbol{r}_i) \cdot \boldsymbol{\sigma}(s_i). \tag{32}$$

Hence, for an inhomogeneous magnetic field in z-direction, that is, $\boldsymbol{B}_{\mathrm{ext}}(\boldsymbol{r}) = (0, 0, B_z(\boldsymbol{r}))$, the expectation value of the spin Zeeman interaction can be evaluated directly from the spin density as

$$\langle \hat{H}_Z \rangle = -\mu_B \int Q(\boldsymbol{r}) B_z(\boldsymbol{r})\, \mathrm{d}^3 r. \tag{33}$$

If one considers an eigenfunction of $\hat{\boldsymbol{S}}^2$ with eigenvalue $S(S+1)\hbar^2$, this eigenvalue is $(2S+1)$-fold degenerate and one can construct a set of $2S+1$ eigenstates of $\hat{S}_z$ with eigenvalues $M_S\hbar$, where $M_S = -S, \ldots, +S$. The total electron densities ρ^{M_S} and the spin densities $Q^{M_S}(\boldsymbol{r})$ of these $\hat{S}_z$ eigenstates are related to each other[60,78,79]: All $2S+1$ states share the same total electron density,

$$\rho^{M_S}(\boldsymbol{r}) = \rho^{M_S=S}(\boldsymbol{r}) \tag{34}$$

and the spin densities are given by

$$Q^{M_S}(\boldsymbol{r}) = \left(\frac{M_S}{S}\right) Q^{M_S=S}(\boldsymbol{r}) \tag{35}$$

where $\rho^{M_S=S}(\boldsymbol{r})$ and $Q^{M_S=S}(\boldsymbol{r})$ are the total electron density and spin density of the state with highest M_S, respectively. Hence, the spin densities have the same functional form and are connected by a simple scaling. It immediately follows that $Q^{M_S}(\boldsymbol{r}) = -Q^{-M_S}(\boldsymbol{r})$ and that the spin density vanishes for states with $M_S = 0$.

Spin in Hohenberg–Kohn DFT

Traditionally, quantum chemistry sets out to calculate approximations to the many-electron wavefunction Ψ of a molecule in its ground state by minimizing the energy expectation value with respect to Ψ, under the constraint that Ψ represents a normalized and antisymmetric N-electron wavefunction, i.e.,

$$E_0 = \min_{\Psi^N} \langle \Psi^N | \hat{H} | \Psi^N \rangle \qquad \text{with} \qquad \langle \Psi^N | \Psi^N \rangle = 1$$
$$\text{and} \quad \hat{\mathcal{A}}\Psi^N = \sqrt{N!}\,\Psi^N, \tag{38}$$

where the nonrelativistic Hamiltonian $\hat{H}$ within the Born–Oppenheimer approximation was given in Eq. (15). In molecular systems, the external potential $v_{\mathrm{ext}}(\boldsymbol{r})$ is given by the Coulomb potential of the nuclei, that is, $v_{\mathrm{ext}}(\boldsymbol{r}) = v_{\mathrm{nuc}}(\boldsymbol{r}) = -q_e \sum_I Z_I/|\boldsymbol{r} - \boldsymbol{R}_I|$, where the sum runs over all nuclei with charges Z_I at positions $\boldsymbol{R}_I$. Thus, the nonrelativistic molecular Hamiltonian assumes the form,

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e} \Delta_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{q_e^2}{r_{ij}} + \sum_{i=1}^{N} q_e\, v_{\mathrm{nuc}}(\boldsymbol{r}_i)$$
$$= \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{nuc}} \tag{37}$$

According to this structure of the Hamiltonian, the energy expectation value in the above minimization is usually split up as

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{\mathrm{nuc}} | \Psi \rangle. \tag{38}$$

However, the wavefunction itself is not directly needed for calculating these expectation values. The evaluation of the first term, corresponding to the kinetic energy, only requires the one-electron reduced density matrix (1-RDM), whereas the second term describing the electron–electron interaction can be calculated from the diagonal two-electron reduced density matrix (2-RDM). Finally, the electron–nuclear attraction energy can be evaluated directly from the multiplicative operator of the electron–nuclei Coulomb interaction and from the electron density only as,

$$\langle \Psi | \hat{V}_{\mathrm{nuc}} | \Psi \rangle = q_e \int \rho(\boldsymbol{r}) v_{\mathrm{nuc}}(\boldsymbol{r})\, \mathrm{d}^3 r. \tag{39}$$

This can be exploited by performing the minimization with respect to the 2-RDM directly,[80] but difficulties arise in enforcing that the 2-RDM corresponds to an actual antisymmetric N-electron wavefunction.

DFT[50–53] provides the theoretical framework for calculating the energy expectation value directly from the electron density $\rho(\boldsymbol{r})$ only. The foundations of this exact theory will be outlined in the following, focussing on its application to open-shell systems.

Hohenberg–Kohn theorems

The first HK theorem[81] states that for each electron density $\rho(\boldsymbol{r})$ that can be obtained from a ground-state wavefunction (such densities are called v-representable densities), the external potential $v_{\text{ext}}(\boldsymbol{r})$ that yields this electron density as the ground state when employed in the Hamiltonian of Eq. (15) is unique up to a constant. Therefore, this potential is a functional of the electron density and since it completely determines the Hamiltonian, also the ground-state wavefunction—which can in turn be determined by solving the corresponding Schrödinger equation—is a functional of the electron density. Furthermore, all observables of the system, in particular the total energy in a given nuclear potential $v_{\text{nuc}}(\boldsymbol{r})$, can be obtained from this wavefunction. This connection between the electron density and the total energy is illustrated in Figure 1a.

a) Hohenberg–Kohn theorem for v-representable densities

$$\rho(\boldsymbol{r}) \xrightarrow{\text{HK}} v(\boldsymbol{r}) \longrightarrow \hat{H} \xrightarrow{\text{SE}} \Psi[\rho](\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_N, s_N) \longrightarrow E[\rho]$$

b) Hohenberg–Kohn theorem for N-representable densities

$$\rho(\boldsymbol{r}) \xrightarrow{\text{constrained search}} \Psi[\rho](\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_N, s_N) \longrightarrow E[\rho]$$

c) Hohenberg–Kohn theorem in the case of spin degeneracies

$$\rho(\boldsymbol{r}) \nearrow \begin{matrix} \Psi^{M_S=+S}[\rho](\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_N, s_N) \\ \vdots \\ \Psi^{M_S=-S}[\rho](\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_N, s_N) \end{matrix} \searrow E[\rho]$$

Figure 1. Connection between the electron density $\rho(\boldsymbol{r})$ and the total energy as stated by the first HK theorem.

Therefore, there exists an energy functional $E[\rho]$ that relates the electron density to the total energy.

According to the second HK theorem,[81] the ground state energy E_0 of a system of electrons in a given nuclear potential $v_{\text{nuc}}(\boldsymbol{r})$ can be determined by minimizing the total energy functional

$$E_0 = \min_{\rho} E[\rho], \tag{40}$$

with

$$E[\rho] = q_e \int \rho(\boldsymbol{r}) \, v_{\text{nuc}}(\boldsymbol{r}) \, \mathrm{d}^3 r + F_{\text{HK}}[\rho], \tag{41}$$

under the constraint that $\rho(\boldsymbol{r})$ integrates to N electrons. The electron density for which this minimum is achieved is the ground-state electron density $\rho_0(\boldsymbol{r})$. In this equation, the total energy functional has been split into a system-specific part (the first term), depending on the nuclear potential, and a system-independent part (the second term), which is called the "universal HK functional" $F_{\text{HK}}[\rho]$.

Following the Levy constrained-search formulation of DFT,[82,83] this universal HK functional is given by

$$F_{\text{HK}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle, \tag{42}$$

where $\hat{T}$ and $\hat{V}_{\text{ee}}$ are the operators of the kinetic energy and of the electron–electron repulsion energy, respectively. The minimization runs over all wavefunctions Ψ that yield the target electron density ρ. From these wavefunctions, the one with the lowest expectation value of $\hat{T} + \hat{V}_{\text{ee}}$ is chosen. The minimization of $E[\rho]$ will lead to the exact ground-state electron density ρ_0, and the exact ground-state wavefunction Ψ_0 is the one for which the minimum in Eq. (42) is obtained. This (nonrelativistic) ground-state wavefunction Ψ_0 has to be an eigenfunction of $\hat{\boldsymbol{S}}^2$. Therefore, it is sufficient to restrict the constrained search to wavefunctions that are eigenfunctions of $\hat{\boldsymbol{S}}^2$.

Using the Levy-constrained search for defining the HK functional also extends the domain in which the above functionals are defined from v-representable densities (i.e., densities that are obtained from a ground state wavefunction) to N-representable densities (i.e., densities that are obtained from any wavefunction, not necessarily a ground state). The resulting generalization of the first HK theorem is illustrated in Figure 1b. More details on the foundations of HK-DFT and on the more general definition of the universal HK functional introduced by Lieb[84] can be found in dedicated reviews on these topics.[51,85,86]

Initially, Hohenberg and Kohn explicitly excluded degeneracies in their derivation of the HK theorems.[81] However, a state with $S > 0$ will be $(2S + 1)$-fold degenerate, with the different degenerate wavefunctions Ψ^{M_S} corresponding to $M_S = -S, \ldots, S$. The necessary generalization of the HK theorems is possible in a straightforward way.[87] The degenerate wavefunctions Ψ^{M_S} and all their linear combinations share the same electron density. For a given ρ, the minimum in Eq. (42) is achieved for all degenerate wavefunctions spanned by the $\hat{S}_z$-eigenfunctions Ψ^{M_S}. This is illustrated in Figure 1c. Therefore, the minimization of the total energy functional $E[\rho]$ will still lead to a unique ground-state density ρ_0. If it is necessary to obtain a unique minimizing wavefunction, the constrained search can be restricted to wavefunctions corresponding to a specific value of M_S. In this case, the wavefunction is again uniquely determined by the electron density.

Spin density in Hohenberg–Kohn DFT

According to the HK theorem only the total electron density is required for obtaining the exact ground-state energy and electron density.[81,88] Therefore, irrespective of the spin state, the

spin density $Q(\mathbf{r})$ or the individual α- and β-electron densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ are not required during the minimization of the total energy functional, and the ground-state spin density $Q_0(\mathbf{r})$ is not directly available. However, if a suitable value of M_S is chosen, the wavefunction Ψ^{M_S} is uniquely determined by the total density $\rho(\mathbf{r})$, that is, $\Psi^{M_S} = \Psi^{M_S}[\rho]$. From this wavefunction, the ground-state α- and β-electron densities,

$$\rho_\alpha^{M_S}[\rho](\mathbf{r}) = N \int \left| \Psi^{M_S}[\rho]\left(\mathbf{r}, +\tfrac{1}{2}, \mathbf{r}_2, s_2, \dots \right) \right|^2 \mathrm{d}^3 r_2 \mathrm{d}s_2 \cdots \mathrm{d}^3 r_N \mathrm{d}s_N \tag{43}$$

$$\rho_\beta^{M_S}[\rho](\mathbf{r}) = N \int \left| \Psi^{M_S}[\rho]\left(\mathbf{r}, -\tfrac{1}{2}, \mathbf{r}_2, s_2, \dots \right) \right|^2 \mathrm{d}^3 r_2 \mathrm{d}s_2 \cdots \mathrm{d}^3 r_N \mathrm{d}s_N, \tag{44}$$

as well as the corresponding spin density

$$Q^{M_S}[\rho](\mathbf{r}) = \rho_\alpha^{M_S}[\rho](\mathbf{r}) - \rho_\beta^{M_S}[\rho](\mathbf{r}) \tag{45}$$

can be calculated. In these expressions, the superscript M_S indicates that a specific value of M_S has to be selected if one is interested in individual α- and β-densities or in the spin density. The chosen value of M_S fixes the number of α- and β-electrons by $M_S = \frac{1}{2}(N^\alpha - N^\beta)$.

To generalize HK-DFT to use the individual α- and β-densities instead of the total density only, the minimization of the total energy can be rewritten as,[50,89]

$$E_0 = \min_\rho E[\rho] = \min_\rho \left\{ q_e \int \rho(\mathbf{r}) v_{\mathrm{nuc}}(\mathbf{r}) \, \mathrm{d}^3 r + \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right\}$$
$$= \min_\rho \left\{ q_e \int \rho(\mathbf{r}) v_{\mathrm{nuc}}(\mathbf{r}) \, \mathrm{d}^3 r + \min_{\rho^\alpha, \rho^\beta \to \rho} \left[\min_{\Psi \to \rho^\alpha, \rho^\beta} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right] \right\}, \tag{46}$$

and by removing the outer minimization with respect to ρ, one obtains

$$E_0 = \min_{\rho^\alpha, \rho^\beta} \left\{ q_e \int \left[\rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \right] v_{\mathrm{nuc}}(\mathbf{r}) \, \mathrm{d}^3 r + \min_{\Psi \to \rho^\alpha, \rho^\beta} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right\}. \tag{47}$$

This defines a universal HK functional in terms of the α- and β-electron densities,

$$F_{\mathrm{HK}}[\rho^\alpha, \rho^\beta] = \min_{\Psi \to \rho^\alpha, \rho^\beta} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \tag{48}$$

In contrast to the HK functional of Eq. (42), the constrained search in this spin-resolved HK functional now runs over all wavefunctions corresponding to a given pair of ρ^α and ρ^β. By minimizing the generalized total energy functional [cf. Eq. (47)],

$$E[\rho^\alpha, \rho^\beta] = q_e \int \left[\rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \right] v_{\mathrm{nuc}}(\mathbf{r}) \, \mathrm{d}^3 r + F_{\mathrm{HK}}[\rho^\alpha, \rho^\beta], \tag{49}$$

under the constraint that ρ^α and ρ^β integrate to N^α and N^β electrons, respectively, it is then possible to obtain the ground-state α- and β-electron densities ρ_0^α and ρ_0^β. Again, in this minimization a specific value of $M_S = \frac{1}{2}(N^\alpha - N^\beta)$ has to be selected.

Instead of using ρ^α and ρ^β, it is also possible to use the total electron density $\rho = \rho^\alpha + \rho^\beta$ and the spin-density $Q = \rho^\alpha - \rho^\beta$ as variables of the spin-resolved HK functional. This gives

$$F_{\mathrm{HK}}[\rho, Q] = \min_{\Psi \to \rho, Q} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \tag{50}$$

Although usually—in particular in practical applications of spin-DFT—it is more common to employ the α- and β-densities as basic variables, in the following such a formulation in terms of ρ and Q will often turn out to be useful, because it allows for an easier comparison to the spin-independent functionals defined only in terms of the density ρ. We will switch between these two representations whenever suitable.

With the spin-resolved HK functional $F_{\mathrm{HK}}[\rho, Q]$, it is now also possible to give a simpler prescription for obtaining the spin-density corresponding to a given total density: $Q^{M_S}[\rho]$ is the spin density for which $F_{\mathrm{HK}}[\rho, Q]$ is minimized, under the constraint that Q^{M_S} integrates to twice the chosen value of M_S, i.e.,

$$Q^{M_S}[\rho] = \arg \min_{Q^{M_S}} F_{\mathrm{HK}}[\rho, Q^{M_S}] \qquad \text{with} \quad \frac{1}{2} \int Q^{M_S}(\mathbf{r}) \, \mathrm{d}^3 r = M_S. \tag{51}$$

Therefore, the spin-independent HK functional $F[\rho]$ can be obtained from the spin-dependent HK functional $F_{\mathrm{HK}}[\rho, Q]$ as

$$F_{\mathrm{HK}}[\rho] = F_{\mathrm{HK}}[\rho, Q[\rho]] = \min_Q F_{\mathrm{HK}}[\rho, Q], \tag{52}$$

where $Q[\rho]$ is any of the spin densities that minimize $F_{\mathrm{HK}}[\rho, Q]$ for the given total density ρ. Of course, as long as no specific M_S is chosen, $Q[\rho]$ is not unique, but any admissible choice must lead to the same energy.

Finally, we have to consider whether there exist extensions of the HK theorems that justify the use of ρ and Q (or of ρ^α and ρ^β) as basic variables. For a generalization of this kind, it is not sufficient to consider wavefunctions generated by an external potential $v_{\mathrm{ext}}(\mathbf{r})$, but also wavefunctions obtained in the presence of an additional external magnetic field $B_z(\mathbf{r})$ have to be taken into account. Such an extension of the HK theorems was first given by von Barth and Hedin,[90] and was only recently put on more firm ground by extensions of Lieb's formulation of DFT.[91,92] Similar to the external potential, which is only known up to a constant, it is also possible to add a constant shift to the external magnetic field $B_z(\mathbf{r})$ without changing the wavefunction or the (spin-)density.[93,94] This leads to a number of peculiarities related to the differentiability of the spin-dependent energy functional.[95,96] However, most of these issues do not appear if the treatment is restricted to eigenfunctions of S_z (the case of interest here)[97] or can be addressed by constraining M_S to a fixed value (as we are always requiring here).[98,99]

Fractional spin conditions on the HK functional

For states that are not a singlet (i.e., for $S > 0$), there are different degenerate wavefunctions $\Psi^{M_S}[\rho]$. These wavefunctions

all share the same electron density, but correspond to different spin densities $Q^{M_S}[\rho]$. These different spin-densities are related by [cf. Eq. (35)]

$$Q^{M_S}[\rho](\boldsymbol{r}) = \left(\frac{M_S}{S}\right) Q^{M_S=S}[\rho](\boldsymbol{r}), \tag{53}$$

and it follows that $Q^{M_S}(\boldsymbol{r}) = -Q^{-M_S}(\boldsymbol{r})$ and that one obtains $Q^{M_S=0}(\boldsymbol{r}) = 0$ for even values of S. For all these degenerate spin-densities, the exact total energy functional $E[\rho, Q]$ must yield the same value.

