

Calculation of magnetic coupling constants with hybrid density functionals

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Abstract

The currently available computational methods for the calculation of magnetic coupling constants with density functional theory have been reviewed. These methods include modern approximations to the exchange-correlation functional, such as hybrid, range-separated and double-hybrid functionals, as well as approaches to treat the severe spin symmetry problems encountered in density functional calculations of magnetic interactions. In addition to the commonly used unrestricted Kohn–Sham formalism, density functional methods based on multireference wave functions and ensemble densities are also discussed. Performance of these models based on various studies has been summarized. The results indicate that self-interaction error plays an important role in the performance of density functional methods and is responsible for many of their shortcomings. If the self-interaction error and problems related to spin symmetry are treated in a theoretically correct manner, density functional theory can offer a very good description of magnetic coupling constants.

Tiivistelmä

Tässä tutkimuksessa on selvitetty mitä tiheysfunktionaaliteoriaan perustuvia laskennallisia menetelmiä käytetään tänä päivänä magneettisten kytkentävakioiden teoreettiseen määrittämiseen. Näihin menetelmiin kuuluvat muun muassa modernit vaihtokorrelaatiofunktionaaliapproksimaatiot (kuten hybridi-, kaksoishybridi- ja etäisyserotetut funktionaalit) ja menetelmät, joilla voidaan ratkaista tai kiertää spin-symmetriasta aiheutuvia ongelmia. Yleisesti käytetyn Kohn–Sham-formalismin lisäksi tutkielmassa on käsitelty tiheysfunktionaalimenelmiä, jotka perustuvat monideterminanttisiin aaltofunktioihin tai laajennettuihin kuvauksiin elektronitiheydestä. Kirjallisuudessa esitettyjen tutkimustulosten yhteenvedo osoittaa, että elektronitiheyden itseisvuorovaikutuksesta aiheutuva virhe on merkittävä tekijä tiheysfunktionaaliteoriaan perustuvien mallien kyvyssä ennustaa magneettisia kytkentävakioita ja johtaa usein suuriin virheisiin tuloksissa. Jos itseisvuorovaikutusvirheestä ja spin-symmetriasta aiheutuvat ongelmat ratkaistaan tai kierretään teoreettisesti oikein, voi tiheysfunktionaaliteorialla laskea tarkkoja arvoja magneettisille kytkentävakioille.

Foreword

This thesis has been written in Jyväskylä during the latter half of 2013. Some preliminary research and drafting was done in July and August but most of the writing took place during a three week period in October and November. This work is inspired by a loosely related computational research project examining the magnetic exchange interactions between organic radicals that was conducted during the summer of 2012.

I would like to express my warm-hearted gratitude to my supervisor Dr. Heikki M. Tuononen for his guidance as well as for making it possible for me to work with this fascinating topic. I also want to thank my girlfriend Susanna for enduring me during the rather intensive and time consuming writing process. Finally, a very special thanks goes to all my friends who have shared with me my all-too-short undergrad years at the University of Jyväskylä and without whom I would have graduated much earlier as a much duller man.

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Contents

Abstract	i
Tiivistelmä	i
Foreword	iii
Contents	v
List of abbreviations	vii
1 Introduction	1
2 Magnetic coupling	4
2.1 Coupling of effective magnetic moments and exchange interaction	4
2.2 Molecular magnetic materials and delocalization of effective magnetic moment	6
2.3 Spin-Hamiltonians	8
3 Magnetic interactions in electronic structure theory	12
3.1 Fundamentals of electronic structure theory	12
3.1.1 Hartree–Fock theory	12
3.1.2 Electron correlation	16
3.1.3 Configuration interaction	17
3.1.4 Other electron correlation methods	19
3.2 Magnetic interactions of singly occupied molecular orbitals .	21
4 Density functional theory	26
4.1 Electron density as the fundamental quantity	26
4.2 Kohn–Sham theory	30
4.3 DFT and multireference systems	34
5 Higher quality approximations to the exchange correlation functional	37
5.1 Hybrid functionals	38
5.2 Range-separated functionals	40
5.3 Double-hybrid functionals	43
5.4 Role of self-interaction error	44

6	Dealing with spin symmetry	48
6.1	Neglect of spin symmetry	48
6.2	Mapping results from unrestricted calculations	50
6.2.1	On the interpretation of the spin symmetry of an UKS reference wave function	50
6.2.2	Projection schemes	51
6.2.3	Mapping based on the Ising model	53
6.3	Alternative DFT formulations that retain spin symmetry of the KS reference wave function	54
6.3.1	Complete active space multireference DFT methods .	55
6.3.2	Ensemble Kohn–Sham formalism	58
6.4	Spin-flip time-dependent DFT	60
7	Performance of models	63
7.1	H–He–H model and projection schemes	63
7.2	Systematic studies	66
7.2.1	Magnetic coupling constant databases	66
7.2.2	Results	68
8	Conclusions	74
	References	76

List of abbreviations

ω B97X	range-separated functional of Chai and Head-Gordon based on Becke's 97 hybrid functional
ω B97X-2	a double-hybrid version of ω B97X
B05	Becke's 2005 SIE-corrected functional
B1B95	Becke's 1995 single-parameter hybrid functional
B1LYP	a single-parameter hybrid functional employing Becke's 1988 exchange part and the correlation part of Lee, Yang and Parr
B1PW91	a single-parameter hybrid functional employing Becke's 1988 exchange part and the correlation part of Perdew <i>et al.</i>
B2-PLYP	Grimme's original double-hybrid functional
B2GP-PLYP	a modified version of Grimme's double-hybrid functional
B3LYP	a three-parameter hybrid functional employing Becke's 1988 exchange part and the correlation part of Lee, Yang and Parr
B3LYP*	a modified version of B3LYP with 15% of exact exchange
B3PW91	a three-parameter hybrid functional employing Becke's 1988 exchange part and the 1991 correlation part of Perdew <i>et al.</i>
BLYP	a GGA functional employing Becke's 1988 exchange part and the correlation part of Lee, Yang and Parr
BMK	a meta-hybrid functional of Boese and Martin
CAM	Coulomb-attenuated method used to separate the Coulomb operator into short and long range parts
CAM-B3LYP	range-separated version of the B3LYP functional
CAMY-B3LYP	range-separated version of the B3LYP functional employing an exponential separation function
CAS	complete active space
CAS-MR-DFT	complete active space multireference density functional theory
CASCI	complete active space configuration interaction
CASCI-DFT	complete active space configuration interaction density functional theory

CASPT2	complete active space with second order perturbation correction
CASSCF	complete active space self-consistent field
CASSCF-DFT	complete active space self-consistent field density functional theory
CC	coupled cluster
CCSD	coupled cluster with single and double excitations
CCSD(T)	coupled cluster with single, double and perturbative triple excitations
CI	configuration interaction
CISD	configuration interaction with single and double excitations
CSF	configuration state function
DFT	density functional theory
DFT-FON	density functional theory with fractional occupation numbers
DS1DH	one-parameter density-scaled double-hybrid functional
FCI	full configuration interaction
GGA	generalized gradient approximation
GTO	Gaussian-type orbital
HDV	Heisenberg–Dirac–van Vleck
HF	Hartree–Fock
HK	Hohenberg–Kohn
HOMO	highest occupied molecular orbital
HS	high-spin
HSE	range-separated functional of Heyd, Scuseria and Ernzerhof
KS	Kohn–Sham
LC- ω PBE	range-separated functional based of Vydrov and Scuseria
LDA	local density approximation
LS	low-spin
LSDA	local spin density approximation
LUMO	lowest unoccupied molecular orbital
LYP	correlation functional of Lee, Yang and Parr
M05	2005 version of the meta-hybrid functional of Zhao and Truhlar

M06	2006 version of the meta-hybrid functional of Zhao and Truhlar
M06-2X	2006 version of the meta-hybrid functional of Zhao and Truhlar with double amount of exact exchange
M06-HF	2006 version of the meta-hybrid functional of Zhao and Truhlar with 100% of exact exchange
M06-L	a meta-GGA functional of Zhao and Truhlar
M08-HF	2008 version of the meta-hybrid of Zhao and Truhlar with 100% of exact exchange
M08-SO	2008 version of the meta-hybrid of Zhao and Truhlar
MAE	mean absolute error
MCSCF	multi-configuration self-consistent field
MCY	one-electron SIE-free functional of Mori-Sanchez, Cohen and Yang
MCY3	a version of MCY that is specially designed to reduce N -electron SIE
MP	Møller–Plesset
MP2	second order Møller–Plesset perturbation theory
mPW2-PLYP	a double-hybrid functional
MRCC	multireference coupled cluster
MRCI	multireference configuration interaction
O3LYP	a hybrid functional based on B3LYP using the parametrization of Cohen and Handy
OPBE0	a hybrid functional of Swart, Ehlers and Lammertsma that uses a modified version of the PBE GGA functional
PBE	GGA functional of Perdew, Burke and Ernzerhof
PBE0	a zero-parameter hybrid version of PBE
PBE0-DH	a zero-parameter double-hybrid version of PBE
PBE1PBE	an alternative name for PBE0
PBEh	an alternative name for PBE0 (the name is used for other functionals as well)
PW86	1986 correlation functional of Perdew <i>et al.</i>
PW91	1991 correlation functional of Perdew <i>et al.</i>
rCAM-B3LYP	a version of CAM-B3LYP that is specially designed to reduce N -electron SIE
REKS	restricted ensemble-referenced Kohn–Sham
RHF	restricted Hartree–Fock
RKS	restricted Kohn–Sham

ROHF	restricted open-shell Hartree–Fock
SCF	self-consistent field
SDV	standard deviation
SF-TDDFT	spin-flip time-dependent density functional theory
SIC-B3LYP	self-interaction corrected B3LYP
SIE	self-interaction error
SOMO	singly occupied molecular orbital
STO	Slater-type orbital
TDDFT	time-dependent density functional theory
TPSSh	meta-hybrid functional of Tao <i>et al.</i>
UHF	unrestricted Hartree–Fock
UKS	unrestricted Kohn–Sham
X3LYP	a functional based on B3LYP using the parametriza- tion of Xu and Goddard
XC	exchange-correlation

1 Introduction

Molecular magnetic materials have attracted a lot of interest over the past years. They show promising applications in a number of technologies such as magnetic memory appliances, quantum computing and optical devices.¹⁻⁶ Rational design of magnetic functionality at the molecular level requires quantum chemical insight into the magnetic coupling mechanism between the molecules that comprise these materials. At the heart of this coupling lies the magnetic coupling constant J that describes the magnitude and type of magnetic interactions.^{7,8} Calculation of J using *ab initio* methods based on reference wave functions with well defined spin states is straightforward.⁸ Coupled cluster^{9,10} and configuration interaction¹⁰⁻¹² theories can produce high quality results but they are computationally extremely exhaustive. Furthermore, most magnetic systems show multireference character and a proper description of such a system cannot be achieved by the lowest levels of approximation in these theories.¹³⁻¹⁵ Methods such as the complete active space self-consistent field (CASSCF)^{16,17} and the multireference perturbation theory (CASPT2)^{18,19} can be applied to systems of moderate size but most molecules with interesting magnetic functionality are relatively large. Density functional theory (DFT) offers a promising alternative to the aforementioned methods as it is fairly cheap in terms of computational costs and can offer very accurate results in a number of different types of chemical problems.

Over the past two decades DFT has risen to become a standard method for accurate quantum chemical treatment of systems that are too large for high level *ab initio* calculations.²⁰⁻²⁵ DFT is, in principle, an exact theory but in any practical implementation—the most common being the Kohn–Sham (KS) formalism²⁶—approximations have to be made. This introduces the concept of the exchange-correlation functional that covers the portion of energy that KS theory cannot describe exactly. Various approximations have been made to its form, starting from the local density approximation (LDA). It was not, however, until the advent of hybrid functionals in the early nineties that DFT became a *de facto* method in the field of quantum chemistry.^{20-22,24} Hybrid functionals introduce a portion of exact exchange energy calculated with the wave function formalism into the functional approximation, much improving their performance. Much of the early success of hybrid DFT can be attributed to the B3LYP exchange-correlation functional²⁷⁻³⁰ that is still the most widely used DFT method in quantum chemistry today.²³ Hybrid functionals have triumphed in their

ability to predict a wide range of molecular properties, in addition to having greater computational efficiency compared to high accuracy *ab initio* methods.^{20,23,25} Nonetheless, calculation of magnetic coupling constant proves a major challenge for DFT.³¹⁻³⁴

Attempts to describe magnetic interactions expose many of the fundamental deficiencies of KS theory.³¹ Magnetic coupling is an exchange phenomenon and thus an accurate description of exchange interaction is vital for quantitative estimates of coupling constants. Exchange is treated accurately in all *ab initio* methods but no mapping between electron density and exchange energy exists.⁷ Another significant problem arises from the description of spin eigenstates in DFT. A correct description of the spectrum of spin eigenstates is essential in order to calculate magnetic coupling constants. A commonly used approach is to treat the spin state of the KS reference wave function (an artificial by-product of a KS calculation³⁵) as an approximation to the true spin state. However, there is no theoretical justification for this.³⁶ Furthermore, in magnetic coupling problems one must employ unrestricted KS formalism which produces KS reference wave functions that are not spin eigenstates. To enforce proper spin symmetry, the unrestricted results must be projected on to the spectrum of spin eigenstates. Currently there is no consensus as to how this problem should be best treated although a variety of approaches exist.^{8,25,31-34} Much of the failure of common exchange-correlation functionals in magnetic coupling problems has also been ascribed to a problem known as self-interaction error that is present in all functional approximations.^{31,37}

The wide range of problems that require some approximate treatment means that numerical results alone cannot be used in validating density functional methods for calculation of magnetic coupling constants. Two incorrectly chosen approximations may lead to error cancellation and good overall numerical results. As Illas *et al.* have pointed out,³³ good results are often obtained for the wrong reasons. Thus, one must have a thorough understanding of the theoretical foundations of DFT and KS theory and how they are related to magnetic coupling phenomena in order to choose the right tools for the right problem.

This study aims to review the currently available density functional methods that are used to calculate magnetic coupling constants and then to discuss their performance. The second and third sections of this study discuss the concepts of magnetic coupling, spin-Hamiltonians and exchange interaction and how they are treated in conventional electronic structure theory. The fourth section introduces the theoretical concepts be-

hind DFT. Sections five and six then introduce the tools that are required to employ Kohn–Sham DFT to magnetic coupling problems. Finally, section seven summarizes and discusses several systematic studies on the performance of DFT models in the calculation of coupling constants of a large number of experimentally or theoretically well-characterized magnetic systems.

2 Magnetic coupling

The ability of certain minerals to attract ferrous bodies—ferromagnetism—is a phenomenon that has been known to mankind since ancient times. By the end of the 19th century the magnetic interactions between macroscopic objects were well understood. However, the microscopic structure of material that is responsible for magnetic properties remained elusive until the advent of quantum mechanics. A true understanding of magnetism was not achieved until relativistic quantum theory introduced the concept of electron spin.^{7,38} Since then much progress has been made in understanding the relationship between the electronic structure of material and its magnetic properties in both relativistic and non-relativistic frameworks. The most commonly applied model of magnetism in quantum chemistry is based on the semi-classical approach proposed by Heisenberg in 1928 that treats spin by a simple vector model.³⁹ The spin vectors couple through exchange interaction which is a form of non-classical interaction that results from the antisymmetry of the electronic many-particle wave function. The coupling mechanisms determine the macroscopic magnetic properties of the bulk material.

2.1 Coupling of effective magnetic moments and exchange interaction

Heisenberg's theory of ferromagnetism considers effective magnetic moments, S_i , that are located at a magnetic center i in a crystal lattice.³⁹⁻⁴¹ The moments arise from the spin and orbital angular momentum of unpaired electrons. The simplest case of such a magnetic center is one that is associated with a single unpaired electron with zero orbital angular momentum and thus has $S_i = 1/2$. If the microscopic moments are aligned they add up, and a macroscopic magnetization ensues in the bulk material. This type of material (as well as the interaction between the moments) is said to be ferromagnetic. If some of the moments add negatively to the net magnetic moment but the overall magnetization still remains positive, the material is said to be ferrimagnetic. The opposite phenomenon to ferromagnetism is antiferromagnetism where the magnetic moments align themselves in a manner such that they point to opposite directions canceling each other and thus resulting in zero macroscopic magnetization. This is the most common alignment in radical systems. Ferro-, ferri- and antiferromagnetism all require ordering of the magnetic moments. Above a certain

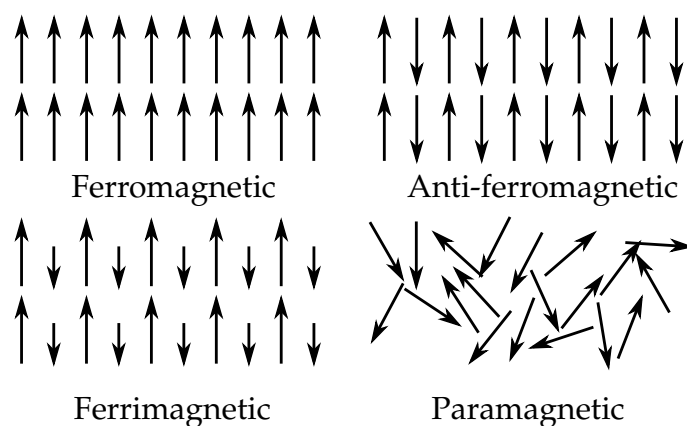


Figure 1: A schematic representation of the alignment of microscopic magnetic moments in ferromagnetic, anti-ferromagnetic, ferrimagnetic and paramagnetic materials.

material-specific threshold temperature (known as the Curie temperature) this ordering disappears and the magnetic moments lie at random directions resulting in a zero macroscopic magnetization. This type of magnetic material is called paramagnetic. A paramagnetic material is attracted to an external magnetic field and can show ordered structure in such a field. In contrast, a diamagnetic material is one that is repelled by an external field. Para- and diamagnetism are much weaker interactions than ferro- or ferrimagnetism.⁴⁰⁻⁴² Figure 1 presents a schematic representation of different magnetic interactions in materials.

The macroscopic magnetization originating from the aligned microscopic magnetic moments can be explained with classical electromagnetism. The classical interaction between the individual microscopic magnetic moments is, however, in most cases far too weak to result in spontaneous alignment. Thus, ferromagnetism is a result of quantum mechanical effects.⁸ The explanation for this lies in the Pauli principle. The microscopic magnetic moment is carried by unpaired electrons that are anti-symmetric relative to particle exchange. Because of this, no two electrons of the same spin may occupy the same point in space. This leads to a lower probability of finding two electrons near each other and thus to a lower Coulombic repulsion between them, resulting in a lower total energy of the system. The lowering of the total energy due to anti-symmetry of electrons is known as the exchange interaction and takes place only between electrons of the same spin. Exchange interaction is a highly important concept in the electronic structure of molecules, and already in the early work of Heitler and London on the H_2 molecule, it was shown that

the anti-symmetry of the two-electron wave function must be enforced in order to make the molecule stable.^{43,44} A quantitative expression for this concept is derived in section 3.1.1. Because of exchange interaction, two electrons that are degenerate in energy have lower total energy if their spins are aligned. Of course, in most chemical systems electrons are not degenerate but lie on orbitals of discrete energy. The energy gained from spin-pairing to a lower energy orbital usually surpasses the energy gained from the exchange interaction and thus spin-alignment takes place only in the presence of near-degenerate orbitals.