This statement can be generalized to linear combinations of these spin-densities. Within an ensemble formulation of spin-DFT, it can be shown[100] that for any properly normalized linear combination of the spin-densities $Q^{M_S}[\rho]$, the same energy should be obtained. Therefore, one finds that

$$E\left[\rho, \alpha Q^{M_S=S}[\rho]\right] = \text{const.} \quad \text{for} -1 \leq \alpha \leq +1, \tag{54}$$

which implies for the spin-dependent HK functional

$$F_{\text{HK}}\left[\rho, \alpha Q^{M_S=S}[\rho]\right] = \text{const.} \quad \text{for} -1 \leq \alpha \leq +1. \tag{55}$$

Such ensemble spin densities correspond to a situation with a non-integer number of α- and β-electrons ("fractional spins"). As has been pointed out by Yang and coworkers, the above constancy conditions for fractional spins, which is a property of the exact energy functional is violated by all contemporary approximations. Therefore, it was suggested that many problems appearing in practical DFT calculations with such approximations might be connected to this violation.[49,101,102]

The use of fractional spins makes it possible to further simplify the relation between the spin-dependent and spin-independent HK functionals given in Eq. (52), because one realizes that

$$F_{\text{HK}}[\rho] = F_{\text{HK}}[\rho, Q = 0]. \tag{56}$$

This equation holds both for systems with an even number of electrons (where one can always choose $M_S = 0$, corresponding to $Q(\boldsymbol{r}) = 0$) and for systems with an odd number of electrons (where $Q(\boldsymbol{r}) = 0$ is only possible if one allows for fractional spins).

Spin states in Hohenberg–Kohn DFT

In their initial formulation,[81] the HK theorems were applicable only to the ground state. In particular, minimizing the total energy functional $E[\rho]$ only yields the ground-state energy and electron density (and if the spin-dependent energy functional is employed, also the spin density). However, as was first shown by Gunnarsson and Lundqvist,[103] HK-DFT can be generalized to the lowest-energy states of a given symmetry. Of particular importance is the calculation of the lowest state of a particular spin symmetry, that is, of the lowest state with a particular eigenvalue of $\hat{\boldsymbol{S}}^2$. Such a generalization is most easily presented within the constrained-search formulation of DFT.

To obtain the energy and electron density of the lowest state corresponding to a given value of S, one has to define the spin-state specific energy functional,

$$E^S[\rho] = q_e \int \rho(\boldsymbol{r}) \, v_{\text{nuc}}(\boldsymbol{r}) \, \mathrm{d}^3 r + F_{\text{HK}}^S[\rho], \tag{57}$$

with the spin-state specific HK functional,

$$F_{\text{HK}}^S[\rho] = \min_{\Psi^S \to \rho} \left\langle \Psi^S \middle| \hat{T} + \hat{V}_{\text{ee}} \middle| \Psi^S \right\rangle \quad \text{with} \quad \hat{\boldsymbol{S}}^2 \Psi^S = S(S+1)\hbar^2 \Psi^S, \tag{58}$$

where the constrained search now only includes wavefunctions Ψ^S which are eigenfunctions of $\hat{\boldsymbol{S}}^2$ with the proper eigenvalue. Therefore, one obtains a different HK functional and thus a different total energy functional for each value of S.

Within spin-DFT, the simplest way of obtaining a functional that at least partly allows one to select certain spin states is by choosing an appropriate value for M_S. This way, only states with $S \geq M_S$ are accessible because for spin states corresponding to a smaller values of S, the chosen value of M_S is not admissible. By minimizing the energy functional $E_v[\rho, Q]$ under the constraint that $Q(\boldsymbol{r})$ integrates to $2M_S$, the lowest-energy state with $S \geq M_S$ is obtained, i.e.,

$$E^{S \geq M_S}[\rho] = E\left[\rho, Q^{M_S}[\rho]\right]. \tag{59}$$

Equivalently, one can, of course, also minimize $E_v[\rho^\alpha, \rho^\beta]$ under appropriate constraints for N^α and N^β. However, fixing M_S to target a specific spin-state is not completely general since the minimization is only restricted to states with $S \geq M_S$, not to states with a specific S. Although it is, for instance, possible to calculate the lowest triplet ($S = 1$) state if the ground-state is a singlet ($S = 0$), it is not possible to target the lowest singlet state if the ground-state is a triplet. Therefore, to be able to calculate the lowest state of a given S, it would in general be necessary to use the true spin-state specific energy functional of Eq. (57).

Spin in Kohn–Sham DFT

Although the HK formulation of DFT is exact, it is very difficult to set up computationally feasible, but nevertheless accurate approximate realizations of it. This is mainly rooted in the difficulty of approximating the kinetic-energy contribution to the HK functional as a functional of the electron density only.[104,105]

A possible way out of this dilemma, that forms the basis of almost every present-day application of (approximate) DFT calculations, was suggested by Kohn and Sham.[106] Instead of considering the kinetic energy of the true system of interacting electrons, they proposed to calculate the kinetic energy of a reference system of noninteracting electrons with the same electron density instead. This then already accounts for the largest part of the kinetic energy, and only a small remainder has to be approximated. The KS approach still allows for the formulation of an exact theory, which will be outlined in this section.

In KS-DFT, one considers two different quantum-mechanical systems at the same time: The true molecular system of interacting electrons and a reference system of noninteracting electrons. The link between these two systems is established by
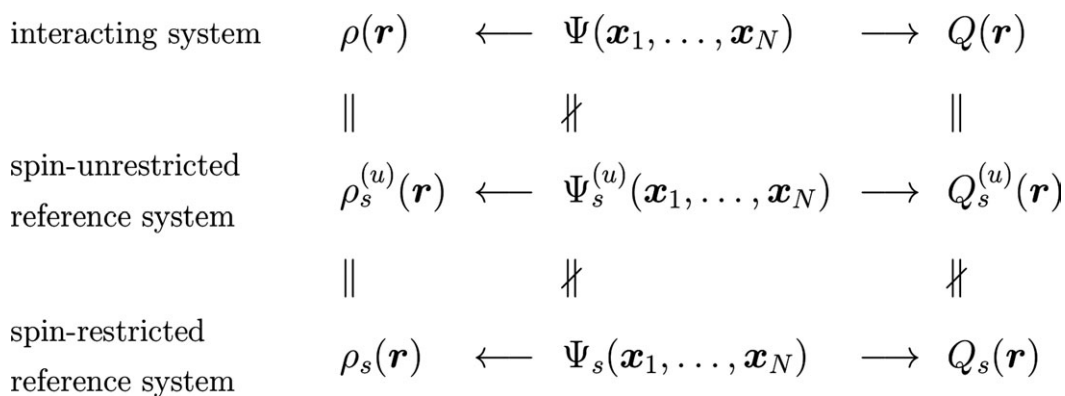
$$\text{interacting system} \quad \rho(\boldsymbol{r}) \quad \longleftarrow \quad \Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \quad \longrightarrow \quad Q(\boldsymbol{r})$$

$$\| \qquad\qquad \nparallel \qquad\qquad \|$$

$$\begin{array}{c}\text{spin-unrestricted}\\\text{reference system}\end{array} \quad \rho_s^{(u)}(\boldsymbol{r}) \quad \longleftarrow \quad \Psi_s^{(u)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \quad \longrightarrow \quad Q_s^{(u)}(\boldsymbol{r})$$

$$\| \qquad\qquad \nparallel \qquad\qquad \nparallel$$

$$\begin{array}{c}\text{spin-restricted}\\\text{reference system}\end{array} \quad \rho_s(\boldsymbol{r}) \quad \longleftarrow \quad \Psi_s(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \quad \longrightarrow \quad Q_s(\boldsymbol{r})$$

Figure 2. Relationship between wave function, total electron density, and spin density of the system of fully interacting electrons and of the spin-restricted and spin-unrestricted KS reference systems of noninteracting electrons.

requiring that their electron densities $\rho(\boldsymbol{r})$ and $\rho_s(\boldsymbol{r})$ are equal (see Fig. 2). Their wavefunctions, however, will in general be different. For open-shell molecules, different options exist for introducing such a reference system: the first option is to require only that the electron densities of the interacting and noninteracting systems agree. This leads to a spin-restricted KS-DFT formulation. The second option is to require that in addition to the total electron densities, also the spin densities of the two systems agree. This results in a spin-unrestricted formulation of KS-DFT. Of course, these two options are equivalent for closed-shell systems (i.e., for singlet states with $S = 0$).

Note that any version of KS-DFT relies on the assumption that such a noninteracting reference system with the same electron density (and possibly also the same spin density) as the interacting system exists. In practice, it is always assumed that this so-called v_s-representability condition is fulfilled, even though this is not guaranteed and several counter-examples are known.[84,107–111] For a detailed discussion of these subtle issues, see, for example, Refs. [85].

Spin-Restricted Kohn–Sham DFT

Noninteracting Reference System. First, we consider a system of N noninteracting electrons in an external potential $v_s(\boldsymbol{r})$. Such a system is described by the Hamiltonian

$$\hat{H}_s = \hat{T} + \hat{V}_s = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\Delta_i + \sum_{i=1}^{N} q_e v_s(\boldsymbol{r}_i), \tag{60}$$

where the subscript s (for "single-particle") is introduced to indicate that the quantities refer to a system of noninteracting electrons. Because this Hamiltonian does not contain terms that couple different electrons, an exact wavefunction is given by an antisymmetrized product of one-electron functions (i.e., by a single Slater determinant), for which the short-hand notation

$$\Phi_s(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \left| \varphi_1\alpha, \varphi_1\beta, \varphi_2\alpha, \varphi_2\beta, \ldots \right| \tag{61}$$

can be used. The spatial parts of the one-electron functions (orbitals) can be obtained as the solutions of the one-electron equation

$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e v_s(\boldsymbol{r}) \right] \varphi_i(\boldsymbol{r}) = \epsilon_i \varphi_i(\boldsymbol{r}), \tag{62}$$

which trivially emerge from the energy eigenvalue equation $\hat{H}_s\Phi_s = E_s\Phi_s$ with $E_s = \sum_i \epsilon_i$. As this one-electron Hamiltonian does not depend on the spin of the electron, each energy eigenvalue is twofold degenerate (i.e., each spatial orbital can be combined with an α- or a β-spin function). In particular, the spatial orbitals are identical for α- and for β-electrons, and the resulting Slater determinant is therefore spin-restricted.

In such a spin-restricted Slater determinant, each spatial orbital φ_i can either be doubly occupied (i.e., it appears both in combination with an α- and with a β-spin function) or it can be singly occupied with either an α- or a β-electron. For the ground state, such singly occupied orbitals can only occur for the highest occupied molecular orbital (HOMO), and more than one singly occupied orbital can only be present if the HOMO is degenerate (for a detailed discussion, see e.g., Ref. [109] and chapters 3.3 and 3.4 in Ref. [53]).

For a single, spin-restricted Slater determinant, the electron density is given by

$$\rho(\boldsymbol{r}) = \sum_i^{\text{occ.}} f_i |\varphi_i(\boldsymbol{r})|^2, \tag{63}$$

where the occupation numbers f_i are either 1 or 2. The spin density is determined only by the singly occupied orbitals, and can be calculated as

$$Q_s(\boldsymbol{r}) = \sum_i^{\text{singly occ.}} s_i |\varphi_i(\boldsymbol{r})|^2, \tag{64}$$

where the sum only runs over the singly occupied orbitals and where $s_i = +1$ for α-spin and $s_i = -1$ for β-spin orbitals, as all doubly occupied orbital contributions drop out because of the identical spatial distribution of these α, β-pairings. Finally, the kinetic energy of a spin-restricted Slater determinant can be calculated as

$$T_s = \sum_i^{\text{occ.}} f_i \langle \varphi_i | \hat{T} | \varphi_i \rangle = -\frac{\hbar^2}{2m_e} \sum_i^{\text{occ.}} f_i \int \varphi_i(\boldsymbol{r}) \Delta\varphi_i(\boldsymbol{r}) \, \mathrm{d}^3r. \tag{65}$$

Thus, it turns out that spin-restricted Slater determinants in which the occupation numbers f_i are identical share the same electron density and have the same kinetic energy. Such determinants—which can only differ in the spin of the singly occupied orbitals—are degenerate with respect to the noninteracting Hamiltonian of Eq. (60).

The noninteracting Hamiltonian $\hat{H}_s$ commutes with both $\hat{S}_z$ and with $\hat{\mathbf{S}}^2$. Therefore, it is always possible to combine degenerate eigenfunctions such that they are also eigenfunctions of $\hat{S}_z$ and $\hat{\mathbf{S}}^2$. A restricted Slater determinant is always an eigenfunction of $\hat{S}_z$ with eigenvalue $M_S\hbar = (N_\alpha - N_\beta)\hbar/2$.[60,58] If all singly occupied orbitals are either α- or β-spin orbitals, then it is also an eigenfunction of $\hat{\mathbf{S}}^2$ with $S = |M_S|$. In all other cases, an eigenfunction of $\hat{\mathbf{S}}^2$ can be constructed as a linear combination of (degenerate) determinants in which the same orbitals are singly occupied and which correspond to the same value of M_S. Such linear combinations are known as configuration state functions (CSF).[10] It is important to understand that for any eigenfunction of the noninteracting Hamiltonian that is an eigenfunction of $\hat{\mathbf{S}}^2$ with eigenvalue $S_{max}(S_{max} + 1)\hbar^2$, degenerate eigenfunctions with $S = 0, 1, \ldots, S_{max}$ (for an even number of electrons) or with $S = \frac{1}{2}, \frac{3}{2}, \ldots, S_{max}$ (for an odd number of electrons) can also be constructed. Thus, for each energy eigenvalue, there is one CSF corresponding to $S = 0$ (i.e., a singlet state) or $S = \frac{1}{2}$ (i.e., a doublet state) for an even or odd number of electrons, respectively.

The HK theorems still hold for a system of noninteracting electrons. Thus, the ground-state density of $\hat{H}_s$ can be determined by minimizing the noninteracting energy functional,

$$E_s[\rho] = T_s[\rho] + q_e \int \rho(\mathbf{r})v_s(\mathbf{r})\, d^3r, \qquad (66)$$

where the noninteracting kinetic-energy functional $T_s[\rho]$ can be defined in the Levy constrained-search formalism as

$$T_s[\rho] = \min_{\Psi_s \to \rho} \langle \Psi_s | \hat{T} | \Psi_s \rangle. \qquad (67)$$

In this definition, the constrained search includes all wavefunctions Ψ_s that correspond to a system of noninteracting electrons with density ρ. As discussed above, this could be further restricted to singlet or doublet wavefunctions. In this definition, $T_s[\rho]$ is independent of the spin density.

The ground-state electron density ρ_0 is obtained from minimizing $E_s[\rho]$ under the constraint that the number of electrons is preserved, and the corresponding ground-state wavefunction $\Psi_{s,0}$ is the one for which the minimum in Eq. (67) is achieved. Again, this wavefunction could always be chosen as a singlet or a doublet for an even or odd number of electrons, respectively.

Interacting Energy Functional and Exchange–Correlation Energy. The (spin-resolved) HK functional of the true system of interacting electrons [Eq. (50)] can now be decomposed as

$$F_{HK}[\rho, Q] = T_s[\rho] + J[\rho] + E_{xc}[\rho, Q], \qquad (68)$$

where $T_s[\rho]$ is the noninteracting kinetic energy introduced in the previous section, $J[\rho]$ is the classical Coulomb interaction of the electron density with itself,

$$J[\rho] = \frac{q_e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3r\, d^3r', \qquad (69)$$

and the exchange–correlation energy $E_{xc}[\rho, Q]$ is defined to account for the remaining energy contributions

$$E_{xc}[\rho, Q] = F_{HK}[\rho, Q] - T_s[\rho] - J[\rho]. \qquad (70)$$

This exchange–correlation functional could also be expressed in terms of the α- and β-electron densities. The noninteracting kinetic energy $T_s[\rho]$ is different from the true kinetic energy of the fully interacting system $T[\rho]$. Therefore, the exchange–correlation energy also contains the difference $T_c[\rho] = T[\rho] - T_s[\rho]$ between the kinetic energy of the interacting system and the kinetic energy of the noninteracting reference system.

With these definitions, the total energy functional of the interacting system can be expressed as

$$E[\rho, Q] = T_s[\rho] + J[\rho] + E_{xc}[\rho, Q] + q_e \int \rho(\mathbf{r})v_{nuc}(\mathbf{r})d^3r. \qquad (71)$$

The spin-independent analogs of the exchange–correlation and the total energy functional, $E_{xc}[\rho]$ and $E[\rho]$, are recovered from these definitions when setting $Q(\mathbf{r}) = 0$ [cf. Eq. (56)].

The ground-state density of the true interacting system can be determined by minimizing the total energy functional $E[\rho]$ with respect to ρ, under the constraint that it integrates to the correct number of electrons. With the exact functionals, this will lead to the exact ground-state electron density $\rho_0(\mathbf{r})$. The corresponding exact wavefunction Ψ_0 is the one for which the minimum in the constraint search in Eq. (50) is obtained. This ground-state wavefunction has to be an eigenfunction of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$, and the corresponding value of S determines the spin multiplicity of the ground-state, whereas the different M_S-states are degenerate. In contrast to the noninteracting case, the ground-state wavefunction is not necessarily a singlet or doublet wavefunction, but could have a higher spin multiplicity.

Kohn–Sham Potential. Minimization of the noninteracting energy functional [Eq. (66)] with respect to the total density ρ, under the constraint that ρ integrates to N electrons, yields the following Euler–Lagrange equation,[50]

$$0 = \frac{\delta E_s[\rho]}{\delta \rho(\mathbf{r})} - \mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + q_e v_s(\mathbf{r}) - \mu. \qquad (72)$$

Conversely, the total energy functional of the interacting system is given by Eq. (71), which upon minimization leads to the condition

$$0 = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + q_e \left(v_{nuc}(\mathbf{r}) + v_{Coul}[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}) \right) - \mu,$$

$$(73)$$

where $v_{\text{Coul}}[\rho](\boldsymbol{r}) = q_e \int \rho(\boldsymbol{r}')/|\boldsymbol{r} - \boldsymbol{r}'| \, \mathrm{d}^3 r'$ is the classical Coulomb potential of the electrons and $v_{\text{xc}}[\rho](\boldsymbol{r}) = (1/q_e) \, \delta E_{\text{xc}}[\rho]/\delta \rho(\boldsymbol{r})$ is the exchange–correlation potential.

As the definition of the noninteracting kinetic energy $T_s[\rho]$ is the same in both minimizations, and because we require that the total densities obtained for the interacting and noninteracting system agree, we obtain for the KS potential

$$v_s[\rho](\boldsymbol{r}) = v_{\text{ext}}(\boldsymbol{r}) + v_{\text{Coul}}[\rho](\boldsymbol{r}) + v_{\text{xc}}[\rho](\boldsymbol{r}). \qquad (74)$$

The ground-state electron density of the fully interacting system can thus be determined by solving the Schrödinger equation of a noninteracting system [i.e., with the Hamiltonian of Eq. (60) including the external potential $v_s[\rho]$ given by Eq. (74)], and the orbitals of this noninteracting system can be obtained from the KS equations

$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e\left(v_{\text{nuc}}(\boldsymbol{r}) + v_{\text{Coul}}[\rho](\boldsymbol{r}) + v_{\text{xc}}[\rho](\boldsymbol{r})\right) \right] \varphi_i(\boldsymbol{r}) = \epsilon_i \varphi_i(\boldsymbol{r}).$$
$$(75)$$

Thus, the ground-state electron density of the true interacting system is obtained from the wavefunction $\Psi_{s,0}$ of the noninteracting reference system. However, this ground-state wavefunction $\Psi_{s,0}$ of the noninteracting reference system does not agree with the ground-state wavefunction Ψ_0 of the interacting system. Moreover, $\Psi_{s,0}$ can always be chosen as a singlet or doublet state (i.e., $S = 0$ or $S = \frac{1}{2}$), whereas Ψ_0 can correspond to any value of S. Therefore, the spin multiplicities of the ground-states of the noninteracting and of the interacting system can be different.

Spin Density. For $S > 0$, the ground state of the true interacting system is degenerate and there is a set of eigenfunctions of $\hat{S}_z$ with different eigenvalues M_S. These wavefunctions $\Psi_0^{M_S}$ have different spin densities $Q_0^{M_S}(\boldsymbol{r})$ that are related by Eq. (35). By construction, the ground-state wavefunction $\Psi_{s,0}$ of the noninteracting reference system and the ground-state wavefunction Ψ_0 of the fully interacting system only share the same electron density. However, the corresponding spin densities $Q(\boldsymbol{r})$ and $Q_s(\boldsymbol{r})$ are in general not equal and the true ground-state spin density cannot be calculated from $\Psi_{s,0}$.

From Eq. (64) it is obvious that $Q(\boldsymbol{r})$ and $Q_s(\boldsymbol{r})$ have to be different: for the spin-restricted noninteracting reference system, the spin density is determined only by the singly occupied orbitals and will thus have the same sign at every point in space (i.e., $Q_s(\boldsymbol{r}) > 0$ for $M_S > 0$). However, it is known both from accurate calculations and from experiment, that for the interacting system the spin density has different signs in different regions in space.[112–114]

To obtain the spin density in a restricted KS-DFT formulation, one has to minimize the spin-resolved HK functional $F_{\text{HK}}[\rho_0, Q]$ defined in Eq. (50) with respect to $Q(\boldsymbol{r})$, under the constraint that the spin density integrates to $2M_s$. As the exchange–correlation energy is the only part of this functional that depends on the spin density, the minimization with respect to $Q(\boldsymbol{r})$ leads to the condition

$$\frac{\delta F_{\text{HK}}[\rho_0, Q]}{\delta Q(\boldsymbol{r})} - \lambda = \frac{\delta E_{\text{xc}}[\rho_0, Q]}{\delta Q(\boldsymbol{r})} = 0, \qquad (76)$$

where the Lagrange multiplier λ is zero because of Eq. (35). This suggests a two-step procedure for determining the spin density in restricted KS-DFT. First, the total ground-state density $\rho_0(\boldsymbol{r})$ is determined by solving the KS equations. Subsequently, the corresponding ground-state spin density $Q_0(\boldsymbol{r})$ can be calculated from the above minimization condition for a chosen value of M_S.

Spin-Unrestricted Kohn–Sham DFT

Noninteracting Reference System. The choice of a reference system of noninteracting electrons with the same total electron density as the interacting system is not the only option. Alternatively, it is also possible to envisage a reference system of noninteracting electrons that has the same α- and β-electron densities as the interacting system.[90,103,112] In this case, a reference system with the Hamiltonian

$$\hat{H}_s^{(u)} = \hat{T}_s + \hat{V}_s^{\text{tot}} + \hat{V}_s^{\text{spin}} = \sum_{i=1}^{N} \frac{\hbar^2}{2m_e}\Delta_i + q_e \sum_{i=1}^{N}\left[v_s^{\text{tot}}(\boldsymbol{r}_i) + v_s^{\text{spin}}(\boldsymbol{r}_i)\sigma_z(s_i)\right]$$
$$= \hat{T}_s + \hat{V}_s^{\alpha} + \hat{V}_s^{\beta} = \sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\Delta_i + q_e\sum_{i=1}^{N}\left[v_s^{\alpha}(\boldsymbol{r}_i)\alpha(s_i) - v_s^{\beta}(\boldsymbol{r}_i)\beta(s_i)\right]$$
$$(77)$$

is used. To distinguish them from those introduced earlier for a spin-restricted reference system, the superscript "(u)" will be used for quantities referring to this spin-unrestricted reference system. Different potentials $v_s^{\alpha}(\boldsymbol{r}) = v_s^{\text{tot}}(\boldsymbol{r}) + v_s^{\text{spin}}(\boldsymbol{r})$ and $v_s^{\beta}(\boldsymbol{r}) = v_s^{\text{tot}}(\boldsymbol{r}) - v_s^{\text{spin}}(\boldsymbol{r})$ for the α- and β-electrons, respectively, are now needed to allow the reference system of noninteracting electrons to have the same spin density as the interacting one. This corresponds to introducing an inhomogeneous external magnetic field in z-direction $B_z(\boldsymbol{r}) = -\frac{q_e}{\mu_B}v_s^{\text{spin}}(\boldsymbol{r})$ that only interacts with the electronic spins (i.e., the interaction due to orbital angular momentum is ignored) [cf. Eq. (32)].

An exact solution to the corresponding Schrödinger equation has the form of a single Slater determinant, but in contrast to the spin-restricted case the spatial orbitals now differ for α- and β-electrons, i.e.,

$$\Phi_s^{(u)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \left| \varphi_1^{\alpha}\alpha, \varphi_1^{\beta}\beta, \varphi_2^{\alpha}\alpha, \varphi_2^{\beta}\beta, \ldots \right| \qquad (78)$$

The spatial parts of the orbitals can be obtained from two separate sets of one-electron equations

$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e\, v_s^{\alpha}(\boldsymbol{r}) \right] \varphi_i^{\alpha}(\boldsymbol{r}) = \epsilon_i^{\alpha}\varphi_i^{\alpha}(\boldsymbol{r}) \quad \text{and}$$
$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e\, v_s^{\beta}(\boldsymbol{r}) \right] \varphi_i^{\beta}(\boldsymbol{r}) = \epsilon_i^{\beta}\varphi_i^{\beta}(\boldsymbol{r}). \qquad (79)$$

Both the resulting α- and β-orbitals form an orthonormal set, $\langle \varphi_i^{\alpha}|\varphi_j^{\alpha}\rangle = \delta_{ij}$ and $\langle \varphi_i^{\beta}|\varphi_j^{\beta}\rangle = \delta_{ij}$, but α- and β-orbitals are in general not orthogonal to each other, that is, $\langle \varphi_i^{\alpha}|\varphi_j^{\beta}\rangle \neq 0$.

The noninteracting Hamiltonian $H_s^{(u)}$ still commutes with $\hat{S}_z$, and any spin-unrestricted Slater determinant is an eigenfunction

of $\hat{S}_z$, with the eigenvalue M_S being determined by the number of α- and β-electrons. However, in contrast to the spin-restricted case, the different $\hat{S}_z$ eigenstates are not degenerate anymore. For constructing the ground-state wavefunction, the N orbitals with the lowest orbital energies have to be occupied, which automatically fixes M_S. By occupying other (α- or β-electron) orbitals, excited state wavefunctions for the noninteracting reference system corresponding to different values of M_S can be obtained.

However, $H_s^{(u)}$ in general does not commute with $\hat{\mathbf{S}}^2$, and the ground-state wavefunction is thus not an eigenfunction of $\hat{\mathbf{S}}^2$ anymore. Instead, the expectation value of $\hat{\mathbf{S}}^2$ can be calculated as (assuming $N_\alpha \geq N_\beta$)[61,115]

$$\langle \hat{\mathbf{S}}^2 \rangle = M_S(M_S + 1)\hbar^2 + \hbar^2 N_\beta - \hbar^2 \sum_{i=1}^{N_\alpha} \sum_{i=1}^{N_\beta} \left| \int \varphi_i^\alpha(\mathbf{r}) \varphi_j^\beta(\mathbf{r}) \, \mathrm{d}^3 r \right|^2.$$

(80)

In the spin-restricted case, where the α- and β-orbitals are equal and therefore mutually orthogonal, the last term equals the number of doubly occupied orbitals, and one obtains $\langle \hat{S}^2 \rangle = M_S(M_S + 1)\hbar^2$. In the unrestricted case, this cancellation is only partial and a larger expectation value is obtained. This is often referred to as "spin contamination."

For an unrestricted Slater determinant, the total electron density is given by,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_\alpha} |\varphi_i^\alpha(\mathbf{r})|^2 + \sum_{i=1}^{N_\beta} |\varphi_i^\beta(\mathbf{r})|^2,$$

(81)

and the spin density can be calculated as

$$Q(\mathbf{r}) = \sum_{i=1}^{N_\alpha} |\varphi_i^\alpha(\mathbf{r})|^2 - \sum_{i=1}^{N_\beta} |\varphi_i^\beta(\mathbf{r})|^2.$$

(82)

In contrast to the spin-restricted case, the spin density can now have different signs at different points in space. The kinetic energy of the unrestricted Slater determinant $\Phi_s^{(u)}$ is

$$T_s^{(u)} = \langle \Psi_s | \hat{T} | \Psi_s \rangle = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_\alpha} \int \varphi_i^\alpha(\mathbf{r}) \Delta \varphi_i^\alpha(\mathbf{r}) \, \mathrm{d}^3 r$$
$$- \frac{\hbar^2}{2m_e} \sum_{i=1}^{N_\beta} \int \varphi_i^\beta(\mathbf{r}) \Delta \varphi_i^\beta(\mathbf{r}) \, \mathrm{d}^3 r,$$

(83)

and a noninteracting kinetic-energy functional can now be defined as

$$T_s^{(u)}[\rho_\alpha, \rho_\beta] = \min_{\Psi_s^{(u)} \to \rho_\alpha, \rho_\beta} \langle \Psi_s^{(u)} | \hat{T} | \Psi_s^{(u)} \rangle$$

(84)

or as

$$T_s^{(u)}[\rho, Q] = \min_{\Psi_s^{(u)} \to \rho, Q} \langle \Psi_s^{(u)} | \hat{T} | \Psi_s^{(u)} \rangle.$$

(85)

In contrast to the spin-restricted case, this functional depends not only on the total electron density $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})$, but

also on the spin density $Q(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$. Usually, $T_s^{(u)}[\rho, Q]$ yields different kinetic energies for systems that share the same total electron density, but have different spin densities.

In terms of α- and β-electron densities, the total energy functional of the noninteracting system is given by

$$E_s^{(u)}[\rho_\alpha, \rho_\beta] = T_s^{(u)}[\rho_\alpha, \rho_\beta] + q_e \int \rho_\alpha(\mathbf{r}) v_s^\alpha(\mathbf{r}) \, \mathrm{d}^3 r$$
$$+ q_e \int \rho_\beta(\mathbf{r}) v_s^\beta(\mathbf{r}) \, \mathrm{d}^3 r.$$

(86)

The ground-state α- and β-densities $\rho_0^\alpha(\mathbf{r})$ and $\rho_0^\beta(\mathbf{r})$ of the noninteracting system can then be determined by minimizing this energy functional with respect to ρ_α and ρ_β, under the constraint that these integrate to the correct number of α- and β-electrons.

Exchange–Correlation Energy Functional. The spin-resolved HK functional [cf. Eq. (48)] of the true system of interacting electrons can now be decomposed as

$$F_{HK}[\rho_\alpha, \rho_\beta] = T_s^{(u)}[\rho_\alpha, \rho_\beta] + J[\rho] + E_{xc}^{(u)}[\rho_\alpha, \rho_\beta],$$

(87)

where the spin-resolved exchange–correlation energy is defined as

$$E_{xc}^{(u)}[\rho_\alpha, \rho_\beta] = F_{HK}[\rho_\alpha, \rho_\beta] - T_s^{(u)}[\rho_\alpha, \rho_\beta] - J[\rho].$$

(88)

As this functional $E_{xc}^{(u)}[\rho_\alpha, \rho_\beta]$ has been defined via the spin-unrestricted reference system, it is in general different from the functional $E_{xc}^{(u)}[\rho_\alpha, \rho_\beta]$ defined in the previous section. This difference arises because different definitions of the noninteracting kinetic energy are used in the two cases.

With this definition of the exchange–correlation energy, the total energy functional of the true system of interacting electrons is given by

$$E[\rho_\alpha, \rho_\beta] = T_s^{(u)}[\rho_\alpha, \rho_\beta] + J[\rho] + E_{xc}^{(u)}[\rho_\alpha, \rho_\beta]$$
$$+ q_e \int \rho(\mathbf{r}) v_{nuc}(\mathbf{r}) \, \mathrm{d}^3 r.$$

(89)

This total energy functional is identical to the spin-resolved version of the total energy functional derived in the spin-restricted case [cf., Eq. (71)], even though it is decomposed in a different fashion.

The ground-state α- and β-electron densities $\rho_0^\alpha(\mathbf{r})$ and $\rho_0^\beta(\mathbf{r})$ can then be determined by minimizing this total energy functional with respect to ρ_α and ρ_β, under the constraint that these integrate to N_α and N_β electrons, respectively. Note that by choosing N_α and N_β, a specific value of M_S is selected. As long as this M_S can be realized for the exact ground state, the resulting total ground-state density $\rho_0(\mathbf{r}) = \rho_0^\alpha(\mathbf{r}) + \rho_0^\beta(\mathbf{r})$ will be independent of the choice of M_S. In addition, the minimization will then yield the exact ground-state spin density $Q_0^{M_S}(\mathbf{r}) = \rho_0^\alpha(\mathbf{r}) - \rho_0^\beta(\mathbf{r})$.

KS Potential. The minimization of the total energy functional $E_s^{(u)}[\rho_\alpha, \rho_\beta]$ of the spin-unrestricted noninteracting reference system leads to these Euler–Lagrange equations

$$\frac{\delta E_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\boldsymbol{r})} - \mu_\alpha = \frac{\delta T_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\boldsymbol{r})} + q_e\, v_s^\alpha(\boldsymbol{r}) - \mu_\alpha = 0 \qquad (90)$$

$$\frac{\delta E_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\boldsymbol{r})} - \mu_\beta = \frac{\delta T_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\boldsymbol{r})} + q_e\, v_s^\beta(\boldsymbol{r}) - \mu_\beta = 0. \qquad (91)$$

For the interacting system, the minimization of $E[\rho_\alpha,\ \rho_\beta]$ with respect to the α- and β-electron densities yields

$$\frac{\delta E[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\boldsymbol{r})} - \mu_\alpha = \frac{\delta T_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\boldsymbol{r})} + q_e\big(v_{\mathrm{nuc}}(\boldsymbol{r})$$
$$+ v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^\alpha[\rho_\alpha, \rho_\beta](\boldsymbol{r})\big) - \mu_\alpha = 0, \qquad (92)$$

$$\frac{\delta E[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\boldsymbol{r})} - \mu_\beta = \frac{\delta T_s^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\boldsymbol{r})} + q_e\big(v_{\mathrm{nuc}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r})$$
$$+ v_{\mathrm{xc}}^\beta[\rho_\alpha, \rho_\beta](\boldsymbol{r})\big) - \mu_\beta = 0. \qquad (93)$$

with the spin components of the exchange–correlation potential

$$v_{\mathrm{xc}}^\alpha[\rho_\alpha, \rho_\beta](\boldsymbol{r}) = \frac{1}{q_e}\frac{\delta E_{\mathrm{xc}}^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\boldsymbol{r})} \qquad \text{and}$$
$$v_{\mathrm{xc}}^\beta[\rho_\alpha, \rho_\beta](\boldsymbol{r}) = \frac{1}{q_e}\frac{\delta E_{\mathrm{xc}}^{(u)}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\boldsymbol{r})}. \qquad (94)$$

If we require that $\rho_\alpha(\boldsymbol{r})$ and $\rho_\beta(\boldsymbol{r})$—and thus both the total and the spin density of the ground state—are the same for the noninteracting reference system and the true interacting system, we find that the spin components of the KS potential are given by

$$v_s^\alpha[\rho^\alpha, \rho^\beta](\boldsymbol{r}) = v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^\alpha[\rho^\alpha, \rho^\beta](\boldsymbol{r}) \qquad (95)$$

$$v_s^\beta[\rho^\alpha, \rho^\beta](\boldsymbol{r}) = v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^\beta[\rho^\alpha, \rho^\beta](\boldsymbol{r}). \qquad (96)$$

Therefore, the exact ground-state α- and β-electron densities of the true interacting system can be calculated by solving the Schrödinger equation of an auxilliary system of noninteracting electrons with the Hamiltonian of Eq. (77). The ground-state wavefunction $\Psi_{s,0}^{(u)}$ of this KS reference system is given by an unrestricted Slater determinant, constructed from the orbitals obtained from the KS equations,

$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e\big(v_{\mathrm{nuc}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^\alpha[\rho_\alpha, \rho_\beta](\boldsymbol{r})\big)\right]\varphi_i^\alpha(\boldsymbol{r}) = \epsilon_i^\alpha \varphi_i^\alpha(\boldsymbol{r})$$
$$\left[-\frac{\hbar^2}{2m_e}\Delta + q_e\big(v_{\mathrm{nuc}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^\beta[\rho_\alpha, \rho_\beta](\boldsymbol{r})\big)\right]\varphi_i^\beta(\boldsymbol{r}) = \epsilon_i^\beta \varphi_i^\beta(\boldsymbol{r}). \qquad (97)$$

Here, the equations for the α- and β-orbitals are coupled through the Coulomb and exchange–correlation potentials.