2.2 Molecular magnetic materials and delocalization of effective magnetic moment

Degeneracy of orbitals is most common in transition-metals. In purely metallic materials, all five d-orbitals can be degenerate, and if they are only partially occupied, the unpaired electrons will align. This leads to paramagnetism but does not ensure ferromagnetism. Degeneracy, as well as near-degeneracy is present also in transition metal complexes with high local symmetry where the d-orbitals split as described by crystal field or ligand field theories.⁴² Paramagnetic transition metal centers are common magnetic building blocks of molecular magnetic materials. These types of materials can also be built with purely organic radicals. In general, paramagnetic organic species are much less stable than paramagnetic transition metal centers, and magnetic properties (other than diamagnetism) are much rarer in organic materials.² Another class of organic compounds that can be characterized by magnetic coupling constants are diradicals. These compounds contain two unpaired electrons lying on different orbitals in singlet or triplet configuration. A diradical system can also be interpreted as a partially dissociated bond. In order for a magnetic material to show spontaneous spin-alignment there must be sufficient exchange interaction between the paramagnetic units. This can take place either through space or by the mediation of other electrons in a process known as superexchange. A textbook example of such a system is MnO where the antiferromagnetic interaction between the Mn atoms is mediated by a p-orbital of the O atom lying on the Mn–O–Mn axis.⁴⁵ In both transition metal centers and organic radicals the magnetic moment is carried by singly occupied molecular orbitals (SOMOs). In transition metal centers these are usually well localized near the atom they are associated with.

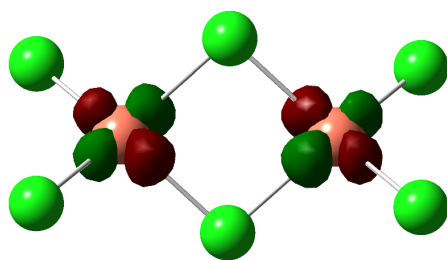


Figure 2: A highly localized singly occupied molecular orbital of $[\text{Cu}_2\text{Cl}_6]^{2-}$ anion.

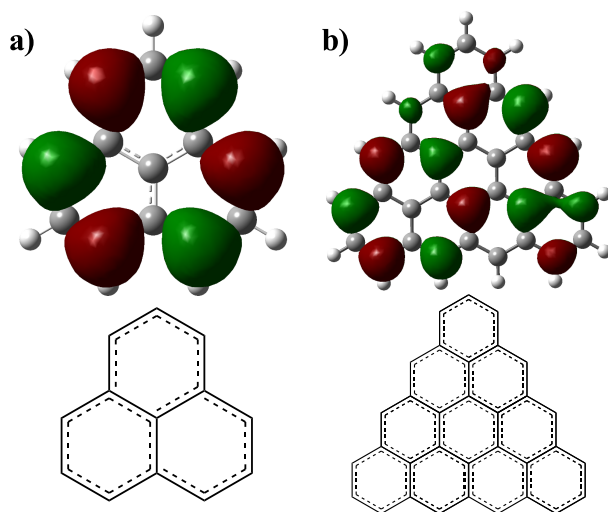


Figure 3: The singly occupied molecular orbital of **a)** a phenalenyl radical and **b)** a graphene sheet.

Figure 2 shows the highly localized singly occupied molecular orbitals of the $[\text{Cu}_2\text{Cl}_6]^{2-}$ anion. In organometallic systems the magnetic moment can however be delocalized into the ligands and in purely organic radicals the SOMOs can be delocalized over the entire molecular skeleton.^{2,3,7} Examples of such systems are the phenalenyl radical (Figure 3a)⁴⁶ and, in a more extreme case, a fragment of a graphene sheet (Figure 3b).⁴⁷

The delocalized nature of the SOMOs in some magnetic systems is contrary to the classical localized nature of magnetic centers in Heisenberg's model. The magnetic centers are well defined points in space whereas the quantum nature of electrons means they are delocalized.³⁶ In order to study interactions between magnetic centers the molecular system under study must be divided into subsystems over which the effective magnetic moment is localized. Transition metal clusters are relatively easy to divide into magnetic units consisting of the transition metal atoms with well localized SOMOs. In highly delocalized organic or organometallic

systems assigning the SOMOs to a single point in space becomes rather arbitrary. In any case, this division is never theoretically rigorous as the spin—defined by the eigenvalues of the operators \hat{S}^2 and \hat{S}_z —is a property of the full many body wave function and not any subsystem of it.³⁶ To overcome this problem, there has been considerable interest over the past decade in developing a method to partition $\langle \hat{S}^2 \rangle$ into atomic contributions.^{48–52}

Despite these inconsistencies the central idea of Heisenberg’s theory—interacting magnetic subunits—remains an attractive approach. In theoretical magneto-chemistry one is usually interested in this interaction and Heisenberg’s theory is by far the most common approach to modeling magnetic interactions in quantum chemistry.⁷ The Heisenberg model is also the basis of the widely successful Heisenberg–Dirac–van Vleck Hamiltonian introduced in the next section.

2.3 Spin-Hamiltonians

The spin of an electron is a relativistic four dimensional property and thus a truly rigorous treatment of magnetic interactions would require use of the Dirac equation.^{36,53–55} In practice, however, spin interactions can often be treated by a spin-Hamiltonian. Such Hamiltonians describe the lower energy spectrum of spin eigenstates. A spin state is defined by the total spin quantum number S and the quantum number corresponding to its z -component M_S . The z -component is chosen by definition and the theory could easily be formulated by choosing any one of the components. The energetics related to properties other than spin are considered by the exact non-relativistic Hamiltonian or some model Hamiltonian based on it. In molecular magnetism the most common spin-Hamiltonian used is the Heisenberg–Dirac–van Vleck (HDV) Hamiltonian

$$\hat{H}_{HDV} = - \sum_{\langle i,j \rangle} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad (1)$$

where J_{ij} is the magnetic coupling constant between magnetic centers i and j , $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are local magnetic moment operators acting on the centers i and j , and the $\langle i,j \rangle$ symbol indicates that the sum runs over lattice neighbors only.^{39,41,56–58} The Hamiltonian describes the lower energy spectrum of isotropic magnetic interactions in a system of localized spins in the absence of an external magnetic field. It should be noted when mak-

ing comparisons with other works that some authors use $2J_{ij}$ instead of J_{ij} and may discard the negative sign in equation (1).

The HDV Hamiltonian is originally phenomenological³⁹ but can be rigorously derived from the exact Hamiltonian through the use of the effective Hamiltonian theory.^{7,8,59-64} The HDV Hamiltonian provides the simplest way to describe magnetic coupling in a large variety of chemical compounds, but it is by no means the most complete description of magnetic interactions. When an effective Hamiltonian is derived in an *ab initio* manner some terms that would need to vanish in order to reproduce equation (1) may not necessarily do so. For example, Moreira *et al.* have shown that in periodic calculations of NiO and K_2NiF_4 systems a biquadratic term remains in the effective Hamiltonian:⁶⁵

$$\hat{H}_{eff} = - \sum_{\langle i,j \rangle} J_{ij} \left\{ \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \lambda (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)^2 \right\}. \quad (2)$$

However, the biquadratic term is a four-particle operator and is not present in any system with less than four magnetic centers. The most common magnetic coupling problems in quantum chemistry involve only two centers. In this case Nesbet has suggested that two magnetic centers with total spin of S at both centers should behave exactly as the HDV Hamiltonian predicts.^{8,66,67} Thus, assuming *a priori* the applicability of the HDV Hamiltonian to a magnetic interaction problem is justified in the case of two interacting magnetic centers. Equation (2) serves to warn that in systems of a large number of interacting magnetic subunits one must be careful when assuming the absence of higher order terms.

As mentioned earlier, the HDV Hamiltonian describes a system of localized magnetic moments. The model is, however, applied also to magnetic systems with some degree of delocalization in the SOMOs.^{7,25,68,69} The numerical results show that the model performs very well in these systems and even systems of highly delocalized magnetic moment such as the phenalenyl radical.^{70,71} For organic magnetic systems, an alternative approach has also been suggested that employs spin-polarization densities in addition to effective magnetic moments.⁷² Spin-polarization density $\rho = n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})$ is the difference between the electron densities of α and β electrons. This introduces a degree of delocalization into the model.

The first model was devised by McConnell⁷² in the early sixties:

$$\hat{H}_{McConnell} = -\hat{\mathbf{S}}^A \cdot \hat{\mathbf{S}}^B \sum_i \sum_j J_{ij}^{AB} \rho_i^A \rho_j^B. \quad (3)$$

$\hat{\mathbf{S}}^A$ and $\hat{\mathbf{S}}^B$ are total spin operators acting on magnetic subunits A and B , and ρ_i^A and ρ_j^B are spin-polarization densities of atoms i and j belonging to subunits A and B . The magnetic coupling constant, J_{ij} , is evaluated in terms of valence bond theory⁴⁴ and is thus not necessarily the same as in the HDV Hamiltonian. Equation (3) is based on equation (1) but cannot be derived from it in any rigorous way. This phenomenological nature of the McConnell Hamiltonian has been criticized.⁷³ Paul and Misra have very recently proposed a rigorous approach to obtaining effective Hamiltonians in terms of spin-polarization density and applied these to calculation of magnetic coupling constants.⁷⁴ Their approach also offers some theoretical justification for equation (3). Practically all modern DFT approaches however employ the HDV Hamiltonian, and it will be the model of choice in this study.^{7,25}

In order to relate the coupling constant J_{ij} of the HDV Hamiltonian to results from quantum chemical calculations, some way to relate J_{ij} to the energy state structure of the full system is required. Eigenstates of the HDV Hamiltonian are the spin eigenstates of the system. Because the squared spin operator, \hat{S}^2 , and the operator of the z -component of spin, \hat{S}_z , commute with the exact Hamiltonian, spin states are also energy eigenstates. Thus, the spin-Hamiltonian and the exact Hamiltonian share the lower end of their spectrum. In a system of two magnetic centers the HDV Hamiltonian takes the simple form

$$\hat{H}_{HDV} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \quad (4)$$

that can be written with the ladder operators $\hat{\mathbf{S}}^+$ and $\hat{\mathbf{S}}^-$ as⁷⁵

$$\hat{H}_{HDV} = -J\left\{\frac{1}{2}[(\hat{\mathbf{S}}_1^+ + \hat{\mathbf{S}}_2^+)(\hat{\mathbf{S}}_1^- + \hat{\mathbf{S}}_2^-) + (\hat{\mathbf{S}}_1^- + \hat{\mathbf{S}}_2^-)(\hat{\mathbf{S}}_1^+ + \hat{\mathbf{S}}_2^+)] + \hat{\mathbf{S}}_{z,1} \cdot \hat{\mathbf{S}}_{z,2}\right\}, \quad (5)$$

where the subscripts 1 and 2 refer to operators acting on magnetic centers 1 and 2 and $\hat{\mathbf{S}}_{z,1}$ and $\hat{\mathbf{S}}_{z,2}$ are operators for the z -component of the spin for centers 1 and 2 respectively. The simplest application of equation (5) is to a system with two magnetic centers with total spins $S_1 = S_2 = 1/2$ such as many copper(II) complexes or organic diradicals.² The system has four possible spin eigenstates: a singlet with $S = 0$ and $M_S = 0$ and three

triplets with $S = 1$ and $M_S = 1, 0, \text{ or } -1$. The triplet states are degenerate in the absence of external magnetic fields. Eigenvalues for these states can be solved by employing equation (5) and they are $\frac{3}{4}J$ and $-\frac{1}{4}J$ for the singlet and triplets respectively. Thus, the magnetic coupling constant for this system is the energy gap between the singlet and triplet states:

$$\Delta E_{S-T} = E(S) - E(T) = \frac{3}{4}J - (-\frac{1}{4}J) = J. \quad (6)$$

Equation (6) shows that if J is positive the triplet state is lower in energy and ferromagnetic (or spin-aligned) coupling is favored whereas if J is negative anti-ferromagnetic coupling leads to lower energy. For larger effective magnetic moments equation (5) becomes more complicated. If $S_1 = S_2$ the Lande interval rule⁷⁶

$$J = \frac{E(S-1) - E(S)}{S} \quad (7)$$

can be used to map energies of the different $2S + 1$ multiplet states to J . This mapping can also be extended—although not straightforwardly—to systems of more than two magnetic centers.⁷⁷⁻⁷⁹

3 Magnetic interactions in electronic structure theory

Equation (6) defines the magnetic coupling constant for a system of two interacting magnetic centers with $S_1 = S_2 = 1/2$ as the energy gap between the singlet and triplet states. The singlet–triplet gap can be related to more chemically intuitive concept of orbital interactions using electronic structure theory. Also, understanding the process of calculating magnetic coupling constants within wave function based framework is important in order to grasp some of the concepts DFT struggles with once applied to the same problem. For this reason, it is necessary to discuss Hartree–Fock and configuration interaction theories in some detail.

In all subsequent derivations relativistic effects are ignored and the Born–Oppenheimer approximation is assumed unless stated otherwise.

3.1 Fundamentals of electronic structure theory

3.1.1 Hartree–Fock theory

The Hartree–Fock (HF) theory approximates the many particle wave function as an antisymmetrized product function of single particle wave functions. An energy expectation value is then calculated for the wave function using the full, many particle electronic Hamiltonian, and this expectation value is treated variationally to obtain the ground state energy. The antisymmetrized product function takes the form of a Slater determinant Φ_{SD} which is the exact ground state wave function of a system of non-interacting fermions. Because in a real system the electrons interact via Coulombic repulsion, this introduces a limit of how close HF theory can get to the real ground state energy known as the Hartree–Fock limit E_{HF} . The difference between E_{HF} and the true ground state energy E_0 is known as the correlation energy

$$E_{corr} = E_0 - E_{HF}, \quad (8)$$

and it is always negative.^{10,12,80}

A Slater determinant for a system of N particles has the form

$$\Phi_{SD}(\mathbf{x}_1, \mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{bmatrix}, \quad (9)$$

where $\phi_i(\mathbf{x}_j)$ is a single particle function i of electron j known as a spinorbital and the factor $1/\sqrt{N!}$ is a normalization constant. The spinorbitals $\phi_i(\mathbf{x}_j)$ consist of a spatial function $\varphi_i(\mathbf{r}_j)$ and a spin function $\sigma_i(\mathbf{s}_j)$:

$$\phi_i(\mathbf{x}_j) = \varphi_i(\mathbf{r}_j)\sigma_i(\mathbf{s}_j), \quad (10)$$

where

$$\sigma_i(\mathbf{s}_j) = \begin{cases} \alpha(\mathbf{s}_j) \\ \beta(\mathbf{s}_j) \end{cases}. \quad (11)$$

The vector \mathbf{r}_j contains the spatial coordinates of electron j . The spin functions $\alpha(\mathbf{s}_j)$ and $\beta(\mathbf{s}_j)$ are orthogonal and their exact mathematical form, as well as the nature of the spin coordinate \mathbf{s}_j , are not relevant to this discussion. important.^{10,12}

The HF energy is calculated by minimizing the energy of the Slater determinant with respect to variations in the spinorbitals. The spinorbitals must remain mutually orthogonal, and thus the minimization is a constrained search. This procedure is performed by the method of Lagrange multipliers. For a system of N electrons this leads to N mutually coupled single particle equations known as the HF equations:

$$\hat{f}_i\phi(\mathbf{x}_i) = \epsilon_i\phi(\mathbf{x}_i), \quad (12)$$

where \hat{f}_i is the Fock operator and ϵ_i is the energy of spinorbital i . The spinorbitals produced as a solution to the HF equations are known as canonical HF orbitals, and they are invariant under a unitary transformation. The Fock operator is an effective single particle operator. It is defined as

$$\hat{f}_i = \hat{h}_i + \frac{1}{2} \sum_{j=1}^N \left(\hat{C}_{ij} - \hat{K}_{ij} \right), \quad (13)$$

where \hat{h}_i , \hat{C}_{ij} and \hat{K}_{ij} are the single electron, Coulomb and exchange operators respectively. The single electron operator corresponds to the kinetic

and nuclear–electron attraction energies, the Coulomb operator to the electrostatic repulsion between electrons i and j and the exchange operator to electron exchange energy between electrons i and j due to the antisymmetry of the N particle wave function. This is the same exchange interaction that is responsible for magnetic interactions. The term arises solely because antisymmetry is enforced on the trial wave function. If a simple product function of the single particle functions was used instead of a Slater determinant Coulombic repulsion would be the only two-electron interaction. It should be noted that most texts use the notation \hat{J}_{ij} for the Coulomb operator, but in order to avoid confusing it with the magnetic coupling constant, \hat{C}_{ij} is used in this study. The operators can be defined by the corresponding matrix elements:

$$\begin{aligned} h_i &= \langle \phi_i(\mathbf{x}) | \hat{h}_i | \phi_i(\mathbf{x}) \rangle \\ &= \int \phi_i^*(\mathbf{x}) \left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) \right] \phi_i(\mathbf{x}) d\mathbf{x} \end{aligned} \quad (14)$$

$$\begin{aligned} C_{ij} &= \langle \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) \rangle \\ &= \iint \phi_i^*(\mathbf{x}_1) \phi_j(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (15)$$

$$\begin{aligned} K_{ij} &= \langle \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \phi_j(\mathbf{x}_1) \phi_i(\mathbf{x}_2) \rangle \\ &= \iint \phi_i^*(\mathbf{x}_1) \phi_j(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_j^*(\mathbf{x}_1) \phi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \end{aligned} \quad (16)$$

where $V_{ext}(\mathbf{r})$ is the Coulombic nuclear–electron attraction potential defined by the nuclear geometry and charges.

It is clear from equations (12)–(16) that the orbital energies ϵ_i depend on all the other orbitals, and thus the HF equations must be solved iteratively with a method known as the self-consistent field (SCF) procedure. The orbital energies and the total energy E_{HF} can be written in terms of the matrix elements in equations (14)–(16):

$$\epsilon_i = h_i + \frac{1}{2} \sum_{j=1}^N (C_{ij} - K_{ij}) \quad (17)$$

$$E_{HF} = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (C_{ij} - K_{ij}). \quad (18)$$

The orbital energy is simply the expectation value of the corresponding Fock operator. The total energy, however, is not the sum of orbital energies as the Fock operator is associated with variations of the total energy, not the energy itself. Simply summing the orbital energies leads to double counting of some terms.

In practical implementations of HF theory, the spatial functions are expanded in a finite basis:

$$\phi_i(\mathbf{r}) = \sum_{j=1}^M c_{ij} \chi_j(\mathbf{r}), \quad (19)$$

where M is the number of basis functions, c_{ij} are the expansion coefficients and $\chi_j(\mathbf{r})$ is the j th basis function of the basis set. The basis functions usually mimic atomic orbitals of a hydrogenic atom. These types of basis sets fall into two categories: Slater type orbitals (STOs), where the radial part of the hydrogenic orbital is an exponential function of the form $r^n e^{-\alpha r}$; and Gaussian type orbitals (GTOs), where the radial part is a Gaussian function of the form $r^n e^{-\alpha r^2}$.¹⁰ In calculations of periodic systems a basis consisting of plane waves can also be used. Once a basis set is chosen to describe the spatial functions, the spin functions must be integrated out. There are three schemes on how to do this: restricted HF (RHF) where all orbitals are set to be doubly occupied (i.e. two electrons of opposite spin share the same spatial orbital); unrestricted HF (UHF), where each electron may have a unique spatial orbital; and restricted open-shell HF (ROHF) where doubly occupied orbitals are described as in RHF and open shell orbitals as in UHF.^{10,12} The latter will not be reviewed here.