Equivalently, the KS potential can be expressed as a component that acts on the total electron density,

$$v_s^{\mathrm{tot}}[\rho, Q](\boldsymbol{r}) = \frac{1}{2}\big(v_s^\alpha(\boldsymbol{r}) + v_s^\beta(\boldsymbol{r})\big)$$
$$= v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{Coul}}[\rho](\boldsymbol{r}) + v_{\mathrm{xc}}^{\mathrm{tot}}[\rho, Q](\boldsymbol{r}), \qquad (98)$$

and one that acts on the spin density,

$$v_s^{\mathrm{spin}}[\rho, Q](\boldsymbol{r}) = \frac{1}{2}\big(v_s^\alpha(\boldsymbol{r}) - v_s^\beta(\boldsymbol{r})\big) = v_{\mathrm{xc}}^{\mathrm{spin}}[\rho, Q](\boldsymbol{r}), \qquad (99)$$

where the total and spin exchange–correlation potential are given by

$$v_{\mathrm{xc}}^{\mathrm{tot}}[\rho, Q](\boldsymbol{r}) = \frac{1}{q_e}\frac{\delta E_{\mathrm{xc}}^{(u)}[\rho, Q]}{\delta \rho(\boldsymbol{r})} \ \text{ and } \ v_{\mathrm{xc}}^{\mathrm{spin}}[\rho, Q](\boldsymbol{r}) = \frac{1}{q_e}\frac{\delta E_{\mathrm{xc}}^{(u)}[\rho, Q]}{\delta Q(\boldsymbol{r})}. \qquad (100)$$

These expressions will be used in the following section for comparing with the spin-restricted theory.

Even though the electron density and spin density calculated from this $\Psi_{s,0}^{(u)}$ are equal to those of the fully interacting system, it is important to realize that $\Psi_{s,0}^{(u)}$ does not agree with the ground-state wavefunction Ψ_0 of the true interacting system. In particular, Ψ_0 can always be chosen as an eigenfunction of $\hat{\mathbf{S}}^2$, whereas by construction, $\Psi_{s,0}^{(u)}$ is not an eigenfunction of $\hat{\mathbf{S}}^2$ for $S > 0$. Thus, within an exact formulation of unrestricted KS-DFT, the wavefunction of the KS reference system is always spin contaminated for $S > 0$.

Comparison of restricted and unrestricted formulation

The restricted and the unrestricted formulation of KS-DFT are based on different definitions of the noninteracting reference system for open-shell systems. In the spin-restricted case, the reference system is chosen such that its total electron density $\rho_s(\boldsymbol{r})$ agrees with the one of the fully interacting system, while its spin density $Q_s(\boldsymbol{r})$ usually differs from the one of the interacting system. Conversely in the spin-unrestricted case, the reference system is defined such that both its total electron density and its spin density agree with those of the fully interacting system.

These different definitions of the noninteracting reference system have implications for the treatment of spin in KS-DFT. In the spin-restricted case, the wavefunction Ψ_s of the noninteracting reference system can always be chosen as an eigenfunction of $\hat{\mathbf{S}}^2$. Nevertheless, the corresponding eigenvalue $\langle\hat{\mathbf{S}}^2\rangle = S(S+1)\hbar^2$ does not necessarily agree with the one obtained for the true interacting system. However, it is possible to require this equality with an additional constraint on the noninteracting reference system. In the spin-unrestricted case, the wavefunction $\Psi_s^{(u)}$ of the reference system is not an eigenfunction of $\hat{\mathbf{S}}^2$, that is, it is spin-contaminated. This is a direct consequence of the requirement that the correct spin density is obtained. Thus, the expectation value of $\hat{\mathbf{S}}^2$ becomes a complicated functional of the electron density.[115,116] Of course, the exact ground state density will still correspond to an interacting wavefunction that is an eigenfunction of $\hat{\mathbf{S}}^2$.

In both the restricted and unrestricted case, the wavefunction of the noninteracting reference system is an eigenfunction of $\hat{S}_z$. Only in the spin-unrestricted case, it is guaranteed that the corresponding eigenvalue M_S is the same as for the fully interacting system, but also in the spin-restricted case it can be chosen accordingly. These differences between the restricted and unrestricted formulation are summarized in Table 1. One important observation is that it is impossible to

Table 1. Comparison of the spin-restricted and spin-unrestricted formulations of KS-DFT. "Correct" indicates that the quantity calculated for the noninteracting reference system agrees with the corresponding one of the fully interacting system.

	Spin-restricted KS-DFT	Spin-unrestricted KS-DFT
Correct $\rho_s(\mathbf{r})$?	Yes	Yes
Correct $Q_s(\mathbf{r})$?	No	Yes
Ψ_s is eigenfunction of $\hat{\mathbf{S}}^2$?	Yes	No
Correct $\langle \hat{\mathbf{S}}^2 \rangle$?	Maybe	No
Ψ_s is eigenfunction of $\hat{S}_z$?	Yes	Yes
Correct $\langle \hat{S}_z \rangle$?	Maybe	Yes

set up a KS-DFT formalism such that for the noninteracting reference system one obtains both the correct spin density and a wavefunction that is an eigenfunction of $\hat{\mathbf{S}}^2$ (see also the discussion of this issue in Refs. [88,112]).

The different definitions of the noninteracting reference system in the restricted and unrestricted formulations of KS-DFT also imply different definitions of the noninteracting kinetic energy, exchange–correlation energy, and exchange–correlation potential. These definitions are collected in Table 2. First of all, the use of different reference systems leads to different definitions of the noninteracting kinetic energy. In the spin-restricted case, $T_s[\rho]$ is defined as the kinetic energy of a system of noninteracting electrons with the total electron density $\rho(\mathbf{r})$ and is independent of the spin density $Q(\mathbf{r})$. In contrast, in the spin-unrestricted case $T_s^{(u)}[\rho, Q]$ is defined as the kinetic energy of a system of noninteracting electrons with the total electron density $\rho(\mathbf{r})$ and the spin density $Q(\mathbf{r})$. These differ by the 'unrestricted' contribution to the noninteracting kinetic energy,

$$T_u[\rho, Q] = T_s[\rho] - T_s^{(u)}[\rho, Q]. \tag{101}$$

Only if the spin density vanishes, the restricted and unrestricted definitions of the noninteracting kinetic energy are identical, that is, $T_u[\rho, Q = 0] = 0$.

Because of these different definitions of the noninteracting kinetic energy, a different decomposition of the HK functional is introduced in the restricted and unrestricted formalisms, respectively, which in turn leads to different definitions of the exchange–correlation energy. These are related by

$$E_{xc}^{(u)}[\rho, Q] = E_{xc}[\rho, Q] + T_u[\rho, Q]. \tag{102}$$

One important difference between the two formalisms is that in spin-restricted KS-DFT, the exchange–correlation energy $E_{xc}[\rho, Q]$ is the only contribution to the HK functional that depends on the spin density, whereas in the spin-unrestricted theory both the exchange–correlation energy $E_{xc}^{(u)}[\rho, Q]$ and the noninteracting kinetic energy $T_s^{(u)}[\rho, Q]$ depend on the spin density. Therefore, the fractional spin condition of Eq. (55), formulated for the HK functional earlier, leads to different exact conditions for the exchange–correlation functional. In the spin-restricted case, the fractional spin condition applies directly to the exchange–correlation energy,

$$E_{xc}\left[\rho, \alpha Q^{M_S=S}[\rho]\right] = \text{const.} \quad \text{for } -1 \leq \alpha \leq +1, \tag{103}$$

whereas in the spin-unrestricted case, it applies to the sum of the exchange–correlation energy and the noninteracting kinetic energy,

$$T_s^{(u)}\left[\rho, \alpha Q^{M_S=S}[\rho]\right] + E_{xc}^{(u)}\left[\rho, \alpha Q^{M_S=S}[\rho]\right] = \text{const.}$$
$$\text{for } -1 \leq \alpha \leq +1. \tag{104}$$

Finally, the exchange–correlation potential (and thus also the resulting KS potential) differs in the two formalisms. In spin-restricted KS-DFT, the exchange–correlation potential $v_{xc}[\rho]$ depends only on the total electron density and acts on electrons of both spin. Conversely, in spin-unrestricted KS-DFT the exchange–correlation potential is different for α- and β-electrons, that is, it has two distinct components. The component of the exchange–correlation potential acting on the total electron density is given by,

$$v_{xc}^{\text{tot}}[\rho, Q](\mathbf{r}) = \frac{1}{q_e} \frac{\delta E_{xc}^{(u)}[\rho, Q]}{\delta \rho(\mathbf{r})} = \frac{1}{q_e} \left(\frac{\delta E_{xc}[\rho, Q]}{\delta \rho(\mathbf{r})} + \frac{\delta T_u[\rho, Q]}{\delta \rho(\mathbf{r})} \right)$$
$$= v_{xc}[\rho, Q](\mathbf{r}) + v_u[\rho, Q](\mathbf{r}). \tag{105}$$

Here, the first term is the exchange–correlation potential in the spin-restricted formalism, while the second term $v_u[\rho, Q](\mathbf{r}) = (1/q_e)\, \delta T_u[\rho, Q]/\delta \rho(\mathbf{r})$ is given by the functional derivative of $T_u[\rho, Q]$. It appears because of the different definitions of the exchange–correlation energy in the restricted and unrestricted theories. The component of the exchange–correlation potential acting on the spin density is given by

Table 2. Definition of the noninteracting kinetic energy, exchange–correlation energy, and exchange–correlation potential in the spin-restricted and spin-unrestricted formulations of KS-DFT.

	Spin-restricted KS-DFT	Spin-unrestricted KS-DFT
Noninteracting kinetic energy	$T_s[\rho] = \min\limits_{\Psi_s \to \rho} \langle \Psi_s | \hat{T} | \Psi_s \rangle$	$T_s^{(u)}[\rho, Q] = \min\limits_{\Psi_s^{(u)} \to \rho, Q} \langle \Psi_s^{(u)} | \hat{T} | \Psi_s^{(u)} \rangle$
Decomposition of HK functional	$F_{HK}[\rho, Q] = T_s[\rho] + J[\rho] + E_{xc}[\rho, Q]$	$F_{HK}[\rho, Q] = T_s^{(u)}[\rho, Q] + J[\rho] + E_{xc}^{(u)}[\rho, Q]$
Exchange–correlation energy	$E_{xc}[\rho, Q] = F_{HK}[\rho, Q] - T_s[\rho] - J[\rho]$	$E_{xc}^{(u)}[\rho, Q] = F_{HK}[\rho, Q] - T_s^{(u)}[\rho, Q] - J[\rho]$
Exchange–correlation potential	$v_{xc}[\rho] = \dfrac{1}{q_e} \dfrac{\delta E_{xc}[\rho, Q]}{\delta \rho(\mathbf{r})}$	$v_{xc}^{\text{tot}}[\rho, Q] = \dfrac{1}{q_e} \dfrac{\delta E_{xc}^{(u)}[\rho, Q]}{\delta \rho(\mathbf{r})}$
		$v_{xc}^{\text{spin}}[\rho, Q] = \dfrac{1}{q_e} \dfrac{\delta E_{xc}^{(u)}[\rho, Q]}{\delta Q(\mathbf{r})}$

$$v_{xc}^{spin}[\rho, Q](\boldsymbol{r}) = \frac{1}{q_e} \frac{\delta E_{xc}^{(u)}[\rho, Q]}{\delta Q(\boldsymbol{r})} = \frac{1}{q_e} \left(\frac{\delta E_{xc}[\rho, Q]}{\delta Q(\boldsymbol{r})} + \frac{\delta T_u[\rho, Q]}{\delta Q(\boldsymbol{r})} \right).$$
(106)

For the ground-state electron and spin densities, the first term vanishes according to Eq. (76), and the above expression for $v_{xc}^{spin}[\rho, Q](\boldsymbol{r})$ reduces to the Euler–Lagrange equation for the spin density [*cf*. Eqs. (92) and (93)].

In summary, the KS potential in the spin-unrestricted case differs from the spin-restricted KS potential $v_{xc}[\rho, Q](\boldsymbol{r})$ by (a) an additional component $v_{xc}^{spin}[\rho, Q](\boldsymbol{r})s_z$ acting on the spin density, and (b) a correction to the spin-independent potential $v_u[\rho, Q](\boldsymbol{r})$. Thus, starting from a spin-restricted reference system with the total electron density $\rho(\boldsymbol{r})$ and with a spin density that differs from the spin density $Q_s(\boldsymbol{r})$ of the interacting system, the KS potential is modified such that its spin density becomes equal to the one of the fully interacting system $Q(\boldsymbol{r})$. To achieve this, the spin potential $v_{xc}^{spin}[\rho, Q](\boldsymbol{r})\sigma_z$ has to be introduced. However, with the total potential kept fixed, this would lead to a change of the total electron density, and to keep $\rho(\boldsymbol{r})$ unchanged, the correction $v_u[\rho, Q](\boldsymbol{r})$ is needed.

Spin states in KS-DFT

So far, we have only considered a spin-state independent theory, that is, with the exact exchange–correlation functionals, the spin-restricted and spin-unrestricted KS-DFT formalism discussed above will lead to the ground-state, irrespective of its spin symmetry. As discussed earlier, targeting the lowest state of a given spin symmetry (i.e., with a specific eigenvalue $S(S + 1)$ of $\hat{\boldsymbol{S}}^2$) requires a spin-state specific HK functional $F_{HK}^S[\rho]$ as defined in Eq. (58).

In the spin-restricted case, this is formally possible by using the spin-state independent definition of the noninteracting kinetic energy, which results in a spin-state specific exchange–correlation functional. In practice, a different strategy is followed: The noninteracting reference system is defined such that it is described by a single Slater determinant with $M_S = S$. This can be achieved by defining the spin-state specific noninteracting kinetic energy as

$$T_s^S[\rho] = \min_{\Phi^{M_S=S} \to \rho} \left\langle \Phi^{M_S=S} | \hat{T} | \Phi^{M_S=S} \right\rangle,$$
(107)

where $\Phi^{M_S=S}$ is a Slater determinant with $M_S = S$. Such a Slater determinant is always an eigenfunction of $\hat{\boldsymbol{S}}^2$ with eigenvalue $S(S + 1)$. Thus, it is ensured that the wavefunction of the noninteracting reference system has the same spin symmetry as the wavefunction of the true interacting system. However, as always in spin-restricted KS-DFT, for $S > 0$ the spin density $\Phi^{M_S=S}$ of the noninteracting reference system will differ from the one of the fully interacting system.

With this definition of a spin-state specific noninteracting kinetic energy, the spin-state specific exchange–correlation energy is given by

$$E_{xc}^S[\rho] = F_{HK}^S[\rho] - T_s^S[\rho] - J[\rho].$$
(108)

One protocol for constructing this spin-state dependent exchange–correlation functional then proceeds using the spin density $\Phi^{M_S=S}$ of the noninteracting reference system to distinguish the different spin states. To this end, $E_{xc}^S[\rho]$ is expressed as

$$E_{xc}^S[\rho] = E_{xc}^{(ss)}\left[\rho, Q_s^{M_S=S}[\rho]\right].$$
(109)

Here, $E_{xc}^{(ss)}[\rho, Q]$ is not equal to the spin-resolved exchange–correlation functional $E_{xc}[\rho, Q]$ defined in Eq. (70). Its dependence on Q does not describe the spin-density dependence of the exchange–correlation energy, but instead introduces the spin-state dependence. This is indicated by the superscript "(ss)." The multiplet-DFT scheme of Daul[117,118] and the restricted open-shell KS (ROKS) scheme[119–124] as well as related approaches[125,126] proceed along these lines, but usually include additional ideas originating from Hartree–Fock theory.[127,128]

It appears that if applied in a spin-restricted formalism, all available approximate exchange–correlation functionals have to be understood as approximations to $E_{xc}^{(ss)}[\rho, Q]$ and not as approximations to $E_{xc}[\rho, Q]$. This has important consequences for the construction of such approximate exchange–correlation functional. In particular, one has to realize that $E_{xc}^{(ss)}[\rho, Q]$ does not fulfill the fractional spin condition and thus this condition should not be included when constructing approximations to it.

In addition, in spin-restricted KS-DFT the ground-state spin density is not directly available and has to be determined after calculating the ground-state electron density by minimizing $E_{xc}[\rho, Q]$ with respect to Q [cf. Eq. (76)]. In this step, one has to use $E_{xc}[\rho, Q]$—which includes the correct spin-density dependence—instead of $E_{xc}^{(ss)}[\rho, Q]$. Thus, the construction of a different class of approximate exchange–correlation functionals that include the spin-density dependence by approximating $E_{xc}[\rho, Q]$ (or its spin-state specific analog $E_{xc}^S[\rho, Q]$) instead of $E_{xc}^{(ss)}[\rho, Q]$ would be required. Of course, the fractional spin condition applies to $E_{xc}[\rho, Q]$ and $E_{xc}^S[\rho, Q]$, and should also be incorporated when constructing such approximations.

In spin-unrestricted KS-DFT, it is not possible to require that the noninteracting reference system is an eigenfunction of $\hat{\boldsymbol{S}}^2$.[88,112] Thus, it is not possible to define a spin-state specific analog of $T_s^{(u)}[\rho, Q]$. Consequently, the spin-state dependence only enters the exchange–correlation functional, which becomes

$$E_{xc}^{(u),S}[\rho, Q] = F_{HK}^S[\rho, Q] - T_s^{(u)}[\rho, Q] - J[\rho].$$
(110)

For constructing approximations to this spin-state specific exchange–correlation functional, usually a strategy similar to the one in spin-restricted KS-DFT is applied. To this end, the description is restricted to the case of $M_S = S$, that is, only the maximal eigenvalue of $\hat{S}_z$ is allowed. Then, the spin-state specific exchange–correlation functional can be expressed as

$$E_{xc}^{(u),S}[\rho, Q] = E_{xc}^{(u,ss)}\left[\rho, Q^{M_S=S}\right].$$
(111)

Here, different spin states can be distinguished based on the integral of the spin density. However, the functional $E_{xc}^{(u),ss}[\rho, Q]$ does not describe the correct spin-density

dependence of $E_{xc}^{(u)}[\rho, Q]$ anymore. Neither does $E_{xc}^{(u),S}[\rho, Q]$, which is limited to spin densities corresponding to $M_S = S$. However, the spin densities Q^{M_S} corresponding to other eigenvalues of $\hat{S}_z$ can be obtained from the scaling relation of Eq. (35). Again, it is important to realize that the fractional spin condition does not apply to $E_{xc}^{(u),ss}[\rho, Q]$.

The idea of using the spin density as a means to distinguish different spin states in a spin-unrestricted KS-DFT formalism is taken even further in broken-symmetry DFT,[24,40,44] where the requirement that the spin density of the noninteracting reference system matches the correct spin density of the fully interacting system is sacrificed in favor of obtaining accurate energetics for low-spin states. Consequently, it has been suggested that in this case, the spin density in fact serves to describe the (spin-state specific) on-top pair density.[129] If broken-symmetry DFT calculations are interpreted in this way, one would need to determine the spin density in a separate step from the minimization of $E_{xc}[\rho, Q]$ (or its spin-state specific analog $E_{xc}^S[\rho, Q]$), as discussed above for spin-restricted KS-DFT.

Spin in Relativistic DFT

Spin and current in relativistic quantum mechanics

So far, the discussion has focused on spin in nonrelativistic DFT. For the sake of completeness, we now consider the generalization to the more fundamental relativistic regime. The relativistic theory relies on Dirac's semiclassical theory of the electron (see Ref. [57] for a detailed account). This quantum theory describes the relativistic motion of the electron in a classical external electromagnetic field, represented by the scalar and vector potentials $\phi_{ext}(\mathbf{r})$ and $\mathbf{A}_{ext}(\mathbf{r})$. The equation of motion reads in this case (in Gaussian units),

$$\hat{h}^D \psi(\mathbf{r}, t) = \left[c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta m_e c^2 + q_e \left(\phi_{ext}(\mathbf{r}) - \boldsymbol{\alpha} \cdot \mathbf{A}_{ext}(\mathbf{r}) \right) \right] \psi(\mathbf{r}, t)$$
$$= i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t), \tag{112}$$

which yields an energy eigenvalue equation for determining the stationary states when the right hand side is replaced by $E\psi(\mathbf{r},t)$. The Dirac Hamiltonian $\hat{h}^D$ consists of the kinetic energy operator $c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}}$, the rest energy term $\beta m_e c^2$, and the interaction operator $q_e(\phi_{ext}(\mathbf{r}) - \alpha \cdot \mathbf{A}_{ext}(\mathbf{r}))$, where c is the speed of light and $\hat{\mathbf{p}} = -i\hbar\nabla$ is the momentum operator as before. The Dirac matrices are contained in the parameters $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β, which are in the standard representation,

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 1_2 & 0 \\ 0 & -1_2 \end{pmatrix}, \tag{113}$$

where σ_i are the the Pauli spin matrices σ_x, σ_y, and σ_z defined in Eq. (4). A consequence of these four-dimensional operators is that the Dirac Hamiltonian $\hat{h}^D$ is a 4×4 matrix operator with a four-component eigenvector $\psi(\mathbf{r},t)$, the so-called 4-spinor. Such a four-component description naturally includes spin, which had to be introduced in an *ad hoc* fashion in the nonrelativistic theory.

In analogy to the nonrelativistic case, one can define the relativistic spin operator as

$$\hat{\mathbf{s}} = \frac{\hbar}{2} \boldsymbol{\sigma}^{(4)} = \frac{\hbar}{2} (\sigma_x^{(4)}, \sigma_y^{(4)}, \sigma_z^{(4)})^T \quad \text{with} \quad \boldsymbol{\sigma}_i^{(4)} = \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}. \tag{114}$$

This operators still obey the commutation relations of an angular momentum. However, in the relativistic case $\hat{\mathbf{s}}^2$ and $\hat{s}_z$ do not commute with the Hamiltonian. Therefore, eigenstates of $\hat{h}^D$ cannot be chosen as eigenfunctions of $\hat{\mathbf{s}}^2$ and $\hat{s}_z$ anymore and spin is thus not a good quantum number in relativistic theory. In spherically symmetric systems such as atoms, one can consider the total angular momentum instead. This also has the consequence that, in contrast to the nonrelativistic case, the expectation value of $\hat{s}_z$ will depend on the choice of the quantization axis.

In the case of many electrons, the relativistic wavefunction again assumes a tensor structure, that is, for N electrons, the wavefunction formally has 4^N components. It has to fulfill the Pauli principle by being antisymmetric with respect to the exchange of any two electron. The relativistic many-electron Hamiltonian is then given by (neglecting projectors on positive-energy solutions for the sake of brevity),

$$\hat{H}^D = \sum_{i=1}^{N} \hat{h}^D(i) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \hat{g}(i,j), \tag{115}$$

where $\hat{h}^D(i)$ is the one-electron Hamiltonian of Eq. (112) acting on electron i and $\hat{g}(i,j)$ is the operator describing the interaction between electrons i and j. The form of the exact electron–electron interaction operator can be derived from quantum electrodynamics, but usually only approximate forms are employed in practice. The simplest approximation is to employ the nonrelativistic Coulomb operator. However, the resulting Dirac–Coulomb Hamiltonian is not Lorentz invariant. This approximation is improved by the Dirac–Coulomb–Gaunt Hamiltonian, which also includes the unretarded magnetic interaction between electrons, whereas the Dirac–Coulomb–Breit Hamiltonian approximately describes the retarded electromagnetic interaction (for a detailed discussion, see chapter 8 in Ref. [57]).

As in nonrelativistic theory, an electron density and a current density can be defined in the relativistic many-electron theory such that they fulfill a continuity equation. This results in the definition of the electron density as[57,130]

$$\rho(\mathbf{r}) = N \int \Psi^\dagger(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N) \, d^3 r_2 ... d^3 r_N \tag{116}$$

and of the current density as

$$\mathbf{j}(\mathbf{r}) = c N \int \Psi^\dagger(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N) \boldsymbol{\alpha}_1 \Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N) \, d^3 r_2 ... d^3 r_N \tag{117}$$

where $\boldsymbol{\alpha}_1$ indicates that the Dirac matrices act on the first electron and the dagger denotes the transposed and complex conjugate spinor. This definition of the current density still holds in the presence of external magnetic fields.

Relativistic current-DFT

A central aspect of relativistic theories is that all fundamental physical equations must preserve their form under Lorentz transformations from one inertial frame of reference to another one. This requires that the equations are castable in tensorial form. Hence, all quantities are joined to 4-vectors, which are basic physical quantities in any relativistic theory. For instance, the electromagnetic potentials are joined to yield the 4-potential $A^\mu = (\phi, \boldsymbol{A})$. This is the reason why a relativistic theory has to include both the scalar and vector potentials simultaneously. The density $\rho(\boldsymbol{r})$ is also part of a 4-vector, namely of the 4-current $j^\mu(\boldsymbol{r})$. The other three components are given by the current density $\boldsymbol{j}(\boldsymbol{r})$ such that $j^\mu = (c\rho, \boldsymbol{j})$.

Now, a similar decomposition of the energy expectation value as in the nonrelativistic case can be performed,

$$E = \langle \Psi | \hat{H}^D | \Psi \rangle = \langle \Psi | \hat{T}^D | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ee}} | \Psi \rangle, \quad (118)$$

where $\hat{T}^D$ is the relativistic "kinetic energy" operator, collecting all terms of the one-electron Hamiltonian $\hat{h}^D$ containing the Dirac matrices α and β (i.e., the kinetic energy and the rest energy terms), $\hat{V}_{\text{ext}}$ consists of the remaining one-electron terms and describes the interaction with the external electromagnetic potentials, and $\hat{V}_{\text{ee}}$ is the electron–electron interaction operator. The second term can be calculated directly from the 4-current, without the need to know the full wavefunction, as

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \frac{q_e}{c} \int j_\mu(\boldsymbol{r}) A_{\text{ext}}^\mu(\boldsymbol{r}) \, \mathrm{d}^3 r$$
$$= q_e \int \rho(\boldsymbol{r}) \phi_{\text{ext}}(\boldsymbol{r}) \, \mathrm{d}^3 r + \frac{q_e}{c} \int \boldsymbol{j}(\boldsymbol{r}) \cdot \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}) \, \mathrm{d}^3 r = V_{\text{ext}}[j^\mu], \quad (119)$$

where Einstein's convention of implicit summation over repeated lower and upper indices has been used. The first term is the same as in the nonrelativistic case and describes the electrostatic interaction of the electron density with the external potential, whereas the second term accounts for the interaction of the current density with the external magnetic field.

A 4-current may be understood as the source of a 4-potential which can be calculated from the relativistic generalization of the Poisson equation of electrostatics,

$$\Box A^\mu(\boldsymbol{r}) = \frac{4\pi}{c} j^\mu(\boldsymbol{r}), \quad (120)$$

with the D'Alembertian operator being the Minkowski space generalization of the three-dimensional Laplacian, that is, it is defined as $\Box = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \Delta$. From the solution of this equation, one obtains for the 4-potential generated by the electronic 4-current j^μ,

$$A^\mu[j^\mu] = \frac{q_e}{c} \int \frac{j^\mu(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}^3 r'. \quad (121)$$

The classical interaction energy $J[j^\mu]$ of the 4-current j^μ with itself (i.e., the relativistic analog of the classical Coulomb interaction in nonrelativistic theory) is then given by

$$J[j^\mu] = \frac{q_e^2}{2c^2} \int \frac{j_\mu(\boldsymbol{r}) j^\mu(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}^3 r \, \mathrm{d}^3 r'$$
$$= \frac{q_e^2}{2} \int \frac{\rho(\boldsymbol{r}) \rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}^3 r \, \mathrm{d}^3 r' + \frac{q_e^2}{2c^2} \int \frac{\boldsymbol{j}(\boldsymbol{r}) \cdot \boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}^3 r \, \mathrm{d}^3 r'. \quad (122)$$

Here, the first term is the classical electrostatic (Coulomb) interaction $J[\rho]$, whereas the second term accounts for the magnetic interaction of the electrons. Note that this second term should only be present if the Gaunt or Breit interaction has been included in the Hamiltonian.

The analogy between $V_{\text{ext}}[j^\mu]$ and $J[j^\mu]$ [Eqs. (119) and (122)] and their nonrelativistic counterparts $V_{\text{ext}}[\rho]$ and $J[\rho]$ suggests that the fundamental quantity for a relativistic formulation of DFT is actually the 4-current, that is, the combination of the electronic density $\rho(\boldsymbol{r})$ and the current density $\boldsymbol{j}(\boldsymbol{r})$. For this reason, the relativistic generalization of standard DFT has been known as current-DFT (CDFT).[131–134]

It can be shown that in relativistic theory, an analog of the HK theorem exists: the 4-current $j^\mu(\boldsymbol{r})$ uniquely determines the external 4-potential $A^\mu(\boldsymbol{r})$ up to a gauge transformation.[131] Therefore, it is possible to consider the energy $E[j^\mu]$ as a functional of the 4-current $j^\mu(\boldsymbol{r})$. As in the nonrelativistic case, one then proceeds by introducing a reference system of noninteracting electrons with the relativistic Hamiltonian

$$\hat{H}_s^D = \sum_{i=1}^{N} c\boldsymbol{\alpha}(i) \cdot \hat{\boldsymbol{p}}_i + \beta(i) m_e c^2 + q_e \left(\phi_s(\boldsymbol{r}_i) - \boldsymbol{\alpha}(i) \cdot \boldsymbol{A}_s(\boldsymbol{r}_i) \right). \quad (123)$$

The eigenfunctions of this noninteracting Hamiltonian are given by Slater determinants $\Psi_s = |\varphi_1, \varphi_2, \dots, \varphi_N|$ constructed from 4-spinors $\varphi_i(\boldsymbol{r})$, which solve the relativistic one-electron KS equations

$$\left[c\boldsymbol{\alpha} \cdot \hat{\boldsymbol{p}} + \beta m_e c^2 + q_e \left(\phi_s(\boldsymbol{r}) - \boldsymbol{\alpha} \cdot \boldsymbol{A}_s(\boldsymbol{r}) \right) \right] \varphi_i(\boldsymbol{r}) = \epsilon_i \varphi_i(\boldsymbol{r}). \quad (124)$$

For the resulting single Slater determinant, the electron density is given by

$$\rho(\boldsymbol{r}) = \sum_i^{\text{occ}} \varphi_i^\dagger(\boldsymbol{r}) \varphi_i(\boldsymbol{r}), \quad (125)$$

an the relativistic current density reads

$$\boldsymbol{j}(\boldsymbol{r}) = c \sum_i^{\text{occ}} \varphi_i^\dagger(\boldsymbol{r}) \, \boldsymbol{\alpha} \, \varphi_i(\boldsymbol{r}). \quad (126)$$

The noninteracting kinetic energy $T_s[j^\mu]$ can then be defined as the kinetic energy $T_s = \langle \Psi_s | \hat{T}^D | \Psi_s \rangle$ of such a noninteracting system with the 4-current j^μ, which allows for a similar decomposition of the total energy functional as in nonrelativistic DFT, i.e.,

$$E[j^\mu] = T_s[j^\mu] + V_{\text{ext}}[j^\mu] + J[j^\mu] + E_{\text{xc}}[j^\mu]. \quad (127)$$

Here, the exchange–correlation energy functional is defined as containing all the energy contributions not accounted for

by the first three terms. In analogy to nonrelativistic KS-DFT, it can then be shown that the 4-current $j^\mu(\mathbf{r})$ of the true interacting system can be determined from the self-consistent solution of the relativistic KS equations for a noninteracting system,[131,135] with the 4-potential

$$A_s^\mu(\mathbf{r}) = A_\text{ext}^\mu(\mathbf{r}) + A^\mu[j^\mu](\mathbf{r}) + \frac{1}{q_e} \frac{\delta E_\text{xc}[j^\mu]}{\delta j^\mu(\mathbf{r})}. \tag{128}$$

The functional derivatives of the exchange–correlation functional with respect to the components of the 4-current defines the exchange–correlation potential $v_\text{xc}^\mu[j^\mu](\mathbf{r})$, which now assumes a four-component form.

Electron density and spin density in relativistic DFT

In view of the previous discussions concerning nonrelativistic KS-DFT, we now face the following question: (i) Is it still possible to formulate a relativistic DFT in terms of the electron density only, (ii) how is the fundamental 4-current related to the density and spin density considered as fundamental quantities in nonrelativistic DFT, and (iii) how do the nonrelativistic restricted and unrestricted formulations of KS-DFT emerge from the relativistic framework?

Regarding the first question, under some additional assumptions it is indeed possible to prove a relativistic HK theorem for the electron density only[135–137]: In the case considered throughout this article, the external potential is the electrostatic potential of all atomic nuclei in a molecule that are at rest (Born–Oppenheimer approximation). As the nuclei are not moving, they do not create magnetic fields. In addition, we neglect any magnetic fields that stem from nuclear spins and assume that there are no additional external electromagnetic fields. As a consequence, the external electromagnetic 4-potential A^μ only contains the time-independent scalar potential of the atomic nuclei, that is, $\phi_\text{ext}(\mathbf{r}) = v_\text{nuc}(\mathbf{r})$ and $\mathbf{A}(\mathbf{r}) = 0$. This assumption is also common practice in almost every relativistic quantum chemical calculation. Then, it can be shown that the external scalar potential $\phi_\text{ext}(\mathbf{r})$ within this specific reference frame is (up to a constant) uniquely determined by the electron density $\rho(\mathbf{r})$ only.[135–137] Within such a framework, the relativistic total energy functional becomes

$$E[\rho] = T_s[j^\mu[\rho]] + V_\text{ext}[\rho] + J[j^\mu[\rho]] + E_\text{xc}[j^\mu[\rho]]. \tag{129}$$

Here, the current density $\mathbf{j}(\mathbf{r})$ is still required, but it is now uniquely determined by the electron density (i.e., $\mathbf{j} = \mathbf{j}[\rho]$), in the same way in which the spin density is determined by the electron density in nonrelativistic DFT. If a magnetic interaction between the electron is not included (i.e., the Dirac–Coulomb Hamiltonian is employed), also the analog of the Coulomb interaction reduces to a functional $J[\rho]$ of the density only.[135] Moreover, it now becomes possible to set up theories in which not only the full 4-current is used as fundamental variable but also the parts of it that are related to the total electron den-

sity and the spin density. This will be discussed further in the following subsection.