In RHF all the HF equations can be combined in a single matrix equation known as the Roothan–Hall equation:^{10,12,81,82}

$$\mathbf{FC} = \mathbf{SC}\epsilon, \quad (20)$$

where

$$\begin{aligned} F_{mn} &= \langle \chi_m(\mathbf{r}) | \hat{f} | \chi_n(\mathbf{r}) \rangle = \int \chi_m(\mathbf{r}) \hat{f} \chi_n(\mathbf{r}) d\mathbf{r} \\ S_{mn} &= \langle \chi_m(\mathbf{r}) | \chi_n(\mathbf{r}) \rangle = \int \chi_m(\mathbf{r}) \chi_n(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (21)$$

\mathbf{F} and \mathbf{S} are the Fock and overlap matrices. \mathbf{C} is a square matrix that contains the expansion vectors (a vector with the coefficients c_{ij} as its ele-

ments) as its columns. The diagonal matrix ϵ contains the orbital energies. The coefficients can be solved by diagonalizing the Fock matrix. In the UHF formalism, the coefficients can be solved by simultaneous diagonalization of two coupled matrix equations using the method of Pople and Nesbet where all the matrices are built separately for spatial orbitals associated to α and β spinorbitals:^{12,83}

$$\begin{aligned}\mathbf{F}^\alpha \mathbf{C}^\alpha &= \mathbf{S}^\alpha \mathbf{C}^\alpha \epsilon^\alpha \\ \mathbf{F}^\beta \mathbf{C}^\beta &= \mathbf{S}^\beta \mathbf{C}^\beta \epsilon^\beta.\end{aligned}\tag{22}$$

The RHF wave function is an eigenfunction of the \hat{S}_z and \hat{S}^2 operators as the exact many-particle wave function. A UHF wave function is however an eigenfunction of \hat{S}_z only and does not have a clearly defined spin state. The UHF wave function is said to be spin contaminated. An UHF solution might also have a lower symmetry than the nuclear geometry. The singlet UHF solution is in such a case called a broken symmetry solution.^{10,12}

The HF method is an independent particle model in the sense that, even though the Fock operator in equation (13) is generated by all of the spinorbitals, all electron–electron interactions are taken into account in an average fashion. In other words, all the electrons move in a constant potential $v_i^{HF}(\mathbf{r})$ formed by all the other electrons, and therefore HF theory is a mean field theory. This restriction is imposed on the model by approximating the true wave function as a single determinant. The HF method is usually able to reproduce about 99% of the total electronic energy of the system. However, energies associated with chemical bonds are often much smaller—and those associated to magnetic coupling constants even smaller—and the remaining 1% becomes important.¹⁰ The solutions to the HF equations can, however, be used as a basis for an expansion of the true wave function.¹²

3.1.2 Electron correlation

Equation (8) defines the correlation energy as the difference between the HF limit and the exact ground state energy. The limit arises from the single determinant approximation in HF theory. Thus, any *ab initio* method that goes beyond this approximation will recover some correlation energy and is said to be correlated. The correlation energy is often divided to dynamic and static electron correlation. Dynamic correlation arises from the movement of electrons as they tend to avoid each other. This leads

to more delocalized charge distributions than the ones produced by variational HF treatment and thus lower electron–electron Coulombic repulsion. Static correlation is a result of the failure of the single determinant wave function approximation and is most prevalent in systems where a single determinant is a very poor approximation to the true wave function. Static correlation is often associated with degeneracy or near-degeneracy of states such as in bond dissociation processes or transition-metal complexes. These types of systems are sometimes called strongly correlated, although this term can be used for other purposes as well. Dynamic correlation is generally seen as a short range interaction and static correlation as a long range effect. The exact division between the two types of electron correlation is somewhat arbitrary.^{10,12}

It is important to note that describing electron correlation is not the same thing as describing electron–electron interactions. HF theory employs the full non-relativistic electronic Hamiltonian which includes all electron-electron interactions. The lack of electron correlation in the HF model results from the failure of the single determinant wave function as an approximation to the true ground state wave function. Electrons do interact in the HF model although the form of the trial wave function forces this interaction to take place in a mean field fashion.

3.1.3 Configuration interaction

When the Roothan–Hall equation (20) is solved, in addition to the $1/2N$ occupied orbitals, $M - 1/2N$ empty virtual orbitals are generated. By promoting electrons from the occupied orbitals to the virtual orbitals, a series of singly, doubly, triply, etc., excited determinants, or configurations, can be generated. The true interacting many particle wave function can be expressed as an infinite expansion in a basis of configurations of the non-interacting solution of the same system. This method is known as configuration interaction (CI).^{10–12} The CI expansion can be written as

$$\begin{aligned}
 |\Psi_{CI}\rangle &= a_0|\Phi_{HF}\rangle + \sum_S a_S|\Phi_S\rangle + \sum_D a_D|\Phi_D\rangle + \sum_T a_T|\Phi_T\rangle + \sum_Q a_Q|\Phi_Q\rangle + \dots \\
 &= \sum_{i=0} a_i|\Phi_i\rangle,
 \end{aligned}
 \tag{23}$$

where a_i is an expansion coefficient and the indices S , D , T and Q refer to singly, doubly, triply and quadruply excited determinants respectively.^{10,12}

Not all of the configurations generated from a given HF reference wave function are eigenfunctions of the \hat{S}^2 operator, and thus not all are spin eigenfunctions. As the full electronic Hamiltonian and the \hat{S}^2 operator commute, these states are unphysical. Spin eigenfunctions can, however, be generated by taking proper linear combinations of the non-eigenfunction configurations. These combinations are known as configuration state functions (CSFs). The simplest example of such a configuration is the singly excited state of the hydrogen molecule which can be written as a linear combination of a configuration where α electron is promoted to the lowest unoccupied molecular orbital (LUMO) and a configuration where a β electron is promoted. For configurations with larger number of excitations, the number of determinants in a CSF increases rapidly.¹²

The expansion coefficients a_i can be solved by diagonalizing the CI matrix:

$$\begin{bmatrix} H_{00} & H_{01} & H_{02} & \dots \\ H_{10} & H_{11} & H_{12} & \dots \\ H_{20} & H_{21} & H_{22} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \\ \vdots \end{bmatrix} = \begin{bmatrix} E_0 & 0 & 0 & \dots \\ 0 & E_1 & 0 & \dots \\ 0 & 0 & E_2 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \\ \vdots \end{bmatrix}, \quad (24)$$

where

$$H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle. \quad (25)$$

Once all the matrix elements are calculated, only a single diagonalization is necessary. For large systems the size of the matrix becomes enormous. Some matrix elements can, however, be eliminated. The Hamiltonian is totally symmetric and does not operate on spin (when absence of external fields and spin-orbit coupling is assumed). This means that matrix elements between CSFs are zero if the direct product of the symmetries of the respective CSFs does not produce the totally symmetric representation or if the CSFs are of different spin symmetry (singlet, doublet, triplet, etc.). Furthermore, Brillouin's theorem¹² states that the matrix elements between the HF reference state and singly excited configurations is zero. Excitations from core orbitals can in most cases also be neglected. While these excitations do affect the total energy, in chemistry one is usually interested of relative energies and most chemically interesting phenomenon take place in the valence orbitals. Thus the error introduced from the neglect of core electron correlation tends to cancel out.

If all possible configurations are included in a CI expansion, all the

electron correlation up to the basis set limit is included. This method is known as full CI (FCI). If the basis set were infinite, the FCI solution would be the *exact* solution to the non-relativistic, time-independent Schrödinger equation within the Born–Oppenheimer approximation. In practice, however, FCI is computationally extremely exhaustive and thus only feasible for very small systems such as diatomics. For larger systems, the expansion has to be truncated at some point. The most common method is CISD where only singly and doubly excited determinants are considered. In most closed shell systems the majority of electron correlation can be recovered with this method. For example, a CISD calculation for water molecule using the cc-pVDZ basis set⁸⁴ reproduces 94.5% of the correlation energy.^{10,85} However, in the water molecule electron correlation rises mainly from dynamic effects. For systems where static electron correlation plays a key part, CISD is a poorer approximation. The higher order excitations also become very important for systems with near-degenerate orbitals such as in diradicals.¹⁰

3.1.4 Other electron correlation methods

A number of other correlation methods besides CI have been developed and are widely used.¹⁰ Results obtained with DFT calculations are often compared to results from these theories and they will be briefly introduced here. Full theoretical descriptions can be found in the accompanying references.

Dynamic electron correlation can be added to the HF wave function using Møller–Plesset (MP) perturbation theory.^{10,12,86} The most commonly used implementation is the MP2 method where the perturbation series is truncated at the second order.⁸⁷ MP methods are not variational and expanding the perturbation series does not necessarily mean convergence towards the exact energy. MP2 is computationally much cheaper than CISD but is in many cases surpassed in accuracy by DFT. An advantage of MP2 over DFT is that MP2 can describe weak long range interactions such as dispersion, though it is known to overestimate these effects.⁸⁸ The MP2 method can also use an unrestricted HF reference wave function but will suffer from the same spin contamination problem as the UHF solution.

Another widely used method to add dynamic electron correlation is the much more accurate coupled cluster (CC) theory.^{9,10} In CC theory the exact wave function is expanded by operating on an HF reference wave function with an exponential cluster operator $e^{\hat{T}}$ that can be expressed as

an infinite series:

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_{SD}\rangle = \left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 \dots\right)|\Phi_{SD}\rangle. \quad (26)$$

The cluster operator has the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots, \quad (27)$$

where \hat{T}_1 creates all the singly excited determinants, \hat{T}_2 all the doubly excited determinants and so on. If all excitations are included to the basis set limit the CC wave function is equivalent to the FCI wave function in that basis. In any practical implementation, the CC expansion is truncated at some point, most commonly at \hat{T}_2 with the CC singles and doubles (CCSD) method,⁸⁹ although theories with higher excitations do exist.^{90,91} A commonly used “hybrid” method is CCSD(T) where the triple excitations are included as a perturbative correction to the CCSD expansion.⁹² The nature of the CC expansion leads, in addition to the connected excitations such as \hat{T}_2 or \hat{T}_3 , to disconnected excitations such as $\hat{T}_2\hat{T}_2$. These terms make the CCSD expansion more accurate than the CISD expansion without the need of additional higher order determinants. The difficulty that arises from the exponential form of the cluster operator is that the optimization problem is highly nonlinear and can no longer be solved by a simple diagonalization as in CI. The computational costs associated with CC methods are largely dependent on the optimization algorithm employed but rank somewhere slightly above the corresponding CI calculation with the same amount of excitations. CC methods are in principle variational, but the commonly used optimization algorithms are not. Regardless of this limitation, some of the most accurate benchmark calculations for medium sized systems are nowadays made using CC methods.^{9,93} The CCSD(T) method is often called the “gold standard of quantum chemistry”. This is true for single reference systems, but systems with high static electron correlation require the triple excitations to be treated iteratively (CCSDT) in order to obtain a quantitative description of the system.^{13–15}

Static electron correlation can be included in the wave function by using the multi-configuration self-consistent field (MCSCF) method.^{10,12,16,17} In a MCSCF calculation, optimization of not only the CI expansion coefficients but also the molecular orbital expansion coefficients is carried out. The most commonly used variation of the MCSCF method is the

complete active space multi-configuration self-consistent field (CASSCF), where only a small number of determinants that contribute significantly to the total wave function (known as the active space) are optimized. This again leads to a nonlinear optimization problem but the MCSCF equations can be solved variationally. The CASSCF method can reliably describe static correlation only if the active space is chosen correctly. This requires chemical intuition and may not always be possible if the space is too large to be computationally feasible.

Both static and dynamic electron correlation can be included in a wave function with dynamic correlation methods using an MCSCF reference wave function. The widely used CASPT2 method adds a second order perturbative correction to an MCSCF wave function.^{18,19} Further correlation can also be added to an MCSCF wave function by using CI theory in MRCI methods⁹⁴⁻⁹⁶ or by using CC theory in MRCC methods.⁹⁷⁻⁹⁹ Most variations of these two approaches are truncated at the singles and doubles level of approximation.

3.2 Magnetic interactions of singly occupied molecular orbitals

The simplest description for magnetic interactions between two unpaired electrons in terms of electronic structure theory can be obtained by using a basis of two SOMOs. These orbitals are assumed to lie well separated in energy from the inner orbitals, and thus the unpaired electrons move in a constant potential formed by rest of the electrons of the system. Most of the interactions do take place in this limited space and this treatment does offer qualitative results but is of course an idealization of the true problem where all orbital interactions should be considered.

The six configurations presented in Figure 4 can be built from two electrons on two orbitals ϕ_1 and ϕ_2 . Configurations Φ_D and Φ_E are not spin eigenstates, but two CSFs can be formed from them:

$$\Phi_{D+E} = \frac{1}{\sqrt{2}}(\Phi_D + \Phi_E) \quad (28)$$

and

$$\Phi_{D-E} = \frac{1}{\sqrt{2}}(\Phi_D - \Phi_E). \quad (29)$$

Φ_A corresponds to the singlet state $|S_0\rangle$ with energy $E(S_0)$. This is the

RHF solution in this orbital basis if ϕ_1 lies lower in energy than ϕ_2 . Φ_F corresponds to a singlet state $|S_2\rangle$ with energy $E(S_2)$ and the CSF Φ_{D-E} to a singlet state $|S_1\rangle$ with energy $E(S_1)$. Configurations Φ_B , Φ_C and the CSF Φ_{D+E} are all degenerate and correspond to the $M_S = 1$, $M_S = 0$ and $M_S = -1$ components of a triplet state $|T\rangle$ with energy $E(T)$.

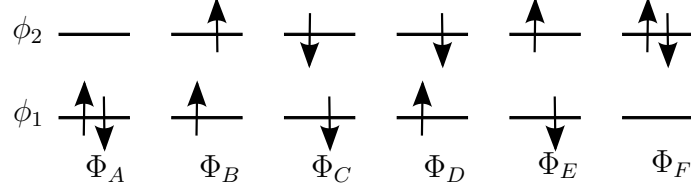


Figure 4: All possible configurations of a system of two orbitals and two electrons.

For the following derivation a somewhat different indexing system as in the previous equations will be employed. For the rest of this section C_{12} will mean a Coulomb integral between an electron lying at orbital ϕ_1 and one lying on ϕ_2 , while C_{11} is the Coulomb integral between two electrons both lying on ϕ_1 . The derivation is based on the one published by Huang and Kertesz.⁷⁰ Using the expression in equation (18) energies for the energy states described above can be written as

$$\begin{aligned}
 E(S_0) &= 2h_1 + C_{11} \\
 E(S_1) &= h_1 + h_2 + C_{12} + K_{12} \\
 E(S_2) &= 2h_2 + C_{22} \\
 E(T) &= h_1 + h_2 + C_{12} - K_{12},
 \end{aligned} \tag{30}$$

where the energy of the inner electrons is roughly constant for all terms and has been excluded. Using equation (17), the orbital energies ϵ_1 and ϵ_2 for ϕ_1 and ϕ_2 respectively can be written as

$$\begin{aligned}
 \epsilon_1 &= h_1 + C_{11} \\
 \epsilon_2 &= h_2 + 2C_{12} - K_{12}.
 \end{aligned} \tag{31}$$

Combining equations (30) and (31), the energies E can be rewritten as

$$\begin{aligned}
 E(S_0) &= 2\epsilon_1 - C_{11} \\
 E(S_1) &= \epsilon_1 + \epsilon_2 - C_{11} - C_{12} + 2K_{12} \\
 E(S_2) &= 2\epsilon_2 - 4J_{12} + 2K_{12} + C_{22} \\
 E(T) &= \epsilon_1 + \epsilon_2 - C_{11} - C_{12}.
 \end{aligned} \tag{32}$$

Owing to Brillouin's theorem and the spin-symmetries of the energy states, a diagonalization of the CI-matrix (equation (24)) produces three possible solutions:

$$\begin{aligned} |\Psi_S\rangle &= a_0|S_0\rangle + a_2|S_2\rangle \\ |\Psi_{S'}\rangle &= |S_1\rangle \\ |\Psi_T\rangle &= |T\rangle \end{aligned} \quad (33)$$

with energies

$$\begin{aligned} E(S) &= |a_0|^2 E(S_0) + |a_2|^2 E(S_2) \\ E(S') &= E(S_1) \\ E(T) &= E(T). \end{aligned} \quad (34)$$

The singlet solution $|\Psi_S\rangle$ describes a fully covalent bond if $a_0 = 1$ and $a_2 = 0$. If $a_0 = a_2 = 1/\sqrt{2}$ the bond is fully dissociated and ϕ_1 and ϕ_2 are degenerate. Any intermediate values of a_0 and a_1 describe a partially dissociated bond between the two SOMOs—i.e. a singlet diradical. $|\Psi_{S'}\rangle$ describes a condition where two non-degenerate SOMOs interact but cannot mix to form a molecular orbital. This situation arises, for example, if the two SOMOs belong to different symmetry representations or are orthogonal because of their nodal properties. This leads to a very weakly bound system where both electrons lie at their respective SOMOs. In general, $|\Psi_S\rangle$ with $a_0 = 1$ is the energetically preferred solution if the SOMOs overlap sufficiently, and the same state with $a_0 \approx a_2$ becomes more favorable when the two interacting orbitals are degenerate and nearly orthogonal. $|\Psi_{S'}\rangle$ is more favorable when the SOMOs are nearly orthogonal but not degenerate. The different possible SOMO–SOMO interactions are presented using molecular orbital diagrams in Figure 5.

Using equations (32) and the normalization condition $|a_0|^2 + |a_2|^2 = 1$, the coupling constant for the $|\Psi_S\rangle$ system can be written as

$$\begin{aligned} J_{12} &= E(S) - E(T) = E(S_0) - E(T) - |a_2|^2[E(S_0) - E(S_2)] \\ &= \epsilon_1 - \epsilon_2 + C_{12} - |a_2|^2[E(S_0) - E(S_2)]. \end{aligned} \quad (35)$$

The negative of the HOMO–LUMO gap $\epsilon_1 - \epsilon_2$ is less than or equal to zero thus favoring a singlet ground state, whereas the $-|a_2|^2[E(S_0) - E(S_2)]$ and C_{12} terms are always positive ($E(S_0) \leq E(S_2)$ by definition) stabilizing the triplet state. In general, J_{12} is positive only if the HOMO–LUMO gap is

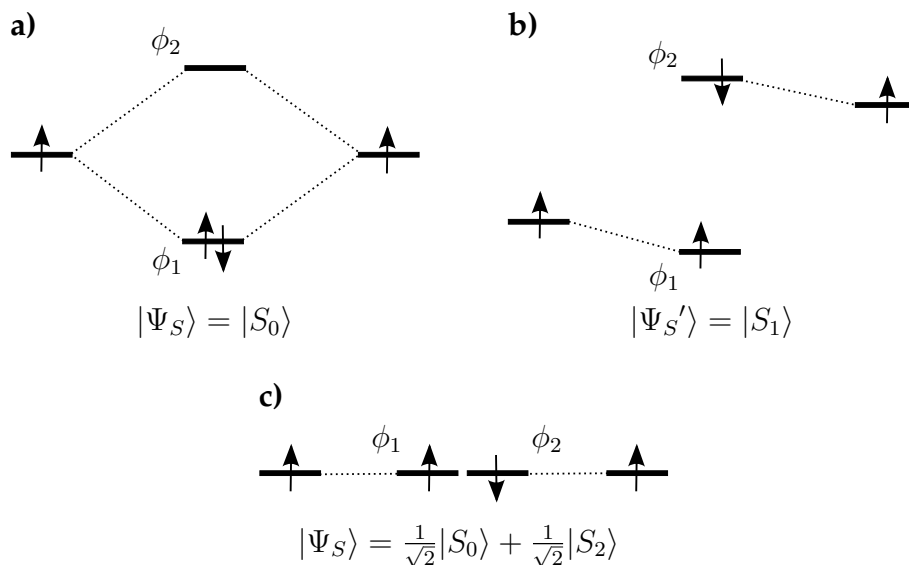


Figure 5: Molecular orbital diagrams of SOMO–SOMO interactions in case of **a)** extensive orbital overlap between the SOMOs resulting in strong bonding interaction, **b)** two non-degenerate orthogonal SOMOs leading to nonexistent orbital mixing and **c)** degenerate orbitals of a fully dissociated bond .

zero or very small as often occurs in transition metal complexes. For the $|\Psi_{S'}\rangle$ system the coupling constant is

$$J_{12} = E(S') - E(T) = 2K_{12}. \quad (36)$$

The exchange integral K_{12} is always positive and thus for these kind of systems a triplet ground state is always favored.