To understand the relation of the 4-current to the spin density, it is important to realize that the definition of the current density (naturally) involves a velocity operator, which is in close analogy to classical mechanics (correspondence principle).[57] The velocity operator in Dirac's theory of the electron follows from the Heisenberg equation of motion applied to the position operator and turns out to be $c\boldsymbol{\alpha}$. Hence, as the Dirac α matrices contain the Pauli spin matrices $\boldsymbol{\sigma}$, we see immediately that the current density $\mathbf{j}$ carries the spin information.[130]

The relation to the spin density can be made more explicit by invoking a Gordon composition of the current density which separates it into a charge- and a spin-related current.[53,131] For the one-electron case, one can carry out this decomposition by rewriting the Dirac eigenvalue equation as,

$$\psi(\mathbf{r}) = \frac{1}{m_e c^2}\left[-c\,\beta\,\boldsymbol{\alpha}\cdot\left(\hat{\mathbf{p}} - \frac{q_e}{c}\mathbf{A}_\text{ext}(\mathbf{r})\right) + \beta\left(E - q_e\phi(\mathbf{r})\right)\right]\psi(\mathbf{r}) \tag{130}$$

and by splitting up the definition of the current in a somewhat artificial way as

$$\mathbf{j}(\mathbf{r}) = c\,\psi^\dagger(\mathbf{r})\,\boldsymbol{\alpha}\,\psi(\mathbf{r}) = \frac{c}{2}\,\psi^\dagger(\mathbf{r})\,\boldsymbol{\alpha}\,\psi(\mathbf{r}) + \frac{c}{2}\,\psi^\dagger(\mathbf{r})\,\boldsymbol{\alpha}\,\psi(\mathbf{r}). \tag{131}$$

Equation (130) can now be used to replace ψ in the first term and $\psi^\dagger$ in the last term. As is shown in the Appendix, by exploiting the commutation relations of the Dirac matrices $\{\alpha^k, \beta\} = 0$ and $\alpha^k\alpha^l = \frac{1}{2}[\alpha^k, \alpha^l] + \frac{1}{2}\{\alpha^k, \alpha^l\} = i\varepsilon_{kln}\sigma_n^{(4)} + \delta_{kl}$, one arrives at[53,131] (see also pages 552–558 in Ref. [138])

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2m_e}\left[\psi^\dagger(\mathbf{r})\beta\left(\hat{\mathbf{p}} - \frac{q_e}{c}\mathbf{A}_\text{ext}(\mathbf{r})\right)\psi(\mathbf{r}) + \left(\hat{\mathbf{p}}^* - \frac{q_e}{c}\mathbf{A}_\text{ext}(\mathbf{r})\right)\psi^\dagger(\mathbf{r})\beta\psi(\mathbf{r})\right]$$
$$+ \frac{\hbar}{2m_e}\nabla\times\psi^\dagger(\mathbf{r})(\beta\boldsymbol{\sigma}^{(4)})\psi(\mathbf{r}), \tag{132}$$

where the 3-vector $\boldsymbol{\sigma}^{(4)} = (\sigma_x^{(4)}, \sigma_y^{(4)}, \sigma_z^{(4)})^T$ contains the 4×4 Pauli matrices $\sigma_i^{(4)}$ introduced in Eq. (114). In a many-electron system described by the Dirac–Coulomb Hamiltonian, a similar decomposition of the current density can be performed (even though the derivation becomes slightly more complicated, see Appendix), and one obtains,

$$\mathbf{j}(\mathbf{r}_1) = N\frac{1}{2m_e}\int\left[\Psi^\dagger\beta_1\left(\hat{\mathbf{p}}_1 - \frac{q_e}{c}\mathbf{A}_\text{ext}(\mathbf{r}_1)\right)\Psi\right.$$
$$\left. + \left(\hat{\mathbf{p}}_1^* - \frac{q_e}{c}\mathbf{A}_\text{ext}(\mathbf{r}_1)\right)\Psi^\dagger\beta_1\Psi\right]d^3r_2...d^3r_N$$
$$+ N\frac{\hbar}{2m_e}\nabla_1\int\Psi^\dagger\beta_1\boldsymbol{\sigma}_1^{(4)}\Psi\,d^3r_2...d^3r_N. \tag{133}$$

The first line of this expression resembles the definition of the current density in nonrelativistic quantum mechanics, whereas the second term can be identified as arising from the electron spin. This can be made more apparent by defining the magnetization (density),

$$\boldsymbol{m}(\boldsymbol{r}_1) = N \int \Psi^\dagger \, \beta_1 \boldsymbol{\sigma}_1^{(4)} \, \Psi \, \mathrm{d}^3 r_2 \ldots \mathrm{d}^3 r_N. \qquad (134)$$

Then, the contribution of the second term of Eq. (133) to the interaction energy with the external electromagnetic potentials [*cf.* Eq. (119)] becomes

$$
\begin{aligned}
V_{\text{ext}}^{\text{spin}}[j^\mu] &= \frac{q_e \hbar}{2 m_e c} \int \left(\nabla \times \boldsymbol{m}(\boldsymbol{r}) \right) \cdot \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}) \, \mathrm{d}^3 r \\
&= -\mu_B \int \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}_{\text{ext}}(\boldsymbol{r}) \, \mathrm{d}^3 r
\end{aligned}
\qquad (135)
$$

where $\boldsymbol{B}_{\text{ext}} = \nabla \times \boldsymbol{A}_{\text{ext}}$ is the external magnetic field. The minus sign originates from the negative charge of the electron. This closely resembles the form of the spin Zeeman interaction in the nonrelativistic case [*cf.* Eq. (32)]. If an inhomogeneous magnetic field in z-direction is considered, Eq. (135) reduces to

$$V_{\text{ext}}^{\text{spin}}[j^\mu] = -\mu_B \int m_z(\boldsymbol{r}) B_z(\boldsymbol{r}) \, \mathrm{d}^3 r, \qquad (136)$$

and by comparison with Eq. (33), we notice that $m_z(\boldsymbol{r})$ can be identified with the spin density $Q(\boldsymbol{r})$ in nonrelativistic theory. However, while in the nonrelativistic case, the spin density is (in the absence of external magnetic fields) independent of the choice of the quantization axis, this is not the case in the relativistic theory, where $\hat{\sigma}_z$ does not commute with the Hamiltonian because of the presence of spin–orbit interactions.

Relativistic spin-DFT

In the relativistic CDFT formalism discussed above, the noninteracting reference system is chosen such that it has the same 4-current $j^\mu(\boldsymbol{r})$ [i.e., the same electron density $\rho(\boldsymbol{r})$ and the same current density $\boldsymbol{j}(\boldsymbol{r})$] as the true interacting system. This results in a noninteracting kinetic-energy functional $T_s[r, \boldsymbol{j}]$ that can be defined as

$$T_s[\rho, \boldsymbol{j}] = \min_{\Psi_s \to \rho, \boldsymbol{j}} \langle \Psi_s | \hat{T}^D | \Psi_s \rangle, \qquad (137)$$

where the constrained search has to be restricted to positive-energy wavefunctions Ψ_s to avoid a variational collaps. In such a formalism, the KS equations then contain a four-component exchange–correlation potential.

However, we also pointed out that in the case of molecular systems in the absence of external magnetic fields, a description relying on the electron density $\rho(\boldsymbol{r})$ only as fundamental variable is sufficient. Therefore, it is formally also possible to develop a relativistic 'density-only' KS-DFT that resembles the nonrelativistic restricted KS-DFT formalism. This can be achieved by only requiring from the noninteracting reference system that it has the same electron density as the interacting system, and consequently defining the noninteracting kinetic energy as,

$$T_s^{(d)}[\rho] = \min_{\Psi_s^{(d)} \to \rho} \langle \Psi_s^{(d)} | \hat{T} | \Psi_s^{(d)} \rangle, \qquad (138)$$

again restricting Ψ_s to positive energy solutions. Then, the total energy functional can be decomposed as,

$$E[\rho] = T_s^{(d)}[\rho] + V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}^{(d)}[\rho], \qquad (139)$$

where we have neglected the magnetic interactions in $J[\rho]$. Note that such a decomposition implies a different definition of the exchange–correlation energy. The resulting KS equations then feature a one-component exchange–correlation potential $v_{\text{xc}}^{(d)}[\rho] = (1/q_e) \, \delta E_{\text{xc}}^{(d)}[\rho]/\delta \rho(\boldsymbol{r})$. However, in such a formalism the current density $\boldsymbol{j}_s(\boldsymbol{r})$ and magnetization $\boldsymbol{m}_s(\boldsymbol{r})$ of the noninteracting reference system do not agree with the true interacting system. Instead, these are again a functional of the density only, just as the spin density is in nonrelativistic restricted KS-DFT.

In between full CDFT and relativistic density-only KS-DFT, different intermediate formulations of relativistic KS-DFT are now also possible. For a relativistic system of noninteracting electrons, the magnetization is given by

$$\boldsymbol{m}(\boldsymbol{r}) = \sum_i^{\text{occ}} \varphi_i^\dagger(\boldsymbol{r}) \, \beta \boldsymbol{\sigma}^{(4)} \, \varphi_i(\boldsymbol{r}). \qquad (140)$$

The noninteracting reference system can then be set up such that, in addition to the electron density, some parts of the magnetization agree with those of the interacting system. For instance, we can require that the z-components of the magnetization $m_z(\boldsymbol{r})$ match, or we can demand that the lengths of the magnetization vector $|\boldsymbol{m}(\boldsymbol{r})|$ at each point in space agree. The choice of what quantity is to be reproduced by a relativistic KS-DFT formalism in addition to the density is our freedom of choice. If we choose to reproduce the z-component of the magnetization density, this approach is called the collinear ["(*cl*)"] approach because an artificial external global quantization axis is introduced for the spin. If we require to reproduce the length of magnetization instead, this is a noncollinear ["(*nc*)"] approach because the magnetization is a vector field representing a magnetic dipole moment whose direction changes with position.[135,137,139,140,141]

Note that these different choices for the noninteracting reference system each implies a different definition of the noninteracting kinetic energy functional, $T_s^{(cl)}[\rho, m_z]$ and $T_s^{(nc)}[\rho, |\boldsymbol{m}|]$, and thus also of the exchange–correlation energy, $E_{\text{xc}}^{(cl)}[\rho, m_z]$ and $E_{\text{xc}}^{(nc)}[\rho, |\boldsymbol{m}|]$, respectively. For the choices mentioned here, where in addition to the electron density one additional quantity is reproduced by the KS system, the resulting exchange–correlation potential has two components. This is in close analogy to the case of nonrelativistic unrestricted KS-DFT. Therefore, approximate exchange–correlation functionals developed in the nonrelativistic domain are usually used in practical applications of such relativistic spin-DFT schemes. However, the exchange–correlation potential is defined differently in nonrelativistic unrestricted KS-DFT and in the relativistic collinear and noncollinear cases. Consequently, also different exact conditions apply to the exchange–correlation functional. The different possible choices for setting up relativistic KS-DFT are summarized in Figure 3.

Finally, we discuss how the nonrelativistic unrestricted KS-DFT formalism emerges from relativistic spin-DFT. This is most easily seen for the collinear approach, although the noncollinear one reduces to the same nonrelativistic limit as well.
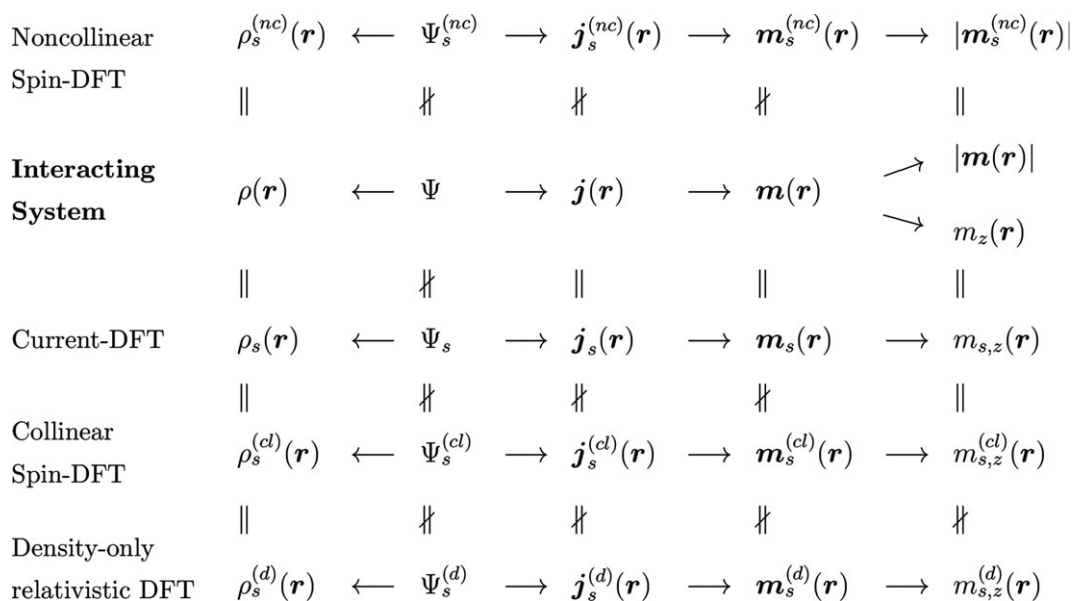
Noncollinear Spin-DFT	$\rho_s^{(nc)}(\boldsymbol{r})$	$\longleftarrow$	$\Psi_s^{(nc)}$	$\longrightarrow$	$\boldsymbol{j}_s^{(nc)}(\boldsymbol{r})$	$\longrightarrow$	$\boldsymbol{m}_s^{(nc)}(\boldsymbol{r})$	$\longrightarrow$	$\|\boldsymbol{m}_s^{(nc)}(\boldsymbol{r})\|$

$$\| \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \|$$

Interacting System	$\rho(\boldsymbol{r})$	$\longleftarrow$	Ψ	$\longrightarrow$	$\boldsymbol{j}(\boldsymbol{r})$	$\longrightarrow$	$\boldsymbol{m}(\boldsymbol{r})$

$$\nearrow \quad |\boldsymbol{m}(\boldsymbol{r})|$$
$$\searrow \quad m_z(\boldsymbol{r})$$

$$\| \qquad\qquad \nparallel \qquad\qquad \| \qquad\qquad \| \qquad\qquad \|$$

Current-DFT	$\rho_s(\boldsymbol{r})$	$\longleftarrow$	Ψ_s	$\longrightarrow$	$\boldsymbol{j}_s(\boldsymbol{r})$	$\longrightarrow$	$\boldsymbol{m}_s(\boldsymbol{r})$	$\longrightarrow$	$m_{s,z}(\boldsymbol{r})$

$$\| \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \|$$

Collinear Spin-DFT	$\rho_s^{(cl)}(\boldsymbol{r})$	$\longleftarrow$	$\Psi_s^{(cl)}$	$\longrightarrow$	$\boldsymbol{j}_s^{(cl)}(\boldsymbol{r})$	$\longrightarrow$	$\boldsymbol{m}_s^{(cl)}(\boldsymbol{r})$	$\longrightarrow$	$m_{s,z}^{(cl)}(\boldsymbol{r})$

$$\| \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \nparallel \qquad\qquad \nparallel$$

Density-only relativistic DFT	$\rho_s^{(d)}(\boldsymbol{r})$	$\longleftarrow$	$\Psi_s^{(d)}$	$\longrightarrow$	$\boldsymbol{j}_s^{(d)}(\boldsymbol{r})$	$\longrightarrow$	$\boldsymbol{m}_s^{(d)}(\boldsymbol{r})$	$\longrightarrow$	$m_{s,z}^{(d)}(\boldsymbol{r})$

Figure 3. Relationship between wave function, total electron density, and the magnetization of the system of fully interacting electrons and of the KS reference systems of noninteracting electrons in different version of relativistic KS-DFT.

The z-component of the magnetization density of the KS reference system is given by

$$m_z(\boldsymbol{r}) = \sum_i^{occ} \varphi_i^\dagger(\boldsymbol{r})\, \beta \sigma_z^{(4)}\, \varphi_i(\boldsymbol{r}). \qquad (141)$$

If spin–orbit coupling is neglected, the Hamiltonian commutes with the spin operators and the KS spinors can each be expressed as (two-component) spin orbitals $\varphi_{i,\alpha} = \varphi_i^\alpha \alpha$ or $\varphi_{i,\beta} = \varphi_i^\beta \beta$, where φ_i^σ are 2-spinors consisting of an upper and a lower component. Then, the spin–orbit coupling free (SOfree) z-component of the magnetization resembles the nonrelativistic spin density,

$$
\begin{aligned}
m_z^{SOfree}(\boldsymbol{r}) &= \sum_{i,\sigma}^{occ} \varphi_{i,\sigma}^\dagger(\boldsymbol{r})\, \beta \sigma_z^{(4)}\, \varphi_{i,\sigma}(\boldsymbol{r}) \\
&= \sum_i^\alpha \varphi_i^{\alpha,\dagger}(\boldsymbol{r})\, \sigma_z\, \varphi_i^\alpha(\boldsymbol{r}) - \sum_i^\beta \varphi_i^{\beta,\dagger}(\boldsymbol{r})\, \sigma_z\, \varphi_i^\beta(\boldsymbol{r}) \\
&= \sum_i^\alpha \left[|\varphi_i^{\alpha,U}(\boldsymbol{r})|^2 - |\varphi_i^{\alpha,L}(\boldsymbol{r})|^2 \right] \\
&\quad - \sum_i^\beta \left[|\varphi_i^{\beta,U}(\boldsymbol{r})|^2 - |\varphi_i^{\beta,L}(\boldsymbol{r})|^2 \right] \\
&= Q(\boldsymbol{r}),
\end{aligned} \qquad (142)
$$

where the superscript 'U' and 'L' denote the upper and lower components, respectively. The neglect of spin–orbit coupling is, of course, an approximation that yields a scalar-relativistic Hamiltonian (which considers kinematic relativistic effects only) or even a nonrelativistic Hamiltonian if the speed of light is taken to be infinity.

The two 2-spinors φ_i^α and φ_i^β considered here can be reduced to one-component spin-orbitals if a unitary transformation[142] is performed to decouple the upper and lower components. This then also requires a unitary transformation

of the operators involved in the calculation of $\boldsymbol{m}_z$.[143] Still, taking the limit $c \to \infty$ yields the nonrelativistic theory and relativistic spin-DFT reduces to nonrelativistic unrestricted KS-DFT.

Future Directions for Spin-DFT

As we have seen, different options exist for setting up KS-DFT for open-shell systems. In the nonrelativistic case, one has to choose between a spin-restricted and a spin-unrestricted formulation of KS-DFT. In the former case, the wavefunction of the noninteracting reference system can always be chosen as an eigenfunction of $\hat{S}^2$, but its spin density differs from the correct one. Alternatively, in spin-unrestricted KS-DFT the noninteracting reference system has the correct spin density, but cannot be an eigenfunction of $\hat{S}^2$. In relativistic DFT even more options in between density-only KS-DFT (with a one-component exchange–correlation potential) and full CDFT (with a four-component exchange–correlation potential) are possible. In particular, one can choose to reproduce either a single component or the magnitude of the magnetization vector in collinear and noncollinear relativistic KS-DFT (which both use a two-component exchange–correlation potential), respectively.

Which choices we make may be determined by our ability to set up a proper approximation to the corresponding exchange–correlation energy functional. However, it is important to understand that these different choices imply different definitions of the noninteracting kinetic energy and the exchange–correlation functional. Thus, different exact conditions apply to these functionals, which must be considered when developing such approximations. This is most obvious for the fractional spin condition in the nonrelativistic case. While in spin-restricted KS-DFT, the constancy condition directly applies to the exchange–correlation functional, in the spin-unrestricted case it does not hold for the exchange–correlation functional alone, but to the sum of noninteracting kinetic and exchange–correlation energy. It

can be expected that in the latter case, devising approximate exchange–correlation functionals that include this condition will be significantly more difficult.

Although exact DFT should always lead to the correct ground-state—irrespective of its spin state—in practice it appears more useful to rely on a theory that is able to target different spin states separately. This should also simplify the development of approximate functionals because it becomes possible to account for the different exact conditions applying to the exchange–correlation hole for different spin states.[129,144] Note that such a spin-state specific DFT always has to operate within a spin–orbit coupling free framework, because in the fully relativistic theory $\hat{S}^2$ does not commute with the Hamiltonian and different spin states do not correspond to the lowest state of a specific symmetry anymore.

Thus, besides finding approximations that accurately account for the spin-density dependence of the (nonrelativistic) exchange–correlation functionals $E_{xc}[\rho, Q]$ or $E_{xc}^{(u)}[\rho, Q]$, finding ways of including the spin-state dependence into these functionals is another important problem for open-shell systems. In common approximations, it appears that the spin-density dependence is actually used to model this spin-state dependence (i.e., the integral of the spin density is used to distinguish spin states). Spin-state and spin-density dependence of the exchange–correlation functional are intermingled in all available approximate functionals, which manifests itself in their violation of the fractional spin condition.[101,102] To make progress in the development of reliable density-functional approximations, we believe it will be essential to consider the spin-state and the spin-density dependence of the exchange–correlation functional separately.

Appendix: Gordon Decomposition of the Current Density

In the one-electron case, the current density is given by

$$\boldsymbol{j}(\boldsymbol{r}) = c\,\psi(\boldsymbol{r})^{\dagger}\boldsymbol{\alpha}\,\psi(\boldsymbol{r}). \tag{A1}$$

For the k-component, we can rewrite this definition in a somewhat artificial way as

$$j^k = c\,\psi^{\dagger}\alpha^k\psi = \frac{c}{2}\,\psi^{\dagger}\alpha^k\psi + \frac{c}{2}\,\psi^{\dagger}\alpha^k\psi, \tag{A2}$$

where we dropped the dependence of ψ on the spatial coordinate to simplify the notation. The eigenvalue equation of the one-electron Dirac Hamiltonian equation can be rewritten to obtain an expression for ψ,

$$\psi = \frac{1}{m_e c^2}\left[-c\,\beta\,\boldsymbol{\alpha}\cdot\left(\hat{\boldsymbol{p}} - \frac{q_e}{c}\boldsymbol{A}\right) + \beta\left(E - q_e\phi\right)\right]\psi, \tag{A3}$$

and by taking the transpose and complex conjugate also an expression for $\psi^{\dagger}$ (exploiting $\alpha_k^{\dagger} = \alpha_k$)

$$\psi^{\dagger} = \frac{1}{m_e c^2}\left[-c\left(\hat{\boldsymbol{p}}^* - \frac{q_e}{c}\boldsymbol{A}\right)\psi^{\dagger}\cdot\boldsymbol{\alpha}\beta + \left(E - q_e\phi\right)\psi^{\dagger}\beta\right]. \tag{A4}$$

These expressions can now be used to replace ψ in the first term and $\psi^{\dagger}$ in the second term of Eq. (A2) to obtain,

$$
j^k = \frac{1}{2m_e c}\,\psi^{\dagger}\alpha^k\left[-c\,\beta\,\boldsymbol{\alpha}\cdot\left(\hat{\boldsymbol{p}} - \frac{q_e}{c}\boldsymbol{A}\right) + \beta\left(E - q_e\phi\right)\right]\psi
$$
$$
+ \frac{1}{2m_e c}\left[-c\left(\hat{\boldsymbol{p}}^* - \frac{q_e}{c}\boldsymbol{A}\right)\psi^{\dagger}\cdot\boldsymbol{\alpha}\beta + \left(E - q_e\phi\right)\psi^{\dagger}\beta\right]\alpha^k\psi, \tag{A5}
$$

and by reordering the different terms we get

$$
j^k = \frac{1}{2m_e}\left[-\psi^{\dagger}\alpha^k\beta\,\boldsymbol{\alpha}\cdot\left(\hat{\boldsymbol{p}} - \frac{q_e}{c}\boldsymbol{A}\right)\psi - \left(\hat{\boldsymbol{p}}^* - \frac{q_e}{c}\boldsymbol{A}\right)\psi^{\dagger}\cdot\boldsymbol{\alpha}\,\beta\,\alpha^k\psi\right]
$$
$$
+ \frac{1}{2m_e c}\left(E - q_e\phi\right)\left[\psi^{\dagger}\alpha^k\beta\psi + \psi^{\dagger}\beta\alpha^k\psi\right]. \tag{A6}
$$

The last term is zero because of $\{\alpha^k, \beta\} = 0$. For the first term, we use

$$\alpha^k\alpha^l = \frac{1}{2}[\alpha^k, \alpha^l] + \frac{1}{2}\{\alpha^k, \alpha^l\} = i\varepsilon_{kln}\sigma_n^{(4)} + \delta_{kl} \tag{A7}$$

to arrive at (using the convention of implicit summation over repeated indices)

$$
j^k = \frac{1}{2m_e}\left[\psi^{\dagger}\beta\alpha^k\alpha^l\left(\hat{p}_l - \frac{q_e}{c}A_l\right)\psi + \left(\hat{p}_l^* - \frac{q_e}{c}A_l\right)\psi^{\dagger}\beta\alpha^l\alpha^k\psi\right]
$$
$$
= \frac{1}{2m_e}\left[\psi^{\dagger}\beta(i\varepsilon_{kln}\sigma_n^{(4)} + \delta_{kl})\left(\hat{p}_l - \frac{q_e}{c}A_l\right)\psi + \left(\hat{p}_l^* - \frac{q_e}{c}A_l\right)\right.
$$
$$
\left. \times \psi^{\dagger}\beta(i\varepsilon_{lkn}\sigma_n^{(4)} + \delta_{kl})\psi\right]. \tag{A8}
$$

After regrouping the different terms, we obtain

$$
j^k = \frac{1}{2m_e}\left[\psi^{\dagger}\beta\delta_{kl}\left(\hat{p}_l - \frac{q_e}{c}A_l\right)\psi + \left(\hat{p}_l^* - \frac{q_e}{c}A_l\right)\psi^{\dagger}\beta\delta_{kl}\psi\right]
$$
$$
+ \frac{1}{2m_e}\left[\psi^{\dagger}\beta i\varepsilon_{kln}\sigma_n^{(4)}\hat{p}_l\psi + \hat{p}_l^*\psi^{\dagger}\beta i\varepsilon_{lkn}\sigma_n^{(4)}\psi\right]
$$
$$
+ \frac{1}{2m_e}\left[\psi^{\dagger}\beta i\varepsilon_{kln}\sigma_n^{(4)}\left(-\frac{q_e}{c}A_l\right)\psi + \left(-\frac{q_e}{c}A_l\right)\psi^{\dagger}\beta i\varepsilon_{lkn}\sigma_n^{(4)}\psi\right], \tag{A9}
$$

where the last term is zero because $\varepsilon_{kln} = -\varepsilon_{lkn}$. Hence, we find

$$
j^k = \frac{1}{2m_e}\left[\psi^{\dagger}\beta\left(\hat{p}_k - \frac{q_e}{c}A_k\right)\psi + \left(\hat{p}_k^* - \frac{q_e}{c}A_k\right)\psi^{\dagger}\beta\psi\right]
$$
$$
+ \frac{1}{2m_e}\left[\psi^{\dagger}\beta i\varepsilon_{kln}\sigma_n^{(4)}\left(-i\hbar\frac{\partial}{\partial r_l}\right)\psi + \left(i\hbar\frac{\partial}{\partial r_l}\right)\psi^{\dagger}\beta i\varepsilon_{lkn}\sigma_n^{(4)}\psi\right]
$$
$$
= \frac{1}{2m_e}\left[\psi^{\dagger}\beta\left(\hat{p}_k - \frac{q_e}{c}A_k\right)\psi + \left(\hat{p}_k^* - \frac{q_e}{c}A_k\right)\psi^{\dagger}\beta\psi\right]
$$
$$
+ \frac{\hbar}{2m_e}\varepsilon_{kln}\frac{\partial}{\partial r_l}\left[\psi^{\dagger}(\beta\sigma_n^{(4)})\psi\right] \tag{A10}
$$

and combining the different components of $\boldsymbol{j}$ again gives

$$\boldsymbol{j} = \frac{1}{2m_e}\left[\psi^\dagger\beta\left(\hat{\boldsymbol{p}} - \frac{q_e}{c}\boldsymbol{A}\right)\psi + \left(\hat{\boldsymbol{p}}^* - \frac{q_e}{c}\boldsymbol{A}\right)\psi^\dagger\beta\psi\right]$$
$$+ \frac{\hbar}{2m_e}\nabla\times\psi^\dagger(\beta\boldsymbol{\sigma}^{(4)})\psi. \tag{A13}$$

For an N-electron system, we start from the definition of the many-electron current density,[130]

$$\boldsymbol{j}(\boldsymbol{r}_1) = cN\int\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)^\dagger\,\boldsymbol{\alpha}_1\,\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\,\mathrm{d}^3r_2\ldots\mathrm{d}^3r_N, \tag{A12}$$

and the wavefunction is an eigenfunction of the many-electron Dirac–Coulomb Hamiltonian

$$\hat{H}^D = \hat{h}^D(1) + \sum_{i=2}^N h^D(i) + \hat{V}_{ee}, \tag{A13}$$

projected onto the electronic (positive-energy) states.

We can now rewrite the corresponding eigenvalue equation in a similar fashion as in the one-electron case to obtain for the wavefunction

$$\Psi = \frac{1}{m_e c^2}\left[-c\beta_1\boldsymbol{\alpha}_1\cdot\left(\hat{\boldsymbol{p}}_1 - \frac{q_e}{c}\boldsymbol{A}(\boldsymbol{r}_1)\right) + \beta_1\left(E - q_e\phi(\boldsymbol{r}_1)\right)\right.$$
$$\left. - \beta_1\sum_{i=2}^N h^D(i) - \beta_1\hat{V}_{ee}\right]\Psi \tag{A14}$$

and for its transpose and complex conjugate

$$\Psi^\dagger = \frac{1}{m_e c^2}\left[-c\left(\hat{\boldsymbol{p}}_1^* - \frac{q_e}{c}\boldsymbol{A}(\boldsymbol{r}_1)\right)\Psi^\dagger\boldsymbol{\alpha}_1\beta_1 + \left(E - q_e\phi(\boldsymbol{r}_1)\right)\Psi^\dagger\beta_1\right.$$
$$\left. - \sum_{i=2}^N\left(h^D(i)\Psi\right)^\dagger\beta_1 - (\hat{V}_{ee}\Psi)^\dagger\beta_1\right]. \tag{A15}$$

Now, we can rewrite the k-component of integrand in Eq. (A12) as

$$c\,\Psi^\dagger\alpha_1^k\Psi = \frac{c}{2}\,\Psi^\dagger\alpha_1^k\Psi + \frac{c}{2}\,\Psi^\dagger\alpha_1^k\Psi. \tag{A16}$$

After substituting Eq. (A14) for Ψ in the first term and Eq. (A15) for $\Psi^\dagger$ in the second term, we obtain, in addition to the term already present in the one-electron case [cf. Eq. (A11)],

$$c\,\Psi^\dagger\alpha_1^k\Psi = (A11) - \frac{1}{2m_e c}\Psi^\dagger\alpha_1^k\left[\beta_1\sum_{i=2}^N\left(h^D(i)\Psi\right)^\dagger + \beta_1\hat{V}_{ee}\Psi\right]$$
$$- \frac{1}{2m_e c}\left[\sum_{i=2}^N\left(h^D(i)\Psi\right)^\dagger\beta_1 + (\hat{V}_{ee}\Psi)^\dagger\beta_1\right]\alpha_1^k\Psi$$
$$= (A11) - \frac{1}{2m_e c}\left[\Psi^\dagger\alpha_1^k\beta_1\sum_{i=2}^N\left(h^D(i)\Psi\right)\right.$$
$$\left. + \sum_{i=2}^N\left(h^D(i)\Psi\right)^\dagger\beta_1\alpha_1^k\Psi\right]$$
$$- \frac{1}{2m_e c}\left[\Psi^\dagger\alpha_1^k\beta_1\hat{V}_{ee}\Psi + (\hat{V}_{ee}\Psi)^\dagger\beta_1\alpha_1^k\Psi\right].$$

With a multiplicative operator acting equally on all components of the wavefunction for $\hat{V}_{ee}$, the last term is zero

because of $\{\alpha^k, \beta\} = 0$. However, if the Gaunt or Breit interaction is included, the corresponding term is not zero and gives an additional contribution to the current that is not present in the one-electron case. This term contains the spin–spin interactions.

For the remaining terms, we now consider one of the terms separately, for instance $h^D(2)$, and note that

$$-\frac{1}{2m_e c}\left[\Psi^\dagger\alpha_1^k\beta_1\left(h^D(2)\Psi\right) + \left(h^D(2)\Psi\right)^\dagger\beta_1\alpha_1^k\Psi\right]$$
$$= -\frac{1}{2m_e c}\left[\Psi^\dagger\alpha_1^k\beta_1\left(h^D(2)\Psi\right) - \left(h^D(2)\Psi\right)^\dagger\alpha_1^k\beta_1\Psi\right], \tag{A17}$$

because of $\{\alpha_1^k, \beta_1\} = 0$. Integrating the expression in square brackets over $\boldsymbol{r}_2$ we now find

$$\int\Psi^\dagger\alpha_1^k\beta_1\left(h^D(2)\Psi\right)\,\mathrm{d}^3r_2 - \int\left(h^D(2)\Psi\right)^\dagger\alpha_1^k\beta_1\Psi\,\mathrm{d}^3r_2$$
$$= \int\Psi^\dagger\alpha_1^k\beta_1\left(h^D(2)\Psi\right)\,\mathrm{d}^3r_2 - \int\Psi^\dagger\alpha_1^k\beta_1\left(h^D(2)\Psi\right)\,\mathrm{d}^3r_2 = 0 \tag{A18}$$

where for the second term, we exploited that $h^D(2)$ is hermitian and commutes with α_1^k and β_1 because these act on different electrons. Combining all of these results, we find that (with the Dirac–Coulomb Hamiltonian),

$$\boldsymbol{j}(\boldsymbol{r}_1) = cN\int\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)^\dagger\,\boldsymbol{\alpha}_1\,\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\,\mathrm{d}^3r_2\ldots\mathrm{d}^3r_N$$
$$= \frac{1}{2m_e}N\int\left[\Psi^\dagger\beta_1\left(\hat{\boldsymbol{p}}_1 - \frac{q_e}{c}\boldsymbol{A}(\boldsymbol{r}_1)\right)\Psi + \left(\hat{\boldsymbol{p}}_1^* - \frac{q_e}{c}\boldsymbol{A}(\boldsymbol{r}_1)\right)\Psi^\dagger\beta_1\Psi\right]$$
$$\times\mathrm{d}^3r_2\ldots\mathrm{d}^3r_N + \frac{\hbar}{2m_e}N\int\nabla\times(\Psi^\dagger\beta_1\boldsymbol{\sigma}_1^{(4)}\Psi)\,\mathrm{d}^3r_2\ldots\mathrm{d}^3r_N \tag{A19}$$

[1] G. Jeschke, Y. Polyhach, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1895.

[2] C. Herrmann, G. C. Solomon, M. A. Ratner, *J. Am. Chem. Soc.* **2010**, *132*, 3682.

[3] C. Herrmann, G. C. Solomon, M. A. Ratner, *J. Chem. Phys.* **2011**, *134*, 224306.

[4] G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. A. Muryn, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte, R. E. P. Winpenny, *Nat. Nanotech.* **2009**, *4*, 173.