This somewhat lengthy excursion into electronic structure theory has led to two mechanisms of ferromagnetic interaction between two singly occupied molecular orbitals. The first requires a very small HOMO–LUMO gap or degeneracy of the SOMOs. The second requires orthogonality or near-orthogonality and non-degeneracy of the SOMOs. In the latter case, the magnitude of the magnetic coupling constant is determined by the magnitude of the SOMO–SOMO exchange integral. Thus, the HOMO–LUMO gaps in transition metal complexes and exchange interactions are both key concepts in calculating quantitative values for magnetic coupling constants. Indeed, Martin and Illas have shown that the values of magnetic coupling constants calculated with DFT are very much dependent on how the exchange interactions are approximated and depend little on the actual implementation of electron correlation.¹⁰⁰ Obtaining reliable es-

estimates of HOMO–LUMO gaps and exchange interactions are both problematic with DFT, and thus understanding these concepts in the framework of electronic structure theory is vital in order to overcome the problems in the DFT framework.^{20,25}

4 Density functional theory

In its original formulation quantum theory is built around a mathematical entity known as the wave function that is used to describe all properties of a system and its time evolution.^{44,55,75,80} The mathematical form of the wave function becomes immensely complex with increasing system size. For a system as simple as the helium atom some approximation has to be made in order to solve an analytical form for the corresponding wave function. Very early in the history of quantum mechanics a rivaling approach emerged that used a quantity known as the electron density instead of wave function as the fundamental entity to describe a quantum system. The electron density is a function of only three coordinates (four if time dependence is included). The early pioneering work on this theory by Thomas, Fermi, Bloch and Dirac^{10,20,101–104} actually precedes the wave function based formulations of Hartree and Fock, which form the foundation of modern electronic structure theory. However, the modern form of density functional theory is a newer product originating from the work of Hohenberg, Kohn and Sham in the sixties.^{26,105}

This section will introduce modern density functional theory in its most common practical implementation, the Kohn–Sham theory. The focus of the discussion is on issues encountered when the theory is applied to calculation of magnetic coupling constants.

4.1 Electron density as the fundamental quantity

The aim of density functional theory is to describe energy and all other properties of a quantum system as functionals of the three-dimensional electron density $n(\mathbf{r})$.^{10,20,21,24,80} In wave function theory, everything that can be known of a given state of a quantum system is contained in the wave function Ψ associated with that state.^{44,75,80} Ψ is a function of $3N$ spatial coordinates, where N is the number of particles in the system, N spin coordinates and a time coordinate. If the system's Hamiltonian is independent of time and Ψ is an energy eigenstate—i.e. it is a stationary state—it can be separated into a time-independent spatial part ψ and a phase factor:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) e^{-iEt}, \quad (37)$$

where E is the energy of the state Ψ . Any observable measured from a stationary state is independent of time. From here on we will assume that any state is stationary unless otherwise specified and discard the time coordinate and the phase factor. ψ is defined by the time-independent Schrödinger equation (also known as the energy eigenvalue equation)^{44,75,80,106}

$$\hat{H}\psi = E\psi. \quad (38)$$

Equation (38) is completely defined by the Hamiltonian which for the electronic part of a many electron system of static nuclei in the absence of external fields takes the form

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \\ &= -\frac{1}{2} \sum_{i=1}^N \nabla^2 - \sum_{i=1}^N \sum_{A=1}^{N_{nuclei}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \end{aligned} \quad (39)$$

where \hat{T} , \hat{V}_{Ne} and \hat{V}_{ee} are the kinetic energy, nuclear–electron attraction and electron–electron repulsion operators respectively. Dimensionality of ψ grows exponentially with system size and for a large system of interacting particles ψ becomes immensely complex. Equation (38) can be solved analytically only for the simplest of systems such as the hydrogen atom. Furthermore, the wave function is a purely mathematical entity and only its squared modulus has a physical interpretation. Density functional theory can—to some extent—offer a mathematically simpler description of many particle systems by using a function of only three dimensions. Furthermore, DFT is built around the electron density, a measurable quantity.^{10,80}

The electron density $n(\mathbf{r})$ for N electron system is defined as

$$n(\mathbf{r}) = N \iint \dots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{s}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (40)$$

where the integration runs over all spin coordinates and all but one spatial coordinate. $n(\mathbf{r})$ gives the probability of finding an electron in a volume element $d\mathbf{r}$ at point \mathbf{r} in space multiplied by N . Thus, $n(\mathbf{r})$ integrates to the total number of electrons. The electron density should not be confused with the $3N$ dimensional conditional probability density

$$P(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (41)$$

which gives the probability of finding electron 1 in a volume element dr_1 at \mathbf{r}_1 when electron 2 is at \mathbf{r}_2 , electron 3 is at \mathbf{r}_3 and so on. $P(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ integrates to unity. The difference between $n(\mathbf{r})$ and $P(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is that the electron density $n(\mathbf{r})$ gives the probability of finding a single electron at a given point when the location of all other electrons is arbitrary whereas $P(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ gives the probability of finding all the electrons at specific points in space.

In practical applications of DFT introduced in the next section, $n(\mathbf{r})$ is usually employed in the form of spin densities

$$n(\mathbf{r}) = n_\alpha(\mathbf{r}) + n_\beta(\mathbf{r}), \quad (42)$$

which are formed by separately integrating over the α and β electrons in equation (40). Only the difference between the spin densities $n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})$ is a measurable quantity and $n_\alpha(\mathbf{r})$ and $n_\beta(\mathbf{r})$ themselves are theoretical entities with no real physical meaning.

If $n(\mathbf{r})$, similar to Ψ , is to be used as an entity that contains all information of every measurable property of a system it is associated with, a mapping of the ground state density $n_0(\mathbf{r})$ to the ground state energy E_0 must exist. E_0 is defined by the ground state wave function Ψ_0 which is completely defined by the Hamiltonian in accordance with equation (38). The Hamiltonian for a system of stationary nuclei and N electrons (in the absence of external fields) is defined by the nuclear charges Z_A , nuclear coordinates R_A and the number of electrons N as shown in equation (39). The electron density integrates to N , has discontinuous cusps at the nuclear coordinates R_A due to the $1/|\mathbf{r}_i - \mathbf{R}_A|$ dependence of the Coulombic potential and is related to the nuclear charges by Kato's theorem:^{24,107}

$$Z_A = -\frac{a_0}{2n(\mathbf{r})} \lim_{\mathbf{r} \rightarrow \mathbf{R}_A} \left\{ \frac{dn(\mathbf{r})}{d\mathbf{r}} \right\}, \quad (43)$$

where a_0 is the Bohr radius. Therefore it can be reasoned that the Hamiltonian is completely defined by the electron density, and thus all measurable properties of the state Ψ can also be extracted from the corresponding electron density.

The existence of a mapping between $n_0(\mathbf{r})$ and E_0 , however, was not rigorously proven until 1964 when Hohenberg and Kohn published their famous theorems.¹⁰⁵ The first theorem proves through *reductio ad absurdum* that two different external potentials (i.e. potentials defined by the

nuclear properties \mathbf{R}_A and Z_A) cannot produce the same electron density, and thus the external potential V_{ext} is a unique functional of $n(\mathbf{r})$. V_{ext} defines the last two terms in the Hamiltonian in equation (39) whereas the first is defined by N . Therefore, the theorem proves that all measurable properties of a given state are defined by its electron density. The second theorem proves that the true ground state density minimizes the energy. In other words, the energy is variational with respect to $n(\mathbf{r})$. For any trial density $\tilde{n}(\mathbf{r})$ the functional will give a value \tilde{E} that is greater than E_0 unless $\tilde{n}(\mathbf{r}) = n_0(\mathbf{r})$. The second proof is not complete in the sense that the variational property of the energy is true only for densities that can be associated with some external potential \hat{V}_{ext} . This property is known as the V -representability of a density. This condition was later replaced by the much weaker condition that the trial densities must originate from an antisymmetric wave function in the constrained-search approach by Levy.¹⁰⁸ This approach also lifts the restriction of the Hohenberg–Kohn theorems to non-degenerate ground states only.

Because E_0 is a functional of $n_0(\mathbf{r})$, so must be the individual components that comprise E_0 :

$$E_0[n_0(\mathbf{r})] = T[n_0(\mathbf{r})] + E_{ee}[n_0(\mathbf{r})] + E_{Ne}[n_0(\mathbf{r})]. \quad (44)$$

T , E_{ee} , E_{Ne} are the kinetic, electron–electron repulsion and electron–nuclear attraction energies respectively. The form of the last term is known since it is the classic electrostatic interaction between a charge density and the nuclear potential. This is also the only term that depends on the nuclear geometry whereas the other two are universal. The energy expression can thus be written

$$\begin{aligned} E_0[n_0(\mathbf{r})] &= \int n_0(\mathbf{r})V_{Ne}d\mathbf{r} + T[n_0(\mathbf{r})] + E_{ee}[n_0(\mathbf{r})] \\ &= \int n_0(\mathbf{r})V_{Ne}d\mathbf{r} + F_{HK}[n_0(\mathbf{r})], \end{aligned} \quad (45)$$

where $F_{HK}[n_0(\mathbf{r})]$ is the universal Hohenberg–Kohn functional. Levy’s constrained-search approach features a functional identical to that of equation (45) except it is defined for all densities originating from an antisymmetric wave function as opposed to the V -representability of the Hohenberg–Kohn approach.

Even though the Hohenberg–Kohn theorems are remarkable from a theoretical point of view, they merely prove the existence of a mapping

between $n_0(\mathbf{r})$ and E_0 . They tell nothing of the actual form of the universal functional $F_{HK}[n_0(\mathbf{r})]$. Furthermore, nothing indicates that, even if the form of $F_{HK}[n_0(\mathbf{r})]$ was known, any practical application of it would be in any way simpler than solving the exact Schrödinger equation (or Dirac equation if relativistic effects are included). Thus, some compromises have to be made in order to employ density functional theory to any practical quantum chemical problem. By far the most common approach is the Kohn–Sham theory introduced in the next section.

4.2 Kohn–Sham theory

Kohn–Sham (KS) theory^{10,20,21,24,26} abandons the purely 3-dimensional approach of DFT and re-introduces a $4N$ -dimensional wave function. KS theory assumes the existence of a wave function in the form of a Slater determinant $\Phi_{KS}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ of N non-interacting electrons that corresponds to the exact ground state electron density $n_0(\mathbf{r})$. The determinant consists of a set of single particle functions $\{\phi_i(\mathbf{r})\}$, and the summation over their squared module produces the exact ground state density:

$$\sum_{i=1}^N \sum_{\mathbf{s}=\alpha,\beta} |\phi_i(\mathbf{r}, \mathbf{s})|^2 = n_0(\mathbf{r}), \quad (46)$$

where the summation runs over both spatial and spin coordinates. It should be noted that the existence of a reference state Φ_{KS} that satisfies equation (46) is an assumption and not proven. This issue will be discussed further in section 6.3.2. The single particle functions (or KS orbitals) can be solved with N single particle eigenvalue equations known as the KS equations. These equations are in many ways analogous to HF equations in equation (12):

$$\begin{aligned} \left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) &= \epsilon_i \phi_i(\mathbf{r}) \\ \hat{f}_{KS} \phi_i(\mathbf{r}) &= \epsilon_i \phi_i(\mathbf{r}). \end{aligned} \quad (47)$$

\hat{f}_{KS} is the KS operator, the eigenvalue ϵ_i is the energy of the corresponding KS orbital $\phi_i(\mathbf{r})$ and $V_{eff}(\mathbf{r})$ is the effective potential. $V_{eff}(\mathbf{r})$ is the potential a single electron experiences as a result of averaged interaction between rest of the electrons and the nuclear charges. The KS potential is analogous to the HF potential. Once the form of $V_{eff}(\mathbf{r})$ is known the KS

equations, and thus the orbital structure, can (in principle) be solved. In other words KS theory transforms the problem of finding the correct wave function that is an infinite series of Slater determinants into a problem of finding an effective potential. The density of the infinitely expanded wave function can then be expressed as a density produced from a single Slater determinant that can be solved by the use of the effective potential. In a strict sense, KS orbitals (and more generally the KS reference wave function) have no physical meaning as they are mere mathematical artifacts of the KS theory. The KS theory cannot reproduce the true wave function of any interacting system.³⁵ However, in practical applications, they have been shown to have similar interpretative power as the canonical HF orbitals.¹⁰⁹

The form of the effective potential can be derived from the exact energy expression in KS theory:

$$\begin{aligned}
E[\{\phi_i(\mathbf{r})\}] &= T_S[\{\phi_i(\mathbf{r})\}] + C[\{\phi_i(\mathbf{r})\}] + E_{Ne}[\{\phi_i(\mathbf{r})\}] + E_{XC}[\{\phi_i(\mathbf{r})\}] \\
&= -\frac{1}{2} \sum_{i=1}^N \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} \\
&\quad + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \iint \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad - \sum_{i=1}^N \int \sum_{A=1}^{N_{nuclei}} \frac{Z_A |\phi_i(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r} + E_{XC}[n(\mathbf{r})]. \tag{48}
\end{aligned}$$

The terms in equation (48) are the non-interacting kinetic energy, Coulombic repulsion between electrons, Coulombic attraction between nuclei and electrons and the exchange-correlation (XC) functional. The first three terms are known exactly but the last is not. The XC functional represents everything that can not be exactly expressed in KS theory: electron correlation energy, exchange energy and the component of kinetic energy arising from these effects. It should be noted that the exchange energy is not the same exchange energy as in HF theory but contains some spurious static electron correlation contributions. If the energy expression in (48) is minimized with respect to $n(\mathbf{r})$, the effective potential in equation (47) takes the form^{24,26}

$$V_{eff}(\mathbf{r}_1) = \int \frac{n(\mathbf{r})}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 - \sum_{A=1}^{N_{nuclei}} \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} + V_{XC}(\mathbf{r}_1), \tag{49}$$

where the XC potential $V_{XC}(\mathbf{r})$ is defined as the functional derivative of $E_{XC}[n(\mathbf{r})]$:

$$V_{XC}(\mathbf{r}) \equiv \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (50)$$

Up to this point KS theory is exact. However, to proceed any further, an approximation to the form of the XC potential has to be introduced. Much of the modern theoretical study of DFT has to do with obtaining better approximations to V_{XC} .^{20,21,24} The number of available approximations and their variants is tremendous.²⁰ It is a common practice to separate the XC functional (and thus the XC potential) into exchange and correlation parts in these approximations:

$$E_{XC}[n(\mathbf{r})] = E_X[n(\mathbf{r})] + E_C[n(\mathbf{r})] \quad (51)$$

and

$$V_{XC}(\mathbf{r}) = V_X(\mathbf{r}) + V_C(\mathbf{r}). \quad (52)$$

It should however be stressed that only the combined XC functional has any real physical meaning and separated exchange and correlation potentials are only mathematical entities.

The simplest approximation to V_{XC} is the local density approximation (LDA), or the local spin-density approximation (LSDA) in the case of open-shell systems, and their variants. In these methods the density is assumed to behave locally like uniform electron gas. The uniform electron gas is a theoretical system for which an exact DFT solution exists. LDA-based variants of XC potentials have enjoyed a wide success in solid state physics but generally perform badly when applied to chemical problems.²⁰ The LDA and LSDA XC functionals are functionals of the density only and can thus be written as $E_{XC}^{LSDA}[n(\mathbf{r})]$. The next step towards a more accurate approximation is to write E_{XC} as a functional of the density and its first derivative. Methods that employ $\nabla n(\mathbf{r})$ (or more exactly $|\nabla n(\mathbf{r})|/n(\mathbf{r})^{4/3}$) in their parametrization are known as generalized gradient approximations (GGA). GGA functionals, such as the BLYP functional (which is a combination of the B88 exchange part by Becke¹¹⁰ and the LYP correlation part by Lee and co-workers^{111,112}), can be built by parameterizing experimental and *ab initio* data. It is a common practice to combine different approximations to exchange and correlation energies, although, only an XC functional with both correlation and exchange parts has physical meaning. Another approach is to set parameters in such a way that

the functional reproduces properties that the exact functional is known to possess. Examples include the PBE functional of Perdew *et al.* and its predecessors PW86 and PW91.^{113–115} LDA, LSDA and GGA functionals are often called pure, local or semi-local functionals. Even though GGA effective potentials can in many cases produce good numerical results, the potentials are in poor agreement with near-exact potentials extracted from high quality *ab initio* wave functions, and thus, the good numerical performance is often due to error cancellation.^{10,116} Functionals employing higher order derivatives of $n(\mathbf{r})$, known as meta-GGA functionals are also used but in general they do not much improve over the GGA.¹⁰ Examples of such a functionals are the TPSS of Tao *et al.*¹¹⁷ and the M06-L of Zhao and Truhlar.¹¹⁸ A much greater increase in accuracy can be obtained by adding exact exchange energy calculated with HF theory to the GGA exchange energy. These functionals are known as a hybrid functionals and will be discussed in detail in section 5.1.

It is worth mentioning at this point that in much of the literature concerning DFT the terms XC functional and functional are used interchangeably. For instance, it is very common to speak of hybrid functionals even though the correct term would be hybrid XC functional. This practice will also be used in this text if the meaning is clear from the context in which the term is used.

It is clear from equation (49) that the form of the effective potential and thus the form of a given single particle wave function in equations (47) depends on all the other single particle wave functions as in HF equations. Thus, the KS equations have to be solved iteratively. The process is analogous to HF theory introduced in section 3.1.1 and will not be repeated in detail here. The KS orbitals are expanded in a chosen basis. The size of the basis introduces a new approximation to the KS solution in addition to the XC functional. The Roothan–Hall equation in KS theory is written as

$$\mathbf{F}_{KS}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon$$

$$F_{mn} = \langle \chi_m(\mathbf{r}) | \hat{f}_{KS} | \chi_n(\mathbf{r}) \rangle = \int \chi_m(\mathbf{r}) \hat{f}_{KS} \chi_n(\mathbf{r}) d\mathbf{r}, \quad (53)$$

where the only difference from HF theory is that instead of the FockK operator, the KS operator is used. Like HF theory, KS theory can be used in restricted (RKS) and unrestricted (UKS) formalisms. Generalization of equation (53) to unrestricted orbitals is completely analogous to HF theory. A detailed discussion of unrestricted KS theory is given in the re-

view of Jacob and Reiher and references therein.⁵⁴ Like UHF, UKS solutions are not spin eigenstates. Spin-contamination in UKS reference wave functions is, however, usually less prevalent than in their UHF counterparts. How the spin-contamination problem should be treated in UKS solutions—especially in the case of magnetic coupling constants where knowing the exact spin state is very important—is discussed in detail in section 6.2.

4.3 DFT and multireference systems

In section 3.1.1 the magnetic coupling between two SOMOs was discussed in terms of configuration interaction theory. The singlet solution $|\Psi_S\rangle = a_0|S_0\rangle + a_2|S_2\rangle$ is a multireference solution when $|a_2|$ is non-negligible and it cannot be described by a single determinant wave function. This is true for practically every magnetic molecular system as the singlet solution to a coupling problem leads to a very weakly bound system with low-lying excited states. Nearly degenerate energy levels lead to high levels of static electron correlation that can only be described by a multi-determinant wave function.²⁵ KS DFT is a single determinant model, and thus the KS reference wave function in a multireference system is very dissimilar to the true wave function. In principle, KS theory is exact, and the KS reference wave function is just a mathematical artifact. If the exact XC functional were known (under the assumptions discussed in section 4.2) it would be able to overcome this problem. Gritsenko and Baerends have shown that using an effective potential extracted from high level *ab initio* calculations, the stretched H₂ molecule can be described by KS theory.¹¹⁹ The stretched H₂ molecule is a text book example of a near-degenerate multireference system. It is necessary in this case that the KS reference wave function should differ considerably from its non-correlated HF counterpart in order to include the correlation effects. However, in practice all approximation to the XC functional will fail if the KS reference wave function differs much from the true wave function. This is most evident in systems with strong static electron correlation. Because of this, the common approximations are in many cases incapable of describing multireference systems. Better approximations such as hybrid or range-separated functionals (described in section 5) can to some extent alleviate the problem but not remove it.¹²⁰

The UKS formalism can considerably mitigate the problem of describing multireference systems as it can introduce static correlation into the KS solutions. Numerical results from UKS calculations on multireference

systems are often remarkably good but this is done at the expense of losing the spin symmetry of the KS reference wave function.¹²⁰ For the same model system as in section 3.1.1 an RKS solution gives a doubly occupied orbital ϕ_1 and a virtual orbital ϕ_2 similar to the HF solution. The UKS (or UHF) solution gives two orbitals γ_1 and γ_2 , both occupied by a single electron. In the following example we will assume that the two orbitals are identical but located at different centers as in the partly dissociated H_2 molecule. These orbitals form a complete set in the same space as the RKS orbitals ϕ_1 and ϕ_2 and thus it must be possible to expand the UKS orbitals in the RKS orbitals:

$$\begin{aligned}\gamma_1 &= (\cos \theta)\phi_1 + (\sin \theta)\phi_2 \\ \gamma_2 &= (\cos \theta)\phi_1 - (\sin \theta)\phi_2,\end{aligned}\tag{54}$$

where θ is a mixing parameter and the trigonometric functions are used to ensure normalization as $\cos^2 \theta + \sin^2 \theta = 1$.¹²¹ The value of θ is determined by solving the Pople–Nesbet equations (22). If $\theta = 0$, then $\gamma_1 = \gamma_2 = \phi_1$ and the RKS and UKS solutions are identical. This solution is the state $|\Phi_S\rangle = |S_0\rangle$ and is found when the orbital overlap S between the SOMOs is strong. At the opposite extreme when $S = 0$, $\theta = \pi/4$ and the bond is fully dissociated. This solution mimics the state $|\Phi_S\rangle = \frac{1}{\sqrt{2}}|S_0\rangle + \frac{1}{\sqrt{2}}|S_2\rangle$. Any value of θ between these two extremes shows some level of singlet diradical character. A UKS solution can also mimic the singly excited $|S_1\rangle$ state if the $|S_0\rangle$ and $|S_1\rangle$ states have different symmetry so that singly excited solution can be located as a minimum constrained to that symmetry species.^{12,121} In addition to unphysical properties arising from the breaking of spin symmetry, any state that is not the true ground state is inherently unphysical since KS theory is a ground state theory. Gunnarsson and Lundqvist have shown that Hohenberg–Kohn theorems and KS theory apply also to the lowest energy state of each spin symmetry.¹²² This means that if a system has a singlet ground state, energy of the triplet state can be obtained *if* triplet spin symmetry can be enforced on the density. However, as mentioned before, a spin symmetry can only be enforced on the KS reference wave function and not on the density itself. Thus one must again make the assumption that the spin state of the KS reference wave function is a good approximation to the spin state of the true wave function. The ground state electron density does include information about all the excited states of the system but there is no known way to access this within the KS formalism. Numerical results do show that a UKS solution

to a triplet state of a system with singlet ground state does offer, in many cases, a good approximation to the true triplet state energy.^{20,21,25}

If the system has higher than C_1 symmetry, in addition to the spin symmetry, the spatial symmetry of the density will also in many cases be broken. This is most easily illustrated by considering the dissociation of the H_2 molecule. Once the nuclei are far enough apart, the UKS solution produces α electron density at one nuclei and β density at the other. No symmetry operation can change α density to β density and thus the resulting total density has only $C_{\infty v}$ symmetry. Furthermore, for singlet densities, the spin polarization density $n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})$ should be zero everywhere, but this is clearly not the case near the nuclei.¹²¹ These problems can be averted by an interpretation developed by Perdew *et al.*¹²³ where the spin polarization density is not taken as a physical prediction of DFT, but the on-top pair density is used instead. In the same paper it is further argued that there is no obvious reason why the KS effective potential should have the same symmetry as the true external potential nor why the KS reference wave function should have the same symmetry as the true Hamiltonian. This is further discussed in section 6.1.

By far the most widespread methods of calculating magnetic coupling constants within the DFT framework employ the UKS method.^{25,121} The lack of proper spin symmetry introduces serious problems in calculation of coupling constants with equation (6) which requires energies of well defined spin states. This problem is discussed in detail in section 6.2.

5 Higher quality approximations to the exchange correlation functional

Even though GGA level approximations to the XC functional introduced in section 4.2 can produce very good results in a variety of situations, it was not until the advent of hybrid functionals in the early nineties when DFT became a *de facto* method in quantum chemistry.^{20,23} The term ‘hybrid’ stems from the fact that these functionals include (in addition to GGA exchange) a portion of exchange energy calculated with the HF formalism.^{27,28} This portion is often called exact exchange as HF theory takes exchange into account in a non-approximate manner by imposing a symmetry constraint on the trial wave function. Since their advent a vast number of hybrid functionals and variations thereof have been developed.^{23,25} These higher quality approximations to the XC functional are essential in order to produce magnetic coupling constants within DFT framework that are in quantitative agreement with experimental results.

In order to impose some hierarchy between different quality approximations Perdew has developed a figurative model known as the “Jacob’s ladder” of DFT summarized in Table 1.^{10,35} Steps on the ladder represent the climb towards the exact XC functional by adding more ingredients to the approximation. The first rung are the LDA and LSDA that are functionals of the density only. The second and third rungs include GGA and meta GGA functionals that add the first and second derivatives of the density. The fourth rung includes the addition of dependence on occupied KS orbitals such as in hybrid functionals and range-separated functionals. The fifth rung adds dependence on unoccupied virtual orbitals also. Double-hybrid functionals can be included in this last category.

Table 1: Perdew’s “Jacob’s ladder” classification of XC functional approximations.

Rung	Name	Variables
1	LDA and LSDA	$n(\mathbf{r})$
2	GGA	$n(\mathbf{r}), \nabla n(\mathbf{r})$
3	Meta GGA	$n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r})$
4	Hybrid and range-separated	$n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}),$ exact exchange
5	Double-hybrid	$n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}),$ exact exchange, dependence on virtual orbitals

This section will introduce the theoretical concepts and rationale behind hybrid functionals, range-separated functionals and double-hybrid functionals. How these functionals mitigate self-interaction error, an important problem in KS theory, and its role in calculation of magnetic cou-

pling constants are also discussed.

5.1 Hybrid functionals

The mixing of exchange energy calculated with GGA approximation with exact energy can be theoretically justified by the adiabatic connection formula.^{20,21,27,28,124} The formula can be derived by considering a Hamiltonian

$$\hat{H} = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{ext,\lambda}, \quad (55)$$

where \hat{T} and \hat{V}_{ee} are the kinetic and electron–electron repulsion energies as in equation (39). λ is a coupling strength parameter that can be used to “switch on” electron–electron interactions. When $\lambda = 0$, there is no Coulombic interaction between the electrons, and the only two-electron term rises from the antisymmetry of the N particle wave function. When $\lambda = 1$ the electrons are fully interacting and fully correlated as in the real physical situation. Intermediate values of λ connect the non-interacting and interacting states in a continuous (adiabatic) fashion by non-physical partially interacting states. The external potential (that includes the Coulombic nuclear–electron attraction) is chosen in such a way for each value of λ that the ground state electron density of the interacting system is retained. Using the Hellmann–Feynman theorem Langreth and Perdew have shown that¹²⁵

$$E_{XC} = \int_0^1 E_{XC,\lambda} d\lambda, \quad (56)$$

where

$$E_{XC,\lambda} = V_{ee,\lambda} - C. \quad (57)$$

$V_{ee,\lambda}$ is the expectation value of the Coulombic electron–electron repulsion for the ground state wave function produced as a solution to the KS equations with coupling constant λ . C is the Coulombic electron–electron repulsion in the expression for the KS energy as in equation (48).

For a hypothetical system for which $\lambda = 0$, the HF and KS reference wave functions would be identical if the approximate exchange energy is replaced by HF exchange. E_{XC} for this system includes only the exchange contribution, and because HF theory considers exchange exactly the exact value for E_{XC} can be calculated by inserting the GGA KS orbitals into equation (18). Since the integration in equation (56) starts from

this limit and because exchange usually plays much larger role in E_{XC} than correlation, it would seem very plausible that if a portion of exact exchange is mixed with the GGA exchange the XC approximation should improve. This approach was first pursued by Becke in 1993 leading to the B3PW91 XC functional.^{27,28} This functional uses Becke’s 1988 exchange functional¹¹⁰ and Perdew and Wang’s 1991 correlation functional¹¹⁵ with the following parametrization:

$$E_{XC}^{B3PW91} = E_{XC}^{LSDA} + a(E_X^{HF} - E_X^{LSDA}) + bE_X^B + cE_C^{PW91}. \quad (58)$$

E_X^{HF} is the exact exchange energy and the subscripts X and C refer to exchange and correlation energies, respectively, calculated with the method in the superscript. The coefficients $a = 0.20$, $b = 0.72$ and $c = 0.81$ have been determined empirically by fitting to a set of atomic data. The same parametrization was used for the B3LYP functional by Stephens *et al.*³⁰ In B3LYP the PW91 correlation part is replaced with the correlation functional of Lee, Yang and Parr.^{111,112} B3LYP has experienced tremendous success and nearly two decades after its appearance it remains by far the most popular DFT method in use.²³

Later Becke parametrized a new functional known as the B1B95 that uses only a single fitting parameter according to equation

$$E_{XC}^{B1B95} = E_{XC}^{GGA} + a(E_X^{HF} - E_{XC}^{GGA}), \quad (59)$$

where E_{XC}^{GGA} is the XC energy calculated with Becke’s 1988 exchange part and a new B95 correlation part.¹²⁶ The empirical parameter is $a = 0.16$ or 0.28 depending on the choice of GGA. Perdew and Ernzerhof used perturbation arguments instead of an empirical fit to obtain a value of $a = 0.25$ for the mixing parameter in equation (59).¹²⁷ This in conjunction with the PBE exchange and correlation functionals¹¹³ gives the zero parameter PBE0 hybrid functional (also known as PBE1PBE and PBEh, although the latter is used for other functionals as well).^{128,129} The same mixing parameter is also used in Adamo and Barone’s B1LYP and B1PW91 functionals.¹³⁰

Zhao *et al.* have more recently developed a suite of meta hybrid functionals generally known as the M06 family (or Minnesota functionals).^{118,131-133} Meta hybrids are functionals that are based on a meta GGA functional. The M06 family is a revise of its original incarnation, the M05 family of functionals, introduced a year earlier.^{134,135} All Minnesota functionals are parametrized by fitting a large number of variables to exper-

imental data. The family consists of four members: M06-L, M06, M06-2X and M06-HF that include 0%, 27%, 54% and 100% of exact exchange respectively. All of these functionals are parametrized and fitted to perform well in specific areas of chemistry, and a more detailed discussion of their properties can be found in the corresponding references. Improved versions of M06 and M06-2X were developed and are known as M08-SO and M08-HF.¹³⁶ However, these functionals are not widely implemented in quantum chemistry codes.

Other hybrid functionals in common use that are not reviewed in detail here include B3LYP*,¹³⁷ X3LYP,¹³⁸ O3LYP,¹³⁹ TPSSh,¹¹⁷ OPBE0¹⁴⁰ and BMK.¹⁴¹

Hybrid and meta hybrid functionals can overcome much of the shortcomings of pure LSDA and GGA functionals—but not all of them. Common hybrid DFT methods such as B3LYP can sometimes fail even in fairly simple problems.^{142,143} Thus, further progress is still required until they can be used as black box methods. The following subsections will introduce some of the more recent developments in the field functional design.

5.2 Range-separated functionals

The exact exchange potential decays asymptotically as $-1/r$.^{144,145} None of the standard approximations to the XC functionals have this property.²⁰ This leads to errors for example in describing charge transfer and higher level excitations within time-dependent DFT formalism.¹⁴⁶ For LSDA and GGA functionals the form of the decay is exponential and they perform very badly for the aforementioned properties. Hybrid functionals have $-c/r$ decay where c is the percentage of exact exchange included. This behavior is much better than that of the GGA but not enough to completely overcome the same problems.¹⁴⁷ Range-separated functionals aim to remedy this problem by splitting the exchange potential to short and long range parts and treating these in a different manner.¹⁴⁸⁻¹⁵¹ Correlation effects usually take place over much shorter range than exchange interactions and thus only exchange potential is considered in the separation process.^{20,147} The separation can be achieved by partitioning the Coulomb operator with the help of the standard error function

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1 - \operatorname{erf}(\omega|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\operatorname{erf}(\omega|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (60)$$

where ω is a parameter defining the range separation. Splitting of the Coulomb operator is known as the Coulomb-attenuated method (CAM). The error function is computationally efficient in quantum chemistry codes that use Gaussian type basis sets. Separation processes also exist that use exponential separation function $\exp(-\omega|\mathbf{r}_1 - \mathbf{r}_2|)$ in conjunction with Slater type basis sets.¹⁵² A process separating the potential into three regions (short, middle and long range) has also been proposed.¹⁴⁷ Range-separated functionals and the hybrid functionals introduced in the previous section both lie on the fourth rung of Perdew’s ladder classification. From here on the term hybrid functional applies to functionals introduced in this and the previous subsection. The term traditional hybrid functional will be reserved for hybrids without range separation.

How the range-separated parts are treated depends on the choice of functional. In periodic systems, the range separation can be used to include exact exchange only at short range which thus avoids many computational difficulties. An example of such a model is the functional of Heyd, Scuseria and Ernzerhof (HSE) that uses a portion of exact exchange at short range and the PBE GGA exchange at long range.^{153–155} In molecular calculations, it is more common to use GGA exchange at short range and exact exchange at long range in order to reproduce the correct asymptotic behavior of the effective potential (the exact exchange decays physically correctly). Such a hybrid functional using the separation process of equation (60) has the form

$$E_{XC}^{LC} = E_X^{GGA}(\omega) + E_X^{HF}(\omega) + E_C^{GGA}, \quad (61)$$

where LC stands for long-range corrected and both of the exchange contributions are now functions of the separation parameter ω . The amount of exact exchange is zero when $|\mathbf{r}_1 - \mathbf{r}_2| = 0$ and the amount of GGA exchange is zero as $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$. The LC- ω PBE model of Vydrov *et al.* uses the functional form of equation (61) with a modified version of the PBE GGA known as ω PBE and a range separation parameter $\omega = 0.4 \text{ bohr}^{-1}$.^{156–158}

The CAM-B3LYP method of Yanan *et al.*¹⁵⁹ uses CAM with two additional parameters, α and β , added to equation (60):

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1 - [\alpha + \beta \operatorname{erf}(\omega|\mathbf{r}_1 - \mathbf{r}_2|)]}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\alpha + \beta \operatorname{erf}(\omega|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (62)$$

This parametrization allows a portion of exact exchange to be included at

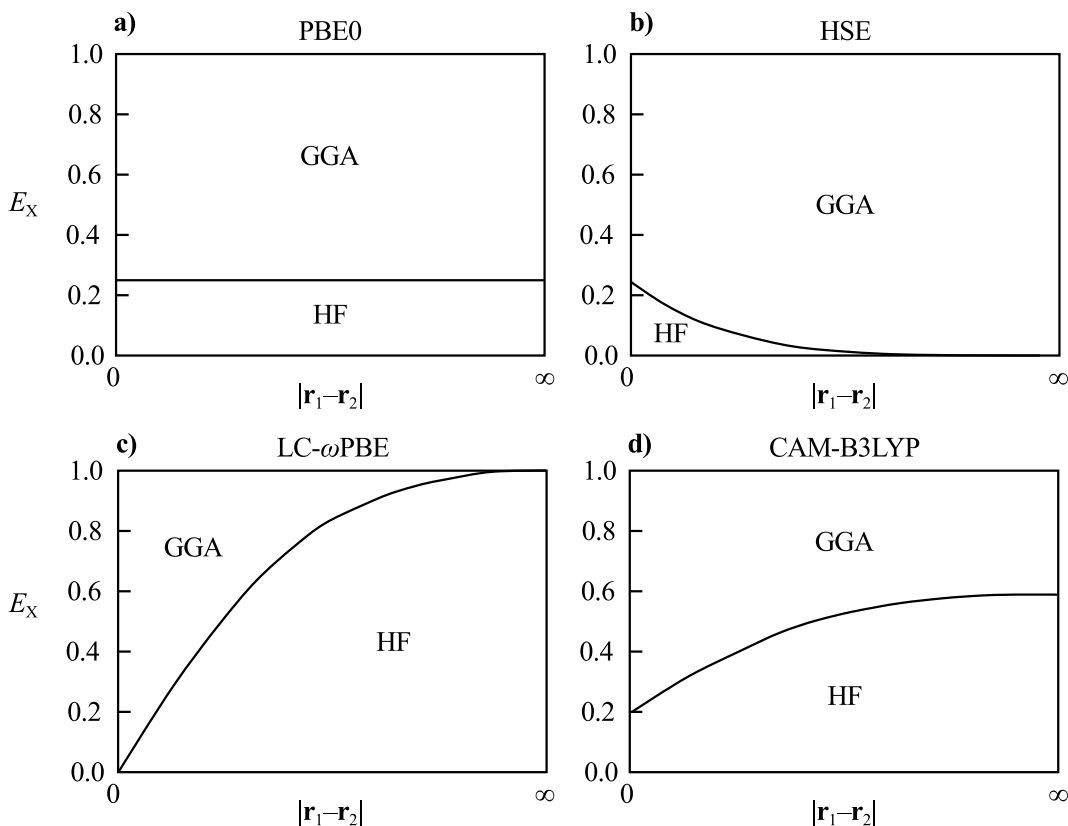


Figure 6: A schematic representation of the range separation of the exchange potential in four different types of hybrid functionals: **a)** the PBE0 model with 25% of exact exchange throughout the range, **b)** the HSE model with 25% of exact exchange at $|\mathbf{r}_1 - \mathbf{r}_2| = 0$ and zero as distance tends towards infinity, **c)** the LC- ω PBE model with zero exact exchange at $|\mathbf{r}_1 - \mathbf{r}_2| = 0$ and zero GGA exchange at long distance and **d)** the CAM-B3LYP model with 20% of exact exchange at $|\mathbf{r}_1 - \mathbf{r}_2| = 0$ and about 60% at long distance.

every distance. α determines how much exact exchange is included over the whole range and β determines how much DFT exchange is present. Values of $\alpha = 0.2$ and $\beta = 1.0$ were used in the original version. A variation of this functional known as CAMY-B3LYP uses exponential functions instead of error functions in the range separation process.^{160,161} Figure 6 gives a schematic representation of the different approaches to the range separation process.

A number of studies have shown that range-separated functionals perform relatively well compared to the traditional hybrid functionals in a variety of chemical problems.^{156,157,161-164} This suggests that enforcing correct asymptotic behavior of the exchange potential does offer an improvement over traditional hybrid functionals. As Riviero *et al.* have shown,¹⁶²

the long range behavior of the exchange potential also plays a key role in calculation of magnetic coupling constants.

5.3 Double-hybrid functionals

Hybrid functionals are orbital-dependent in the sense that the exact exchange energy depends on the exact form of the occupied KS orbitals. The next logical step in improving the approximation is to include dependence also on the unoccupied virtual KS orbitals. In a similar way, the HF energy depends only on the occupied orbitals, whereas the fully correlated CI energy depends on all the orbitals. The inclusion of the virtual KS orbitals would bring DFT methods closer to wave function based correlation methods. Coupled cluster and second order perturbation theory versions of KS theory have been proposed but none of them has achieved wide-spread success.^{165–168} This prompted Grimme to design an empirical version of a hybrid that includes a portion of correlation energy calculated with second order perturbation theory.¹⁶⁹ The functional—known as B2-PLYP—has the general form

$$E_{XC}^{B2-PLYP} = aE_X^{HF} + (1 - a)E_X^{GGA} + (1 - b)E_C^{GGA} + bE_C^{MP2}, \quad (63)$$

where E_C^{MP2} is the correlation energy calculated with the MP2 method using the GGA orbitals. The GGA part uses Becke’s 1988 exchange functional and the LYP correlation functional as in B3LYP. The two empirical parameters $a = 0.53$ and $b = 0.27$ have been optimized by fitting to experimental data. The first three terms are calculated in the usual self-consistent manner, and the perturbation term is added non-iteratively as in a conventional wave function based MP2 calculation.