[5] J. P. McEvoy, G. W. Brudvig, *Chem. Rev.* **2006**, *106*, 4455.

[6] P. M. Vignais, B. Billoud, *Chem. Rev.* **2007**, *107*, 4206.

[7] M. T. Stiebritz, M. Reiher, *Chem. Sci.* **2012**, *3*, 1739.

[8] Y. Hu, M. W. Ribbe, *Acc. Chem. Res.* **2010**, *43*, 475.

[9] D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139.

[10] T. Helgaker, P. Jørgensen, J. Olsen, Molecular Electronic Structure Theory; Wiley: Chichester, **2000**.

[11] W. Koch, M. C. Holthausen, A Chemist's Guide to Density Functional Theory, 2nd ed.; Wiley-VCH: Weinheim, **2001**.

[12] M. Reiher, *Chimia* **2009**, *63*, 140.

[13] B. O. Roos, V. Veryazov, J. Conradie, P. R. Taylor, A. Ghosh, *J. Phys. Chem. B* **2008**, *112,* 14099.

[14] M. Radoń, K. Pierloot, *J. Phys. Chem. A* **2008**, *112,* 11824.

[15] M. Radoń, E. Broclawik, K. Pierloot, *J. Phys. Chem. B* **2010**, *114,* 1518.

[16] X. Sala, M. Z. Ertem, L. Vigara, T. K. Todorova, W. Chen, R. C. Rocha, F. Aquilante, C. J. Cramer, L. Gagliardi, A. Llobet, *Angew. Chem. Int. Ed.* **2010**, *49,* 7745.

[17] N. Planas, L. Vigara, C. Cady, P. Miró, P. Huang, L. Hammarström, S. Styring, N. Leidel, H. Dau, M. Haumann, L. Gagliardi, C. J. Cramer, A. Llobet, *Inorg. Chem.* **2011**, *50,* 11134.

[18] L. Vigara, M. Z. Ertem, N. Planas, F. Bozoglian, N. Leidel, H. Dau, M. Haumann, L. Gagliardi, C. J. Cramer, A. Llobet, *Chem. Sci.* **2012**, *3,* 2576.

[19] G. K.-L. Chan, J. J. Dorando, D. Ghosh, J. Hachmann, E. Neuscamman, H. Wang, T. Yanai, In Frontiers in Quantum Systems in Chemistry and Physics, *Vol. 18, 1st ed.; S. Wilson, P. J. Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch, Eds.; Springer: Dordrecht,* **2008**; pp. 49–65, arXiv:0711.1398 [cond-mat.str-el].

[20] K. H. Marti, M. Reiher, *Z. Phys. Chem.* **2010**, *224,* 583.

[21] K. H. Marti, M. Reiher, *Phys. Chem. Chem. Phys.* **2011**, *13,* 6750.

[22] G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100,* 717.

[23] T. Ziegler, J. Autschbach, *Chem. Rev.* **2005**, *105,* 2695.

[24] F. Neese, *Coord. Chem. Rev.* **2009**, *253,* 526.

[25] M. Podewitz, M. Reiher, *Adv. Inorg. Chem.* **2010**, *62,* 177.

[26] M. Podewitz, T. Weymuth, M. Reiher, In Modeling of Molecular Properties; P. Comba, Eds.; Wiley-VCH: Weinheim, **2011**; pp. 137–163.

[27] A. Ghosh, *J. Biol. Inorg. Chem.* **2006**, *11,* 671.

[28] C. J. Cramer, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2009**, *11,* 10757.

[29] M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* **2001**, *107,* 48.

[30] M. Reiher, *Inorg. Chem.* **2002**, *41,* 6928.

[31] A. Ghosh, P. R. Taylor, *Curr. Opin. Chem. Biol.* **2003**, *7,* 113.

[32] J. N. Harvey, *Struct. Bond.* **2004**, *112,* 151.

[33] C. Herrmann, L. Yu, M. Reiher, *J. Comput. Chem.* **2006**, *27,* 1223.

[34] M. Swart, *J. Chem. Theory Comput.* **2008**, *4,* 2057.

[35] S. Ye, F. Neese, *Inorg. Chem.* **2010**, *49,* 772.

[36] M. Swart, *Int. J. Quantum Chem.* (in press). DOI: 10.1002/qua.24255.

[37] J. Conradie, A. Ghosh, *J. Phys. Chem. B* **2007**, *111,* 12621.

[38] K. Boguslawski, Ch. R. Jacob, M. Reiher, *J. Chem. Theory Comput.* **2011**, *7,* 2740.

[39] K. Boguslawski, K. H. Marti, O. Legeza, M. Reiher, *J. Chem. Theory Comput.* **2012**, *8,* 1970.

[40] L. Noodleman, *J. Chem. Phys.* **1981**, *74,* 5737.

[41] G. Jonkers, C. A. de Lange, L. Noodleman, E. J. Baerends, *Mol. Phys.* **1982**, *46,* 609.

[42] L. Noodleman, J. G. Norman, J. H. Osborne, A. Aizman, D. A. Case, *J. Am. Chem. Soc.* **1985**, *107,* 3418.

[43] L. Noodleman, E. R. Davidson, *Chem. Phys.* **1986**, *109,* 131.

[44] M. Reiher, *Faraday Discuss.* **2007**, *135,* 97.

[45] L. Noodleman, C. Y. Peng, D. A. Case, J. M. Mouesca, *Coord. Chem. Rev.* **1995**, *144,* 199.

[46] C. van Wüllen, *J. Phys. Chem. A* **2009**, *113,* 11535.

[47] D. A. Pantazis, M. Orio, T. Petrenko, S. Zein, E. Bill, W. Lubitz, J. Messinger, F. Neese, *Chem. Eur. J.* **2009**, *15,* 5108.

[48] S. Schinzel, J. Schraut, A. V. Arbuznikov, P. E. M. Siegbahn, M. Kaupp, *Chem. Eur. J.* **2010**, *16,* 10424.

[49] A. J. Cohen, P. Mori-Sánchez, W. Yang, *Chem. Rev.* **2012**, *112,* 289.

[50] R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules; Oxford University Press: Oxford, **1989**.

[51] E. K. U. Gross, R. M. Dreizler, Density Functional Theory: An Approach to the Quantum Many-Body Problem; Springer: Berlin, **1990**.

[52] C. Fiolhais, F. Nogueira, M. A. L. Marques, A Primer in Density Functional Theory, Lecture Notes in Physics; Springer: Berlin, **2003**.

[53] E. Engel, R. M. Dreizler, Density Functional Theory: An Advanced Course; Springer: Heidelberg, **2011**.

[54] W. Pauli, *Z. Phys.* **1927**, *43,* 601.

[55] C. Cohen-Tannoudji, B. Diu, F. Laloe, Quantum Mechanics, *Vol. 1;* Wiley: New York, **1978**.

[56] R. McWeeny, Spins in Chemistry; Dover Publications: Mineola, N. Y., **2004**.

[57] M. Reiher, A. Wolf, Relativistic Quantum Chemistry: The Fundamental Theory of Molecular Science; Wiley-VCH: Weinheim, **2009**.

[58] A. Szabo, N. S. Ostlund, Modern Quantum Chemistry; Dover Publications: Mineola, N.Y., **1996**.

[59] P. A. M. Dirac, *Proc. Roy. Soc. Ser. A* **1929**, *123,* 714.

[60] R. McWeeny, B. T. Sutcliffe, Methods of Molecular Quantum Mechanics; Academic Press Inc: San Diego, **1969**.

[61] P.-O. Löwdin, *Phys. Rev.* **1955**, *97,* 1490.

[62] W. Heisenberg, *Z. Phys.* **1926**, *38,* 411.

[63] W. Heisenberg, *Z. Phys.* **1926**, *39,* 499.

[64] F. A. Matsen, *Adv. Quantum Chem.* **1964**, *1,* 59.

[65] R. Pauncz, Spin Eigenfunctions; Plenum Press: New York, **1979**.

[66] R. Pauncz, The Symmetric Group in Quantum Chemistry; CRC-Press: Boca Raton, **1995**.

[67] A. Schweiger, G. Jeschke, Principles of Pulse Electron Paramagnetic Resonance; Oxford University Press, **2001**.

[68] M. Kaupp, M. Bühl, V. G. Malkin, Calculation of NMR and EPR Parameters. Theory and Applications; Wiley-VCH: Weinheim, **2004**.

[69] F. Rastrelli, A. Bagno, *Chem. Eur. J.* **2009**, *15,* 7990.

[70] J. Autschbach, S. Patchkovskii, B. Pritchard, *J. Chem. Theory Comput.* **2011**, *7,* 2175.

[71] F. Aquino, B. Pritchard, J. Autschbach, *J. Chem. Theory Comput.* **2012**, *8,* 598.

[72] J.-M. Gillet, *Acta Cryst. A* **2007**, *63,* 234.

[73] A. Zheludev, V. Barone, M. Bonnet, B. Delley, A. Grand, E. Ressouche, P. Rey, R. Subra, J. Schweizer, *J. Am. Chem. Soc.* **1994**, *116,* 2019.

[74] V. Baron, B. Gillon, O. Plantevin, A. Cousson, C. Mathonière, O. Kahn, A. Grand, L. Öhrström, B. Delley, *J. Am. Chem. Soc.* **1996**, *118,* 11822.

[75] Y. Pontillon, A. Caneschi, D. Gatteschi, R. Sessoli, E. Ressouche, J. Schweizer, E. Lelievre-Berna, *J. Am. Chem. Soc.* **1999**, *121,* 5342.

[76] N. Claiser, M. Souhassou, C. Lecomte, B. Gillon, C. Carbonera, A. Caneschi, A. Dei, D. Gatteschi, A. Bencini, Y. Pontillon, E. Lelièvre-Berna, *J. Phys. Chem. B* **2005**, *109,* 2723.

[77] O. Zaharko, P. J. Brown, M. Mys'kiv, *Phys. Rev. B* **2010**, *81,* 172405.

[78] R. McWeeny, Y. Mizuno, *Proc. Roy. Soc. Ser. A* **1961**, *259,* 554.

[79] E. R. Davidson, Reduced Density Matrices in Quantum Chemistry; Academic Press: New York, **1976**.

[80] D. A. Mazziotti, *Chem. Rev.* **2011**, *112,* 244.

[81] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136,* B864.

[82] M. Levy, *Proc. Natl. Acad. Sci. USA* **1979**, *76,* 6062.

[83] J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz, Jr., *Phys. Rev. Lett.* **1982**, *49,* 1691.

[84] E. H. Lieb, *Int. J. Quantum Chem.* **1983**, *24,* 243.

[85] R. van Leeuwen, *Adv. Quantum Chem.* **2003**, *43,* 25.

[86] H. Eschrig, The Fundamentals of Density Functional Theory, 2nd ed.; Eagle, Ed. am Gutenbergplatz: Leipzig, **2003**.

[87] W. Kohn, In Highlights of Condensed-Matter Theory, F. Bassani, F. Fumi, M. P. Tosi, Eds.; Elsevier: Amsterdam, **1985**, pp. 1–15.

[88] J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun, G. I. Csonka, *J. Chem. Theory Comput.* **2009**, *5,* 902.

[89] J. P. Perdew, A. Zunger, *Phys. Rev. B* **1981**, *23,* 5048.

[90] U. von Barth, L. Hedin, *J. Phys. C: Solid State Phys.* **1972**, *5,* 1629.

[91] P. W. Ayers, W. Yang, *J. Chem. Phys.* **2006**, *124,* 224108.

[92] A. Holas, R. Balawender, *J. Chem. Phys.* **2006**, *125,* 247101.

[93] H. Eschrig, W. E. Pickett, *Solid State Commun.* **2001**, *118,* 123.

[94] K. Capelle, G. Vignale, *Phys. Rev. Lett.* **2001**, *86,* 5546.

[95] T. Gál, P. Geerlings, *Phys. Rev. A* **2010**, *81,* 032512.

[96] T. Gál, P. Geerlings, *J. Chem. Phys.* **2010**, *133,* 144105.

[97] N. I. Gidopoulos, *Phys. Rev. B* **2007**, *75,* 134408.

[98] T. Gál, *Phys. Rev. B* **2007**, *75,* 235119.

[99] T. Gál, P. W. Ayers, F. De Proft, P. Geerlings, *J. Chem. Phys.* **2009**, *131,* 154114.

[100] W. Yang, Y. Zhang, P. W. Ayers, *Phys. Rev. Lett.* **2000**, *84,* 5172.

[101] A. J. Cohen, P. Mori-Sanchez, W. Yang, *Science* **2008**, *321,* 792.

[102] A. J. Cohen, P. Mori-Sanchez, W. Yang, *J. Chem. Phys.* **2008**, *129,* 121104.

[103] O. Gunnarsson, B. I. Lundqvist, *Phys. Rev. B* **1976**, *13,* 4274.

[104] Y. A. Wang, E. A. Carter, In Theoretical Methods in Condensed Phase Chemistry; S. D. Schwartz, Ed.; Kluwer: Dordrecht, **2000**, pp. 117–184.

[105] J. Xia, C. Huang, I. Shin, E. A. Carter, *J. Chem. Phys.* **2012**, *136,* 084102.

[106] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140,* A1133.

[107] M. Levy, *Phys. Rev. A* **1982**, *26,* 1200.

[108] H. Englisch, R. Englisch, *Phys. Stat. Sol. B* **1984**, *124,* 373.

[109] P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99,* 329.

[110] R. C. Morrison, *J. Chem. Phys.* **2002**, *117,* 10506.

[111] J. Katriel, S. Roy, M. Springborg, *J. Chem. Phys.* **2004**, *121,* 12179.

[112] J. A. Pople, P. M. W. Gill, N. C. Handy, *Int. J. Quantum Chem.* **1995**, *56,* 303.

[113] D. M. Chipman, *J. Chem. Phys.* **1983**, *78,* 3112.

[114] D. M. Chipman, *Theor. Chem. Acc.* **1992**, *82,* 93.

[115] J. Wang, A. D. Becke, V. H. Smith, Jr., *J. Chem. Phys.* **1995**, *102,* 3477.

[116] A. J. Cohen, D. J. Tozer, N. C. Handy, *J. Chem. Phys.* **2007**, *126,* 214104.

[117] C. Daul, *Int. J. Quantum Chem.* **1994**, *52,* 867.

[118] C. A. Daul, K. G. Doclo, A. C. Stückl, In Recent Advances in Density Functional Methods, Part 2; D. P. Chong, Ed.; World Scientific: Singapore, **1995**, pp. 61–113.

[119] M. Filatov, S. Shaik, *Chem. Phys. Lett.* **1998**, *288,* 689.

[120] M. Filatov, S. Shaik, *Chem. Phys. Lett.* **1999**, *304,* 429.

[121] F. Illas, I. Moreira, J. Bofill, M. Filatov, *Theor. Chem. Acc.* **2006**, *116,* 587.

[122] I. Frank, J. Hutter, D. Marx, M. Parrinello, *J. Chem. Phys.* **1998**, *108,* 4060.

[123] S. Grimm, C. Nonnenberg, I. Frank, *J. Chem. Phys.* **2003**, *119,* 11574.

[124] C. Nonnenberg, S. Grimm, I. Frank, *J. Chem. Phys.* **2003**, *119,* 11585.

[125] F. Della Sala, A. Görling, *J. Chem. Phys.* **2003**, *118,* 10439.

[126] V. Vitale, F. Della Sala, A. Görling, *J. Chem. Phys.* **2005**, *122,* 244102.

[127] P. S. Bagus, B. I. Bennett, *Int. J. Quantum Chem.* **1975**, *9,* 143.

[128] T. Ziegler, A. Rauk, E. J. Baerends, *Theor. Chim. Acta* **1977**, *43,* 261.

[129] J. P. Perdew, A. Savin, K. Burke, *Phys. Rev. A* **1995**, *51,* 4531.

[130] S. Fux, M. Reiher, *Struct. Bond.* **2012**, *147,* 99.

[131] A. K. Rajagopal, J. Callaway, *Phys. Rev. B* **1973**, *7,* 1912.

[132] A. H. MacDonald, S. H. Vosko, *J. Phys. C: Solid State Phys.* **1979**, *12,* 2977.

[133] E. Engel, In Relativistic Electronic Structure Theory Part 1: Fundamentals, P. Schwerdtfeger, Ed.; Elsevier: Amsterdam, **2002**, pp. 523–621.

[134] E. Engel, R. M. Dreizler, S. Varga, B. Fricke, In Relativistic Effects in Heavy-Element Chemistry and Physics, B. A. Hess, Ed.; Wiley: Chichester, **2003**, pp. 123–161.

[135] T. Saue, T. Helgaker, *J. Comput. Chem.* **2002**, *23,* 814.

[136] E. Engel, R. Dreizler, *Top. Curr. Chem.* **1996**, *181,* 1.

[137] C. Van Wüllen, In Relativistic Methods for Chemists, Challenges and Advances in Computational Chemistry and Physics; M. Barysz, Y. Ishikawa, Eds.; Springer: Dordrecht, **2010**; pp. 191–214.

[138] G. Baym, Lectures on Quantum Mechanics; Benjamin–Cummings: New York, **1969**.

[139] C. Van Wüllen, *J. Comput. Chem.* **1999**, *20,* 51.

[140] C. Van Wüllen, *J. Comput. Chem.* **2002**, *23,* 779.

[141] G. Scalmani, M. J. Frisch, *J. Chem. Theory Comput.* **2012**, *8,* 2193.

[142] D. Peng, M. Reiher, *Theor. Chem. Acc.* **2012**, *131,* 1081.

[143] R. Mastalerz, R. Lindh, M. Reiher, *Chem. Phys. Lett.* **2008**, *465,* 157.

[144] E. J. Baerends, O. V. Gritsenko, *J. Phys. Chem. A* **1997**, *101,* 5383.