A number of functionals that employ the form of equation (63) have been proposed using different exchange or correlation GGA parts and coefficients determined by fits to different sets of chemical data. These include mPW2-PLYP that uses the modified exchange functional of Perdew and Wang (mPW)¹⁷⁰ and coefficients $a = 0.55$ and $b = 0.25$ and B2GP-PLYP of Karton *et al.*¹⁷¹ with coefficients $a = 0.65$ and $b = 0.36$. It is worth noting that the percentages of exact exchange in these functionals are much higher than in traditional hybrids (20% in B3LYP and 25% in PBE0 for example). XC functionals that include perturbative correlation energy in an empirical fashion are collectively known as double-hybrids. Chai and Head-Gordon^{172,173} have combined the range separation and double-

hybrid schemes to give a double-hybrid version of their earlier long-range corrected functional ω B97X designated as ω B97X-2 in its double-hybrid incarnation.¹⁷⁴

Sharkas *et al.*¹⁷⁵ have derived a theoretically rigorous way of building a one-parameter density-scaled double-hybrid (DS1DH) of the form

$$E_{XC}^{DS1DH} = aE_X^{HF} + (1-a)E_X^{GGA}[n] + E_C^{GGA}[n] - a^2 E_C^{GGA}[n_{1/a}] + a^2 E_C^{MP2}. \quad (64)$$

$E_C^{GGA}[n_{1/a}]$ is the GGA correlation functional that is evaluated with a scaled density $n_{1/a}(\mathbf{r}) = (\frac{1}{a})^3 n(\frac{\mathbf{r}}{a})$. a is the only empirical parameter present in the DS1DH model. A connection to the model in equation (63) can be drawn by neglecting the density scaling and setting $E_C[n_{1/a}] \approx E_C[n]$. Bremond and Adamo have very recently built a double-hybrid based on the PBE0 hybrid functional with zero empirical parameters.¹⁷⁶ The coefficients have been determined theoretically starting from the adiabatic connection formula. The model—denoted PBE0-DH—has the form

$$E_{XC}^{PBE0-DH} = \frac{1}{2}(E_X^{HF} + E_X^{GGA}) + \frac{1}{2} \left(\frac{7}{4} E_C^{GGA} + \frac{1}{4} E_C^{MP2} \right). \quad (65)$$

This model was further theoretically rationalized by Toulouse *et al.*¹⁷⁷ To date, PBE0-DH remains the only zero-parameter double-hybrid.

Double-hybrids represent the cutting edge of approximations to the exact XC functional.¹⁷⁸ They are also a relatively new addition to the ever growing field of functional design and have not been tested by time like traditional hybrids which have been standard quantum chemical tools for well over a decade. It should also be noted that the perturbation correction does add to the computational cost of the method. Nevertheless double-hybrids offer new promising possibilities, including more accurate ways to calculate values for magnetic coupling constants.^{179,180}

5.4 Role of self-interaction error

Self-interaction error (SIE) means the unphysical interaction of a charge density with itself that is present in all common approximations to the XC functional.^{20,31} The Coulombic term

$$C[\{\phi_i(\mathbf{r})\}] = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \iint \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (66)$$

in equation (48) does not vanish when $i = j$ and thus the term produces a Coulombic repulsion between an electron and itself. In HF theory this problem is avoided because when $i = j$ the Coulombic and exchange terms become identical and the term

$$\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (C_{ij} - K_{ij}) \quad (67)$$

in equation (18) vanishes. Thus, HF theory is SIE-free as are all electron correlation methods based on it. Because of the approximate manner in which KS theory treats exchange (as well as correlation) the self-interaction does not vanish in common approximations used in KS formalism. The self-interaction manifests itself as a spurious form of static electron correlation.¹⁸¹⁻¹⁸³ This problem becomes much more severe for systems with non-integer numbers of electrons (a situation that can physically arise when a system is partitioned into subsystems).¹⁸⁴ SIE can be divided into two categories: one-electron SIE and N -electron SIE.^{31,185,186} One-electron SIE is easily understood by considering the hydrogen atom. In the one electron limit there should be no electron–electron interactions and the Coulombic and XC terms in equation (48) should cancel:

$$C[\{\phi_i(\mathbf{r})\}] = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \iint \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = -E_{XC}[n(\mathbf{r})]$$

$$\implies C[\{\phi_i(\mathbf{r})\}] + E_{XC}[n(\mathbf{r})] = 0 \quad (68)$$

However, all common approximations to the XC functional, including hybrid, range-separated and double-hybrid functionals, fail to reproduce this limit correctly. Approximations that are one-electron SIE-free reproduce the correct ground state density and energy for the hydrogen atom. This does not, however, mean that they would produce the correct SIE-free energy for N -electron systems. The N -electron SIE is a much more complicated property of KS theory and very difficult to formulate mathematically.¹⁸⁵ N -electron SIE results in a phenomenon known as the delocalization error. This behavior leads to energies for delocalized densities that are too low.^{25,187} In HF theory an opposite problem known as localization error arises which leads to localized charge distribution being energetically more favorable.¹⁸⁷ If an approximation to the XC functional that was N -electron SIE-free existed, it would also be one-electron SIE-free.

Hybrid functionals are generally thought to suffer from SIE less than pure functionals. The inclusion of exact exchange should include a partial cancellation of the terms in equation (68). The reduction of SIE is dependent on the percentage of exact exchange included. However, even if the percentage is 100%, SIE would still not be absent because of the correlation contribution to E_{XC} . Range-separated functionals that treat the long-range exchange exactly (as in LC- ω PBE) are practically SIE-free at the long range limit. The correlation potentials decay very quickly as dynamic correlation is a short-range effect but a minor part still remains at the long range limit and contributes to SIE. Range-separated functionals that include GGA exchange at long range (as in CAM-B3LYP) suffer from SIE throughout their range. SIE is absent only in regions where correlation is zero and only exact exchange is used. It is worth noting that functionals that are largely empirically built (such as the M06 family) are likely to suffer less from SIE as it is treated indirectly in the fitting process.

One-electron SIE can be corrected for any XC approximation with the method proposed by Perdew and Zunger.¹⁸⁸ This method removes the SIE for each orbital individually:

$$E_{XC}^{PZ} = E_{XC} - \sum_{i=1}^{N/2} \sum_{\sigma=\alpha,\beta} (C[n_{i,\sigma}(\mathbf{r})] + E_X[n_{i,\sigma}(\mathbf{r})]), \quad (69)$$

where the summation runs over all KS orbitals i and both spins and $n_{i,\sigma}(\mathbf{r})$ is a density produced from electron σ on orbital i :

$$n_{i,\sigma}(\mathbf{r}) = |\phi_{i,\sigma}(\mathbf{r})|^2. \quad (70)$$

The Perdew–Zunger correction removes all of the one-electron SIE for any XC functional without tampering with the functional, but it is difficult and computationally expensive to implement in practical quantum chemistry codes. To alleviate this problem scaled versions of the correction have been designed.^{189,190} SIE free functionals have also been devised. These include Becke’s B05¹⁹¹ and Mori-Sanchez, Cohen and Yang’s MCY functional.¹⁹² Both of the functionals include 100% of exact exchange and employ orbital-dependent correlation schemes. However, all of these approaches only treat the one-electron SIE and thus still suffer from N -electron SIE that can be just as—or more so—disastrous to results in certain chemical problems such as homolytic bond cleavage.¹⁸⁵ In fact, the Perdew–Zunger SIE correction can worsen the performance of many func-

tionals on thermochemical properties. This may be a consequence of disturbing the balance of error cancellations in the functional approximation by removing the one-electron SIE component.¹⁹³ No definite cure exists for N -electron SIE within the standard KS formalism. Cohen *et al.*¹⁹⁴ have tried to alleviate the problem by designing two range-separated functionals called MCY3 and rCAM-B3LYP that are especially designed to reduce N -electron SIE.

Ruiz *et al.*³⁷ claim that SIE can lead to overestimation of magnitudes of magnetic coupling constants by a factor of roughly two, although this error can be compensated by projection schemes (to be introduced in section 6.2). These results have led to some controversy.^{195,196} In any case, the N -electron SIE is by no means a minor problem. It is also rooted deep in the foundations of KS theory, and thus a simple remedy to it is unlikely to surface anytime soon. Acknowledging its existence is very important in any first-principles application of KS theory to calculation of magnetic coupling constants.

6 Dealing with spin symmetry

The magnetic coupling constant of a system with two magnetic centers for which $S_1 = S_2 = 1/2$ was defined in section 2.3 as the gap between the energies of the lowest singlet and triplet states:

$$J = \Delta E_{S-T} = E(S) - E(T) \quad (71)$$

This simplest case of magnetic coupling will be considered exclusively in this section. Generalization to larger values of S can be found in the corresponding references for non-trivial cases. Calculation of singlet–triplet splitting is very straightforward with wave function based methods. As discussed in section 4.3 the calculations of coupling constants requires an unrestricted approach in the standard KS formalism. This leads to ill-defined spin states which are eigenstates of the \hat{S}_z operator but not of the \hat{S}^2 operator and thus the use of some mapping—or a projection—of the energies of these states to the true spin states might be required in order to use them in equation (71). However, no consensus currently exists in the scientific community as to how this problem should be solved. A number of approaches have been proposed and the most common ones will be reviewed in this section. In addition to these, alternative formulations of KS theory that circumvent the spin symmetry problem will also be described. Finally, an approach that involves the time-dependent DFT will also be briefly discussed.

In this section $E(LS)$ and $E(HS)$ will be used to denote low-spin and high-spin states of a system when no clear spin state is defined and thus the use of $E(S)$ and $E(T)$ would be incorrect.

6.1 Neglect of spin symmetry

The simplest approach to dealing with spin symmetry is neglecting it and thus setting

$$E(LS) \simeq E(S) \quad (72)$$

$$E(HS) \simeq E(T). \quad (73)$$

For the ground state this approach can be justified. The ground state density is produced by a Hamiltonian of a non-interacting KS model system with the same density as the real system. Thus, the Hamiltonian used

in the KS approach is not the true Hamiltonian of the system. The real Hamiltonian must commute with \hat{S}^2 and \hat{S}_z , but KS theory sets no such limitation on the model Hamiltonian.³⁵ The theory does not offer us any access to the real wave function. With this reasoning the KS reference wave function is a mere mathematical artifact, and its spin state serves no physical interpretation. If the ground state of the system is a singlet, then KS theory produces (in principle) the singlet density and energy. Thus, $E(LS) = E(S)$ applies for the ground state. However, this reasoning only applies to the ground state and equation (71) requires the energy of the first excited singlet or triplet state. If the ground state is a singlet then in order to realize equation (73) an assumption has to be made that if a high-spin configuration is enforced on the KS reference wave function the energy minimization process produces $E(T)$ and thus $E(HS) = E(T)$. There is no theoretical justification for this other than numerical results.¹⁹⁷⁻²⁰⁰ Illas *et al.* have argued that the numerical success is a simple coincidence and this approach gives good results for the wrong theoretical reasons.³³ Ruiz *et al.* have claimed that the good numerical results are due to error cancellation because of double-counting of static correlation as a result of the N -electron SIE.³⁷ This reasoning has, however, raised some controversy.^{195,196} Moreira and Illas have further argued that if one cannot assign definite multiplicities to UKS descriptions, then KS theory should be abandoned altogether as means to predicting magnetic coupling constants.⁸ Thus, some physical meaning must be placed on the $\langle S^2 \rangle$ values derived from the KS reference wave function.

On the other hand, it can also be argued that because the standard KS theory is non-relativistic, it is an incomplete theory and a correct treatment of a relativistic property such as spin symmetry can never arise from it. Thus, one cannot make the assumption that the KS minimization process would converge to a solution with the correct spin state even if it would produce the correct ground state energy; the spin state must be enforced in some *ad hoc* manner in order to prevent the variational procedure from collapsing to a non-physical solution.^{33,36} This line of reasoning leads back to the argument of Moreira and Illas that either some physical meaning must be ascribed to the KS reference wave function or the UKS approach needs to be abandoned.

6.2 Mapping results from unrestricted calculations

6.2.1 On the interpretation of the spin symmetry of an UKS reference wave function

A spin projection technique to extract the value of a magnetic coupling constant from an unrestricted single determinant calculation was first proposed by Noodleman *et al.*^{201–204} This model was originally used in conjunction with HF theory as well as the Hartree–Fock–Slater method.* The HF wave function is by definition an approximation to the true wave function and thus imposing the same symmetry constraints on it is theoretically justified. However, to apply this reasoning to KS theory one must assume that the spin state of the KS reference wave function is a reasonable approximation to the spin state of the exact wave function. In other words:

$$\langle \psi_{exact} | \hat{S}^2 | \psi_{exact} \rangle \simeq \langle \Phi_{KS} | \hat{S}^2 | \Phi_{KS} \rangle. \quad (74)$$

No theoretical justification for this exists other than that Φ_{KS} and ψ_{exact} both produce (in principle) the exact ground state density.

A single unrestricted determinant is an eigenfunction of the S_z operator so this value can at least be uniquely defined for the KS reference wave function. The \hat{S}^2 operator, however, is a two-particle operator and KS theory is an effective one-electron model. Whether a two particle operator acting on an effective single particle wave function can produce any physical result is very much questionable.³⁶ A method has been developed to calculate $\langle \hat{S}^2 \rangle$ directly from the density using one- and two-particle density matrices.^{205,206} This would seem a very promising way to evaluate spin contamination in the true wave function corresponding to the density, but unfortunately two-particle density matrices are not available in KS calculations and have to be approximated in some manner.

The commonly used projection schemes presented in the next subsection all assume, in some sense, that the spin-state of the KS reference wave function has physical meaning.

*The Hartree–Fock–Slater method is an early density functional approach that predates the Hohenberg–Kohn theorems and KS theory. It has enjoyed some success in the field of solid state physics.²⁰

6.2.2 Projection schemes

Noodleman's theory (also derived by Ginsberg²⁰⁷) aims to express the energies of the pure singlet and triplet states with the energies of broken symmetry states.²⁰¹ In the following derivation we will once again limit the discussion to the simplest case of two SOMOs and two electrons.

Let us consider two low-spin broken symmetry determinants with UKS orbitals γ_1 and γ_2

$$\begin{aligned} |LS_1\rangle &= \begin{bmatrix} \gamma_1(\mathbf{r}_1)\alpha(\mathbf{s}) & \gamma_2(\mathbf{r}_1)\alpha(\mathbf{s}) \\ \gamma_1(\mathbf{r}_2)\beta(\mathbf{s}) & \gamma_2(\mathbf{r}_2)\beta(\mathbf{s}) \end{bmatrix} \text{ and} \\ |LS_2\rangle &= \begin{bmatrix} \gamma_1(\mathbf{r}_1)\beta(\mathbf{s}) & \gamma_2(\mathbf{r}_1)\beta(\mathbf{s}) \\ \gamma_1(\mathbf{r}_2)\alpha(\mathbf{s}) & \gamma_2(\mathbf{r}_2)\alpha(\mathbf{s}) \end{bmatrix}. \end{aligned} \quad (75)$$

The determinants have opposite spins but are otherwise identical. In the high-spin state spin contamination is usually much less prevalent than in the low-spin configuration and thus it will be assumed that

$$|T\rangle \simeq |HS\rangle. \quad (76)$$

It is possible to express the pure singlet and triplet states as linear combinations of the broken symmetry low-spin states²⁰¹

$$\begin{aligned} |S\rangle &= \frac{|LS_1\rangle + |LS_2\rangle}{\sqrt{2 + 2\langle LS_1|LS_2\rangle}} \\ |T\rangle &= \frac{|LS_1\rangle - |LS_2\rangle}{\sqrt{2 - 2\langle LS_1|LS_2\rangle}}, \end{aligned} \quad (77)$$

where the denominator is a normalization constant ($|LS_1\rangle$ and $|LS_2\rangle$ are not orthogonal in general) and $\langle LS_1|LS_2\rangle$ is the overlap integral between the broken symmetry states. By taking the energy expectation values of equations (77), the following expressions are obtained:

$$\begin{aligned} E(S) &= \langle S|\hat{H}|S\rangle = \frac{E(LS) + \langle LS_1|\hat{H}|LS_2\rangle}{1 + \langle LS_1|LS_2\rangle} \\ E(T) &= \langle T|\hat{H}|T\rangle = E(HS) = \frac{E(LS) - \langle LS_1|\hat{H}|LS_2\rangle}{1 - \langle LS_1|LS_2\rangle}. \end{aligned} \quad (78)$$

By combining equations (71) and (78), the unknown matrix element $\langle LS_1|\hat{H}|LS_2\rangle$ vanishes, and the magnetic coupling constant can be written

as

$$J = E(S) - E(T) = \frac{2[E(LS) - E(HS)]}{1 + \langle LS_1 | LS_2 \rangle}. \quad (79)$$

If spin-polarization in the orbitals outside the magnetic space defined by γ_1 and γ_2 is assumed to be negligible the overlap integral reduces to the overlap of the two interacting SOMOs:³⁴

$$\langle LS_1 | LS_2 \rangle = \langle \gamma_1 | \gamma_2 \rangle. \quad (80)$$

In the strongly localized (weakly interacting) limit of the SOMOs, the overlap can be taken to be zero and equation (79) takes the simple form^{201,202}

$$J = E(S) - E(T) = 2[E(LS) - E(HS)]. \quad (81)$$

Equation (81) is the Noodleman's projection scheme in its most often employed form. Caballol *et al.* have, however, shown through explicit calculations of the overlap integral that its value is rarely small enough to be neglected.³⁴ The expression for the magnetic coupling constant in the weak interaction limit generalized to two spins with magnitudes S_A and S_B is

$$J = \frac{E(LS) - E(HS)}{2|S_A||S_B|}. \quad (82)$$

For the derivation of equation (82) see reference 201.

Ruiz *et al.*²⁰⁸ have suggested that in the strong interaction limit the low-spin broken symmetry state represents the singlet state sufficiently well and thus renders equation (82) to the unprojected form

$$J = E(LS) - E(HS) \quad (83)$$

for the $S_1 = S_2 = 1/2$ case.

Yamaguchi *et al.*²⁰⁹⁻²¹² have proposed another spin projection scheme that is valid regardless whether the interaction is strong or weak:

$$J = \frac{2[E(LS) - E(HS)]}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{LS}}. \quad (84)$$

$\langle \hat{S}^2 \rangle_{HS}$ and $\langle \hat{S}^2 \rangle_{LS}$ are the expectation values of the \hat{S}^2 operator calculated for the high and low-spin determinants, respectively. A typical spin contamination in a broken symmetry singlet KS reference wave function is $\langle \hat{S}^2 \rangle_{LS} \approx 1$. This means that the low-spin KS reference wave function is

a roughly 50:50 mix of the pure singlet and triplet states.³³ For the triplet state, spin contamination is much less prevalent and thus $\langle \hat{S}^2 \rangle_{HS} \approx 2$. When these values are inserted into equation (84), it reduces to Noodleman’s projection in the weak interaction limit in equation (81). In the strongly interacting case the interaction approaches that of a covalent bond and $\langle \hat{S}^2 \rangle_{LS} \approx 0$. At this limit, equation (84) reduces to the unprojected form of equation (83). Thus, Yamaguchi’s projection scheme reproduces the results of Noodleman’s projection at both interaction extremes. The main difference between the two projection schemes is that Noodleman’s theory connects the extremes with the overlap integral $\langle LS_1 | LS_2 \rangle$ or $\langle \gamma_1 | \gamma_2 \rangle$ whereas Yamaguchi’s theory connects them by spin contamination of the low-spin state. Equation (84) has also been generalized by Shoji *et al.* to systems with more than two interacting magnetic centers.²¹³

In addition to schemes that project the energies of low- and high-spin states after they have been optimized separately, research ongoing in to develop schemes that project the energies during the self-consistent process with the projected Hartree–Fock method.^{214,215} This theory has originally been designed to be used in conjunction with UHF, but a DFT implementation is also under development.²¹⁶ Very recent development has also been made by Saito and Thiel²¹⁷ who implemented analytical gradients to Yamaguchi’s projection method. This enables geometry optimization of high and low-spin states to be carried out within the projection scheme.

6.2.3 Mapping based on the Ising model

Another approach to mapping UKS results to the eigenstates of the HDV Hamiltonian is to simplify the model Hamiltonian.⁸ Such an approach can be achieved by using the Ising Hamiltonian which has the form

$$\hat{H}_{Ising} = -J\hat{S}_{z,1}\hat{S}_{z,2} \quad (85)$$

for a system of two magnetic centers. Equation (85) acts on the magnetic centers 1 and 2 only with the single-particle \hat{S}_z operator that produces a well-defined value from a UKS reference wave function. This avoids the need to introduce the ill-defined two-particle \hat{S}^2 operator to the calculation. The Ising Hamiltonian can be approximated from the HDV Hamiltonian by neglecting the ladder operators in the expansion of equation (5). It should be noted that the spectra of the HDV Hamiltonian and the Ising Hamiltonian are not identical. For example, the Ising model predicts the

two electron states with $S = 1, M_S = 0$ and $S = 0, M_S = 0$ to be degenerate whereas the HDV model does not.⁸ Several authors have employed the Ising Hamiltonian to map results from UHF calculations^{218–220} and more recently from UKS calculations.^{33,221}

For two interacting electrons it is trivial to show, that once applied on the low- and high-spin broken symmetry states, the Ising Hamiltonian produces energies

$$E(LS) = -\frac{1}{4}J \quad \text{and} \quad E(HS) = \frac{1}{4}J \quad (86)$$

and thus

$$J = 2[E(LS) - E(HS)]. \quad (87)$$

This is again the same result that both Noodleman’s and Yamaguchi’s projection schemes produce in the weak interaction limit. The result in equation (87) has now been derived from three different contexts, although two of these only in the weak interaction limit. Dai and Whangbo have shown that the magnetic coupling constants between two magnetic sites calculated both with the Ising Hamiltonian and the HDV Hamiltonian are identical if the magnetic orbitals at the two sites do not significantly overlap.^{222,223} This adds theoretical justification for the use of equation (87) which is the most commonly used mapping approach (although not necessarily derived from the same theoretical starting points). One serious problem with the Ising model approach still remains. In the strong interaction limit the low-spin state approaches that of a covalent bond and thus $|LS\rangle \rightarrow |S\rangle$. Equation (87) does not reproduce this limit while both equations (79) and (84) do.

6.3 Alternative DFT formulations that retain spin symmetry of the KS reference wave function

The third alternative to treating spin symmetry problems that arise in UKS calculations is to reformulate KS theory to a form that does not suffer from these problems. This of course does not remove the fundamental problem that true spin states are not defined in KS DFT. Two such approaches will be described below. Both of them improve the standard KS theory by expanding the variational entity. Complete active space multireference DFT methods use a CI expansion of the reference wave function whereas the restricted ensemble KS formalism expands the density as a linear combina-

tion of the densities of several states. Neither of the methods has seen even remotely as widespread success in static correlation problems as the UKS approach has, and they remain—at the moment—theoretical curiosities. They do, however, offer a way to circumvent the spin symmetry problems present in the UKS solutions. These methods can also be seen as additions to the list of higher quality approximations to the XC functional reviewed in section 5.

6.3.1 Complete active space multireference DFT methods

Complete active space multireference DFT (CAS-MR-DFT) methods combine DFT with a complete active space (CAS) expansion of a wave function. The standard wave function based CAS method partitions the orbital space to active and inactive subspaces. The active orbitals are the ones which include most of the chemically interesting interactions, and they are usually chosen by using chemical intuition. The wave function within the active space is expanded in a full CI fashion, whereas the orbitals in the inactive space are treated with the HF formalism. Thus, the active space includes all correlation and the inactive none. This is a very efficient mean of including static electron correlation.^{10,12} In electronic structure theory a CAS wave function can be optimized in two ways. In a CASCI procedure, only the CI expansion coefficients are optimized, and thus the energy minimization can be done in a single diagonalization as in the standard CI method (introduced in section 3.1.3). To further relax the wave function the molecular orbital coefficients can also be optimized in the variational process with the CASSCF method (briefly introduced in section 3.1.4). CASSCF presents a highly non-linear optimization problem that must be solved in a self-consistent manner. Both of these methods can be combined with DFT to yield the CASCI-DFT and CASSCF-DFT methods. In these approaches the inactive orbitals are correlated with DFT while the active ones are treated as in the wave function approach. This should, in principle, increase the accuracy of the results compared to wave function based CASCI and CASSCF methods and offer an alternative way of treating multireference problems in DFT framework.

The problem of combining correlation energies calculated with CASCI/CASSCF and DFT formalisms is far from trivial as wave function based methods and DFT approaches treat correlation completely differently. In any simple combination of these methods some correlation effects end up being counted twice.^{224,225} There are in general two approaches

to overcome the double counting problem: i) employing a scheme that projects the doubly counted energy from the XC approximation^{224–230} or ii) employing a range-separated approach where the short range part is treated with DFT and the long range part with a CAS method.^{231–235}

In the first CAS-MR-DFT approach, the universal Hohenberg–Kohn functional $F_{HK}[n(\mathbf{r})]$ is divided into a modified universal functional $F^{CAS}[n(\mathbf{r})]$ and a residual correlation functional $E_{RC}^{CAS}[n(\mathbf{r})]$:^{224–230}

$$F_{HK}[n(\mathbf{r})] = F^{CAS}[n(\mathbf{r})] + E_{RC}^{CAS}[n(\mathbf{r})]. \quad (88)$$

The modified universal functional is evaluated by minimizing the expectation value of the kinetic energy and electron–electron Coulombic operators on a CAS wave function ψ_{CAS} that is constrained to the ground state density $|\psi_{CAS}|^2 = n_0(\mathbf{r})$:

$$F^{CAS}[n_0(\mathbf{r})] = \min_{\psi_{CAS} \rightarrow n_0(\mathbf{r})} \langle \psi_{CAS} | \hat{T} + \hat{V}_{ee} | \psi_{CAS} \rangle. \quad (89)$$

The CAS wavefunction ψ_{CAS} is built by generating all possible determinants in the active orbital subspace. The residual correlation energy represents all correlation that is not included in $F^{CAS}[n(\mathbf{r})]$. The modified functional accounts for all correlation included in a wave function based CASCI calculation and the residual correlation term adds correlation beyond this limit. In order to evaluate $E_{RC}^{CAS}[n(\mathbf{r})]$, the correlation effects covered by $F^{CAS}[n(\mathbf{r})]$ must be projected out from the XC functional used to approximate the DFT part of correlation. How the projection is handled depends on the form of the XC approximation. Furthermore, the XC energy must be scaled to the length of the CAS expansion. Details of this process can be found in references 225 and 224. The value of $E_{RC}^{CAS}[n(\mathbf{r})]$ depends on the CAS wave function, and thus equation (88) must be evaluated in a self-consistent manner in both CASCI-DFT and CASSCF-DFT. Earlier multireference DFT methods employing this approach optimized the CI coefficients only, but newer developments gravitate towards a CASSCF-DFT model.^{236,237}

In the second CAS-MR-DFT approach the \hat{V}_{ee} operator is split into short range (*SR*) and long range (*LR*) parts using the standard error function in the same way as introduced in the context of range-separated functionals:^{231–235}

$$\hat{V}_{ee,LR} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{\text{erf}(\mu|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (90)$$

The short range part is treated with KS formalism and the long range part using a CAS expansion of the wave function. The minimization is again done under the constraint that the CAS wave function produces the ground state density. In this approach the universal Hohenberg–Kohn functional has the form

$$F_{HK}[n(\mathbf{r})] = \min_{\psi_{CAS \rightarrow n_0}(\mathbf{r})} \left\{ \langle \psi_{CAS} | \hat{T} + \hat{V}_{ee,LR} | \psi_{CAS} \rangle + C_{SR}[n(\mathbf{r})] + E_{XC,SR}[n(\mathbf{r})] \right\}, \quad (91)$$

where $C_{SR}[n(\mathbf{r})]$ treats the short range electron–electron interaction and $E_{XC,SR}[n(\mathbf{r})]$ is the XC functional evaluated on the short range part of the density.

Sharkas *et al.* have recently proposed a multireference DFT approach that is very similar to the single-parameter double-hybrid of equation (64).²³⁸ This hybrid adds a portion λ of exact exchange as well as exact static correlation to the DFT approximation. In this approach the universal functional takes the form

$$F_{HK}[n(\mathbf{r})] = \min_{\psi_{CAS \rightarrow n_0}(\mathbf{r})} \left\{ \langle \psi_{CAS} | \hat{T} + \lambda \hat{V}_{ee} | \psi_{CAS} \rangle + (1 - \lambda)E_X^{HF} + (1 - \lambda^2)E_C[n(\mathbf{r})] \right\}. \quad (92)$$

All CAS-MR-DFT methods depend on the virtual orbitals and are thus rung five approximations in Perdew’s ladder classification. Double-hybrid functionals include a portion of exact dynamic correlation in the functional, whereas CAS-MR-DFT methods add a portion of exact static correlation. Standard hybrid DFT can describe dynamic correlation reasonably well, but it struggles in the description of static correlation that is very important in near-degeneracy problems present in the calculation of magnetic coupling constants. However, much like with double-hybrid functionals, CAS-MR-DFT is still an emerging method and applications of it are not yet (if they ever will be) widespread. The CAS-MR-DFT approaches have not yet been subject to large systematic studies, although they have been applied to some magnetic coupling problems.^{71,239}

6.3.2 Ensemble Kohn–Sham formalism

In section 4.2, it was mentioned that the KS theory makes the assumption that it is always possible to find a single Slater determinant that produces the ground state density. As Perdew has pointed out,³⁵ there is no guarantee that this is the case. However, a rigorous proof does exist that any physical density can be represented as an ensemble of densities produced from various single-determinant states:^{240–243}

$$n(\mathbf{r}) = \sum_i w_i n_i(\mathbf{r}). \quad (93)$$

A classic example of the success of ensemble densities over conventional single determinant KS theory is the calculation of energies of orbitals that are degenerate due to symmetry reasons. For instance, a Sc^{2+} ion with a d^1 configuration should have the same energy regardless of which of the five d-orbitals the electron occupies. However, all common approximations to the XC functional will produce a different energy if the d_{z^2} orbital is occupied as opposed to the other four d-orbitals. This problem can be solved by expanding the total density as an ensemble of five densities; each of which have the unpaired electron occupying a different d-orbital.^{20,244}

In the KS approach the ensemble is built of densities produced from KS orbitals

$$n(\mathbf{r}) = \sum_k p_k |\phi_k(\mathbf{r})|^2, \quad (94)$$

where p_k is the occupation number of orbital k and has a value between 0 and 2. The summation runs over all orbitals, occupied and virtual.²⁴³ The expansion of equation (94) offers a way of representing the density of a system with strong static correlation without the need to resolve to an unrestricted approach. This avoids all the spin symmetry problems associated with the UKS method. Ensemble densities are the DFT analogue of a CI expansion of the wave function. An ensemble density is used as the variational entity in the restricted ensemble-referenced Kohn–Sham (REKS) method of Filatov and Shaik.^{245,246}

The REKS method will be formulated here for a system of two magnetic centers with spins $S_1 = S_2 = 1/2$.^{33,34,245,246} This system can be described by an active orbital subspace of two orbitals ϕ_r and ϕ_s occupied by two electrons. These orbitals are the HOMO and LUMO of a conventional KS calculation. This is again analogous to the wave function formulation of the same system described in section 3.2. The ensemble density of such

a system is

$$n_{REKS}(\mathbf{r}) = 2 \sum_{k=1}^{(N-2)/2} |\phi_k(\mathbf{r})|^2 + p_r |\phi_r(\mathbf{r})|^2 + p_s |\phi_s(\mathbf{r})|^2, \quad (95)$$

where the summation runs over all doubly occupied orbitals of the inactive subspace. The active orbitals are occupied by numbers p_r and p_s . The REKS energy expression for this particular type of system is

$$\begin{aligned} E_{REKS} = & \frac{p_r}{2} E_{KS}[\dots, \phi_r^{\alpha\beta}, \phi_s^0, \dots] + \frac{p_s}{2} E_{KS}[\dots, \phi_r^0, \phi_s^{\alpha\beta}, \dots] \\ & + f(p_r, p_s) \left\{ E_{KS}[\dots, \phi_s^\alpha, \phi_r^\alpha, \dots] \right. \\ & \left. - \frac{1}{2} E_{KS}[\dots, \phi_s^\alpha, \phi_r^\beta, \dots] - \frac{1}{2} E_{KS}[\dots, \phi_s^\beta, \phi_r^\alpha, \dots] \right\}, \quad (96) \end{aligned}$$

where the superscripts of the orbitals indicate their occupations; $\alpha\beta$ means that the orbital is doubly occupied, α means the orbital is occupied by a single α electron and 0 means that the orbital is vacant. The energy expression consists of the energies of the two doubly occupied states weighted by their occupation numbers and a coupling term that includes energies of the singly excited KS determinants. $f(p_s, p_r)$ is a factor measuring the coupling strength. The REKS energy is an ensemble of energies of individual states (microstates) represented by single determinants. In the optimization process the energy is minimized in terms of the orbital coefficients as well as the fractional occupation numbers of the active orbitals. Energies for the microstates are evaluated with the standard KS formalism using any standard approximation to the XC functional. The functional form of E_{REKS} introduces static correlation in addition to the correlation included in E_{XC} . Much like in CAS-MR-DFT approaches, this leads to double counting of some static correlation.

The error introduced from double counting can be minimized by a proper choice of the coupling factor $f(p_s, p_r)$. When the KS orbitals ϕ_r and ϕ_s are degenerate and thus $p_r = p_s = 1$, the coupling strength is

$$f(p_s, p_r) = \sqrt{p_s p_r}. \quad (97)$$

Combining equations (96) and (97) yields an expression used to evaluate the energy of a CASSCF wave function with a two-orbital-two-electron active subspace. When the orbitals are well separated in energy (the system

has a large HOMO–LUMO gap) the coupling strength can be extracted from the energy functional of DFT-FON (DFT with fractional occupation numbers) method:²⁴⁷

$$f(p_s, p_r) = p_r p_s. \quad (98)$$

Originally a geometric average

$$f(p_s, p_r) = (p_r p_s)^{3/4} \quad (99)$$

of the forms (97) and (98) was used,²⁴⁶ but later a more advanced form which interpolates between the asymptotic regions of (97) and (98) has been developed:²⁴³

$$f(p_s, p_r) = (p_r p_s)^{1 - \frac{1}{2p_r p_s} + \frac{\delta}{1+\delta}}, \quad (100)$$

where $\delta = 0.4$. This model is shown to more efficiently reduce double counting than that in equation (99).

The REKS method offers a very attractive approach to DFT calculations on systems with high static electron correlation. The clear advantage of this method as compared to CAS-MR-DFT approaches is that it can employ any XC approximation used in standard KS calculations. Furthermore, it employs a functional form very similar to that used in wave function based CASSCF method that is implemented in a wide range of quantum chemical codes.²⁴⁸ Equation (96) does however include the coupling factor $f(p_r, p_s)$ that introduces a new approximation to the DFT approach in addition to the XC functional. The REKS method has been applied to strong static correlation problems including the calculation of magnetic coupling constants.^{243,248} Despite its formally correct way of treating spin symmetry, the REKS method has not, however, been shown to considerably improve results compared to the UKS approach.

6.4 Spin-flip time-dependent DFT

The spin-flip time-dependent DFT (SF-TDDFT) method^{249–252} uses a time dependent DFT formalism^{21,253–257} to build the singlet and triplet states as excitations from a reference state. The main advantage of this approach is that it produces a singlet state that is nearly completely free of spin contamination. TDDFT will not be reviewed in detail here; a more thorough description can be found, for example, in references 257 and 21. The foundation of TDDFT is in the Runge–Cross theorem, which proves that at

any given time t the time-dependent density $n(\mathbf{r},t)$ uniquely determines the external potential as in the time-independent approach.²⁵³ This allows a time-dependent perturbation, such as a semi-classical interaction with the electric field, to be included in the ground-state Hamiltonian, which makes it possible to use DFT as a tool in predicting excitation energies. In SF-TDDFT the interaction is further assumed to be weak enough so that the response function is linear. Also, the XC potential is assumed to be independent of the frequency of the excitation so that the conventional ground-state potential can be employed. An in-depth description of the theoretical formulation of SF-TDDFT requires knowledge of TDDFT and will thus be described here in a superficial manner. A detailed discussion can be found in the review of Bernard *et al.*²⁵²

Figure 4 in section 3.2 shows all possible spin states that can be formed in an orbital space of two orbitals and two electrons. The determinants Φ_A and Φ_F represent the ground state singlet $|S_0\rangle$ and the doubly excited singlet $|S_2\rangle$ respectively. These are the two states used to describe two-electron systems of strong static correlation as described in section 3.2. The determinants Φ_B and Φ_C describe degenerate triplet states $|T_1\rangle$. A third triplet state can be built as a CSF by combining the two singly excited determinants Φ_D and Φ_E that are not by themselves spin eigenstates:

$$\Phi_{D+E} = \frac{1}{\sqrt{2}}(\Phi_D + \Phi_E). \quad (101)$$

This CSF corresponds to triplet state $|T_2\rangle$. The states $|T_1\rangle$ and $|T_2\rangle$ are degenerate in the wave function approach but not necessarily so in SF-TDDFT and are thus treated separately here. The SF-TDDFT approach uses the $|T_1\rangle$ state calculated with standard KS formalism as a reference state. Single determinant KS reference wave functions corresponding to states $|S_0\rangle$, $|S_2\rangle$ and also $|T_2\rangle$ can be generated from the $|T_1\rangle$ determinant by a single excitation and a spin-flip. The excitation energy can also be negative in the antiferromagnetic case, when the singlet state has lower energy than the triplet reference state. The approximations introduced above allow only single excitations, and thus the $|S_2\rangle$ state cannot be generated from a $|S_0\rangle$ reference state.

Recently two different implementations of SF-TDDFT—collinear Tamm–Dancoff SF-TDDFT^{249,258,259} and second order spin-flip constricted variational DFT^{260,261}—have been used to calculate magnetic coupling constants.^{261–264} The results are comparable or slightly better than ones

obtained with the UKS approach. What is remarkable about these results, however, is that in all the cases spin contamination in the reference wave function is negligible. SF-TDDFT can be seen as a way to optimize singlet and triplet wave functions in a manner that does not lead to a variational collapse to an unphysical spin state as happens in the standard UKS procedure does.

7 Performance of models

DFT has been applied to a tremendous number of magnetic coupling problems with varying results. In all these studies different methodologies such as XC functionals, basis sets and projection schemes have been applied to very different types of problems. The amount of adjustable parameters present in these models makes it possible to produce practically any predefined result. Thus, reviewing these studies in any systematic way that would provide some wider insight into the performance of DFT methods in coupling problems would be neither feasible nor of practical use. Many such case studies have been briefly described in the references 25, 68 and 69 and the references therein. Fortunately there exist two databases which have been used (at least in part) in a number of systematic studies.^{163,179,243,262,265–268} The first of these has been collected by Valero *et al.*,²⁶⁵ originally for a validation study of the M06 family of functionals, and the second by Rudra *et al.*²⁶⁹

The following subsections first discuss the performance of the commonly applied projection schemes applied to a simple H–He–H model system. The next subsection introduces the two databases mentioned above. The final subsection discusses, in detail, the performance of various DFT methods that have been used to calculate coupling constants for the compounds in these databases.

7.1 H–He–H model and projection schemes

The problem with numerical validation of any projection scheme is that the performance of an individual projection model is always coupled with the performance of the XC functional with which it is used. There is no way of separating these two approximations, and thus one must always study the performance of a functional–projection pair. Of course this applies vice versa to validations of XC approximations. The errors arising from the inaccurate treatment of exchange and correlation can—to some extent—be minimized by using simple enough system such that these properties can be reasonably well described. One of the simplest magnetic systems available is the hypothetical H–He–H moiety. It is small enough for a full CI calculation of its singlet and triplet energies to be computationally feasible.²⁷⁰ Comparing the coupling constants calculated with DFT methods to those calculated with the full CI approach, as opposed to experimental values, offers the added advantage of neglecting all possible

Table 2: Magnetic coupling constants (in wave numbers) calculated for the H–He–H system with various methods, basis sets, projection schemes and H–He bond distances.

Projection	R(H–He)	B3LYP ³⁴ 6-31++G**	B3LYP ^{37,212} 6-311++G**	SIC-B3LYP ³⁷ 6-311++G**	UHF ³⁴ 6-31++G**	Full CI ²⁷⁰ 6-311G**
$J = E(LS) - E(HS)$	1.250 Å	4196	4367	2660	1928	4860
	1.625 Å	497	513	315	213	544
	2.000 Å	55	57	210	21	50
$J = 2[E(LS) - E(HS)]$	1.250 Å	8393	8734	5320	3856	
	1.625 Å	994	1026	630	425	
	2.000 Å	110	114	64	42	
$J = \frac{2[E(LS) - E(HS)]}{1 + \langle \gamma_1 \gamma_2 \rangle}$	1.250 Å	6712			3655	
	1.625 Å	971			423	
	2.000 Å	109			42	
$J = \frac{2[E(LS) - E(HS)]}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{LS}}$	1.250 Å	6944				
	1.625 Å	1198				
	2.000 Å	138				

errors that can arise from experimental procedures, structural properties of the molecule or the size of the basis set; the DFT result is simply compared with the best possible computational result within the chosen basis set.

The H–He–H system has been used by several authors as a model system for magnetic studies.^{34,37,163,212,265,271} This study will focus on the results of Caballol *et al.*,³⁴ Ruiz *et al.*³⁷ and Soda *et al.*²¹² Unfortunately all of these studies use slightly different basis sets. This means that the different calculations cannot be quantitatively compared but differences in the size of the chosen basis sets in these studies should not effect the qualitative trends. All studies use Pople-type split valence basis sets. Caballol *et al.* have used a valence double- ζ set with two sets of diffuse functions and two sets of polarization functions (6-31++G**). Ruiz *et al.* have used a valence triple- ζ set with the same number of diffuse and polarization functions (6-311++G**). The study of Soda *et al.* as well as the full CI calculations both use a triplet- ζ basis set with two sets of polarization functions but without any diffuse functions (6-311G**). A detailed description on notation of basis sets can be found in reference 10. The results of these studies are summarized in Table 2 and Table 3.

The B3LYP functional shows a very large deviation from the full CI results with all projection schemes and the best result is obtained without projection. Noodleman’s projection in the weak interaction limit (equation (81), second row in Table 2) shows the worst performance. The same pro-

Table 3: SOMO–SOMO overlaps and $\langle \hat{S}^2 \rangle$ values for both high and low-spin states of H–He–H calculated with B3LYP and UHF.³⁴

$R(\text{H–He})$	$\langle \gamma_1 \gamma_2 \rangle$	B3LYP		UHF		
		$\langle \hat{S}^2 \rangle_{LS}$	$\langle \hat{S}^2 \rangle_{HS}$	$\langle \gamma_1 \gamma_2 \rangle$	$\langle \hat{S}^2 \rangle_{LS}$	$\langle \hat{S}^2 \rangle_{HS}$
1.250 Å	0.5004	0.750	2.001	0.2347	0.945	2.001
1.625 Å	0.1544	0.976	2.000	0.0761	0.994	2.000
2.000 Å	0.0484	0.998	2.000	0.0247	0.999	2.000

jection scheme that explicitly includes the overlap of the SOMOs (equation (79), third row) performs much better although still fails to reproduce the CI results even in a remotely quantitative manner. Yamaguchi’s projection (equation (84), bottom row) follows close behind. In stark contrast, the Perdew–Zunger one-electron SIE-corrected B3LYP (SIC-B3LYP) with equation (81) shows the best performance. This suggests that the single-electron SIE plays an important role in the calculation of magnetic coupling constants and leads to the failure of the B3LYP approximation as discussed in section 5.4. Values calculated with UHF are also included in Table 2 for comparison. As opposed to B3LYP, UHF underestimates the magnitude of the coupling constants. This behavior is most likely due to the localization error present in UHF whereas the UKS results suffer from the delocalization error as a consequence of the N -electron SIE. Increasing the size of the basis set in a B3LYP calculation from valence double- ζ to valence triplet- ζ shows negligible improvement.

The SOMO–SOMO overlaps listed in Table 3 show that UHF produces more localized orbitals than B3LYP. For both methods, the SOMOs are clearly not orthogonal at bond lengths 1.250 Å and 1.625 Å. Only at the 2.000 Å distance can the $1 + \langle \gamma_1 | \gamma_2 \rangle \simeq 1$ assumption of Noodleman’s weak interaction limit be made. This is the reason for large deviations between the coupling constants calculated with (79) at the 1.250 Å bond length. For both methods the low-spin states are highly spin contaminated. B3LYP suffers from spin contamination slightly less at the 1.250 Å bond length where the SOMO–SOMO overlap is about 0.5. At all other calculated distances $\langle \hat{S}^2 \rangle_{LS} \approx 1$ for both models whereas the triplet states are practically free of spin contamination. This justifies the $|T\rangle \simeq |HS\rangle$ assumption made in both Noodleman’s and Yamaguchi’s projections. Values for the SOMO–SOMO overlap and spin contamination are not available for the SIC-B3LYP results.

The results in Table 2 suggest that the non-projected approach is numerically the most justifiable. On the other hand, the one-electron SIE free method provides better results with the Noodleman’s projection at

the weak interaction limit. Ruiz *et al.* have also calculated the coupling constants of H–He–H with other hybrid functionals. For example, the unprojected values calculated with B3LYP and PBE0 at 1.250 Å distance are 4367 cm⁻¹ and 3663 cm⁻¹, respectively.³⁷ Thus, even for this very simple magnetic system there are considerable functional-dependent variations.

7.2 Systematic studies

7.2.1 Magnetic coupling constant databases

The two databases discussed in this study are summarized in Table 4; the structures of the molecular systems involved are illustrated in Figure 7. The compounds are identified in this study by the IDs they have in the Cambridge Structural Database²⁷² except in cases for which there is no deposited structure.

The database of Valero *et al.* contains two organic diradicals^{273,274} and seven binuclear Cu complexes.²⁷⁵⁻²⁸² The first organic diradical, α -4-dehydrotoluene (DHT), shows strong intramolecular ferromagnetic interaction, whereas the second, biverdazyl, shows antiferromagnetic coupling between two π -electrons localized in two separate rings. The Cu complexes cover a wide range of magnetic coupling strengths, from highly antiferromagnetic (BISDOW) to ferromagnetic (YAFZOU), as well as a large variety of bridging ligands and coordination geometries.

The second database of Rudra *et al.* consists of ten binuclear complexes of the first row transition-metals. In addition to Cu-only complexes this set includes Cu–Cr, Cu–MnV–V, Fe–Fe, and Mn–Mn systems. The Mn ions are present in varying oxidation states. Like the database of Valero *et al.*, it covers a large variety of coupling magnitudes.

With the exception of the two organic diradicals, both databases consist solely of first row transition-metals with heavy emphasis on copper. The reason is that these compounds have fairly simple, well characterized structures with minimal zero field splitting effects that would complicate the magnetic spectrum. Also, calculations on heavier transition metal centers require some approximation of relativistic effects.²⁵ This would introduce yet another ingredient to the ever growing pool of approximations one must use to calculate magnetic coupling constants with DFT. However, this fairly narrow focus does introduce some bias in validation studies conducted with these databases. The low- and high-spin energies have been calculated as single points on the potential energy surface with no ge-

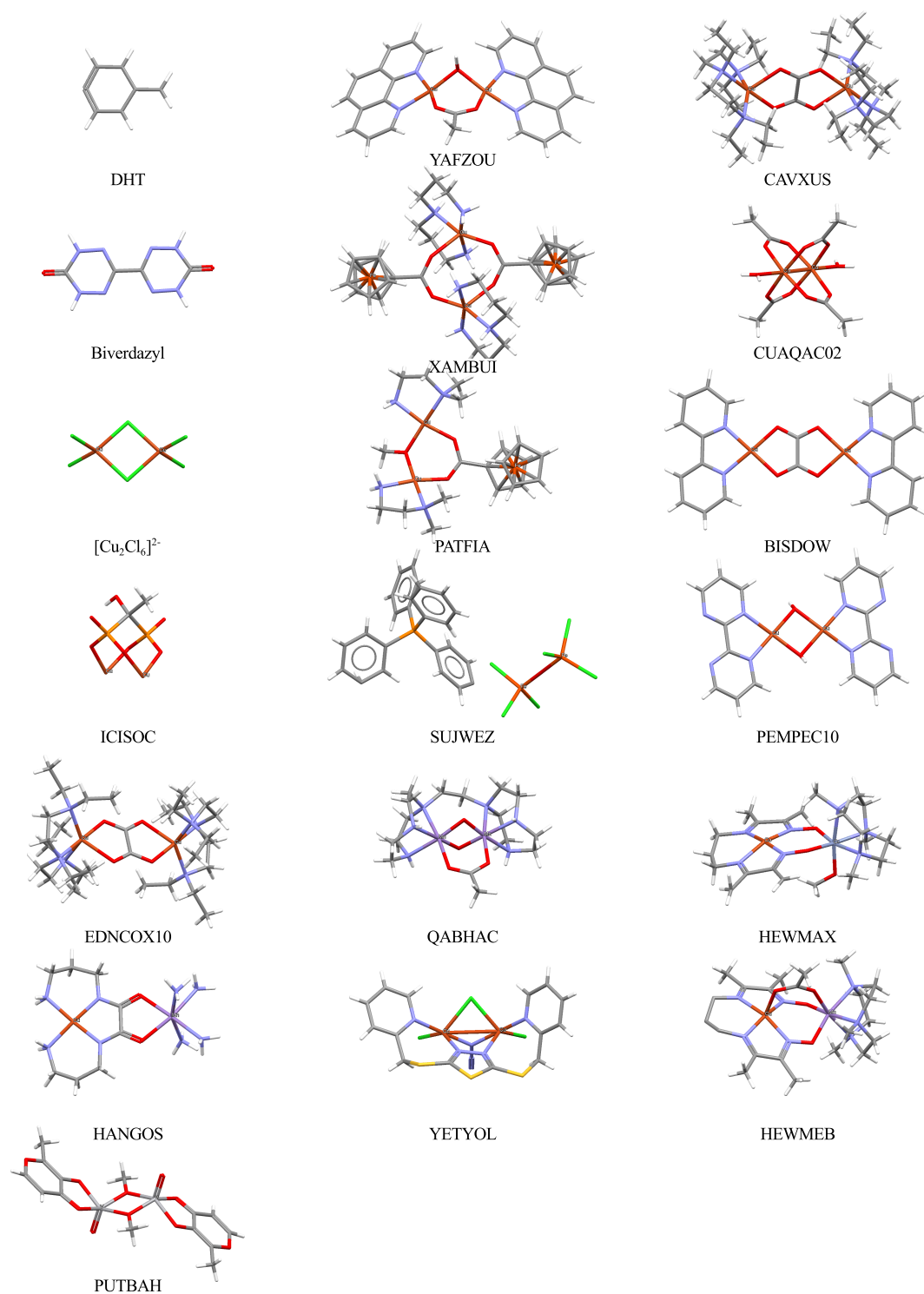


Figure 7: Structures of the open shell systems in the databases of Valero et al.²⁶⁵ (first three rows) and Rudra et al.²⁶⁹ (last four rows). Solvent molecules and small coordinated species such as water and nitroxide have been omitted for clarity. For full crystal structures see the references in Table 4.

Table 4: A summary of the magnetic coupling constant database of Valero et al.²⁶⁵ (listed first) and of Rudra et al.²⁶⁹ (listed second).

ID ^a	Name/formula	J [cm ⁻¹]	Ref.
DHT	α -4-dehydrotoluene	1050 to 1749	273
Biverdazyl	1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl	-769	274
[Cu ₂ Cl ₆] ²⁻	[Cu ₂ Cl ₆] ²⁻	-40 to 0	275
YAFZOU	[[Cu(phen)] ₂ (μ -AcO)(μ -OH)](NO ₃) ₂ ·H ₂ O	111	276
XAMBUI	[[Cu(dpt)] ₂ (μ -O ₂ C-(η^5 -C ₅ H ₄)Fe(η^5 -Cp)) ₂]	2	277
PATFIA	[[Cu(dmen)] ₂ (μ -OMe)(μ -O ₂ C-(η^5 -C ₅ H ₄)Fe(η^5 -Cp))](ClO ₄) ₂	-11	278
CAVXUS	[[Cu(petdien)] ₂ (μ -C ₂ O ₄)](PF ₆) ₂	-19	279, 280
CUAQAC02	[[Cu(H ₂ O)] ₂ (μ -AcO) ₄]	-286	281
BISDOW	[[Cu(bpy)(H ₂ O)(NO ₃)] ₂ (μ -C ₂ O ₄)]	-382	282
ICISOC	[Cu ₂ (MeC(OH)(PO ₃) ₂) ₂] ⁴⁻	-62	283
EDNCOX10	[(petdien) ₂ Cu ₂ (μ -C ₂ O ₄)] ²⁺	-74	284
HANGOS	[Mn(NH ₃) ₄ Cu(oxpn)] ²⁺	-32	285
PUTBAH	[(μ -OCH ₃)VO(maltolato)] ₂	-214	286
SUJWEZ	[Ph ₄ P] ₂ [Fe ₂ OCl ₆]	-224	287
QABHAC	[Mn ₂ (μ -O) ₂ (μ -OAc)dtne] ²⁺	-220	288
YETYOL	[Cu ₂ (DMPTD)(μ_2 -N ₃)(μ_2 -Cl)Cl ₂]CH ₃ CN	168	289
PEMPEC10	[Cu ₂ (μ -OH) ₂ (bipym) ₂](NO ₃) ₂ ·4H ₂ O	114	290
HEWMAX	[(Dopn)Cu(\bar{O} H ₂)Cr(\bar{O} CH ₃)L](ClO ₄) ₂ ·H ₂ O	38	291
HEWMEB	[(Dopn)Cu(μ -CH ₃ COO)-MnL](ClO ₄) ₂ ·H ₂ O	110	291

phen = 1,10-phenanthroline

petdien = *NNN'N'N'*-pentaethyldiethylenetriamine

dpt = dimethylpropylenetriamine

Cp = cyclopentadienyl

dmen = *NN*-dimethylethylenediamine

bpy = 2,2'-bipyridine

L = 1,4,7-trimethyl-1,4,7-triazacyclononane

^a The IDs are those used in the Cambridge Structural Database except for the first three compounds which have no deposited structure.

oxpn = *N,N'*-bis(3-aminopropyl)oxamide

maltolato = 3-hydroxy-2-methyl-4H-pyran-4-one

DTNE = 1,2-bis(1,4,7-triazacyclonon-1-yl)ethane

DMPTD = 2,5-bis(pyridylmethyl)thio

bipym = 2,2'-bipyrimidine

Dopn = oximate dianion

ometry optimizations. The only exception to this is the structure of DHT which is obtained from theoretical calculations.²⁷³

7.2.2 Results

Table 5 summarizes the results from six different studies on the databases introduced in the previous subsection. The coupling constants calculated with B3LYP, PBE0, M06, M06-2X and M06-HF for the first database are from the original paper of Valero *et al.*²⁶⁵ Results with the range-separated functionals HSE and LC- ω PBE and double-hybrids B2-PLYP and B2GP-PLYP on the same database are from the papers of Rivero *et al.*¹⁶³ and Schwabe and Grimme,¹⁷⁹ respectively. The results obtained for the second database with B3LYP, HSE and LC- ω PBE are calculated by Peralta and Melo.²⁶⁶ All the results with the REKS formalism have been calculated by Moreira *et al.*,²⁴³ and the SF-TDDFT calculations have been performed by Valero *et al.*²⁶²

As a whole, the results mix three different types of basis sets. Valero *et al.* have originally used Pople-type basis sets on their database. For DHT, a 6-31++G** basis has been used for all atoms, whereas for the biverdazyl 6-31G* has been used for C, N and O atoms and 6-31++G** for H atoms. For the transition-metal complexes, 6-3111+G has been used for the metal centers and 6-31G* for all other atoms. The above choice of basis sets has been employed in the B3LYP, PBE0, M06, M06-2X, M06-HF, HSE and LC- ω PBE calculations on the first database as well as in all REKS and SF-TDDFT calculations. The double-hybrid calculations employ Ahlrichs' def2-SVP²⁹²⁻²⁹⁵ valence double- ζ basis set. The B3LYP, HSE and LC- ω PBE calculations on the second database use Ahlrichs' def-TZVP²⁹⁶ for transition metal centers and def-SVP²⁹² for the rest of the atoms. The def-SVP and def2-SVP sets are somewhat smaller than the Pople-type basis sets originally used by Valero *et al.* All UKS results are projected using Noodleman's projection in the weak interaction limit (equation (81)). SF-TDDFT results are calculated with Yamaguchi's projection (equation 84) although spin contamination in results calculated with SF-TDDFT formalism is, in general, negligible. REKS formalism produces pure spin states and thus no projection has been employed for REKS data.

It is evident from Table 5 that different XC functionals and DFT formalisms produce highly varying results. The most extensive and consistent set of data available is for the complexes YAFZOU to BISDOW. These structures also have clearly defined experimental magnetic coupling constants and therefore these complexes will be examined here in further detail.

A common statistical approach to evaluating functional performance on a set of experimentally characterized systems is to calculate the mean absolute error (MEA) which is the average deviation of calculated values from experimental values. Table 6 lists the MEA values and standard deviations of MEA for the calculated coupling constants of YAFZOU to BISDOW using various functionals and DFT formalisms. The values are listed first with Noodleman's projection and for comparison also without projection. Based on these numbers the best results are obtained with LC- ω PBE and B2-PLYP. PBE0 and HSE also perform reasonably well. Interestingly, three of these functionals are based on the non-empirical PBE GGA functional. If no projection is used B3LYP performs the best, followed by HSE and PBE0.

A number of authors have pointed out that plots of experimental vs. calculated magnetic coupling constants show very high linear correla-

Table 5: Magnetic coupling constants (in wave numbers) calculated for various compounds using hybrid, range-separated and double hybrid functional with the UKS, SF-TDDFT and REKS formalisms with experimental values listed for comparison..^{163,179,243,262,265,266,273–291}

Compound	Exp.	B3LYP	PBE0	M06	M06-2X	M06-HF	HSE	LC- ω PBE
DHT	1050–1749	1924	2339	2632	2599	2641	2345	2963
Biverdazyl	-769	-1224	-1313	-1184	-1185	-1226	-1336	-1636
[Cu ₂ Cl ₆] ²⁻	-40–0	-91	-49	5	0.1	-18	-55	-15
YAFZOU	111	194	170	294	75	11	169	154
XAMBUI	2	4	3	3	0.8	0.2	3	1.5
PATFIA	-11	-61	-35	-15	-19	-39	-38	-39
CAVXUS	-19	-21	-16	-28	-6	-1	-17	-14
CUAQAC02	-286	-429	-346	-436	-143	-44	-357	-273
BISDOW	-382	-634	-492	-218	-177	-64	-514	-371
ICISOC	-62	-168.4					-127	-80.6
EDNCOX10	-74	-203.6					-166.8	-116.4
HANGOS	-32	-72.8					-59.4	-37
PUTBAH	-214	-200.4					-174.8	-124.8
SUJWEZ	-224	-342					-285	-305.4
QABHAC	-220	207					267.6	495.4
YETYOL	168	263.8					238.4	240.4
PEMPEC10	114	29.2					338.2	16.2
HEWMAX	38	151.2					21.6	93.8

Compound	B2-PLYP	B2GP-PLYP	REKS ^a B3LYP	REKS ^b B3LYP	SF-TDDFT B3LYP	SF-TDDFT M06	SF-TDDFT M06-2X	SF-TDDFT M06-HF
DHT	1769	1627						
Biverdazyl	-214	32						
[Cu ₂ Cl ₆] ²⁻	-121	-61			-342	-210	-13	35
YAFZOU	164	123	269	264	96	91	65	90
XAMBUI	-15	-11	7	6.2	-1	1	0	3
PATFIA	15	19	247	139	-399	-198	-22	32
CAVXUS	-17	-14	19.6	3.3	-65	-37	-8	-2
CUAQAC02	-262	-177	-158	-285	-721	-523	-129	-31
BISDOW	-336	-222	-1126	-743	-181	-40		
ICISOC					-426	-226	-29	-8
EDNCOX10					-397	-280	-56	-8
HANGOS								
PUTBAH					-444	-290	-81	-3
SUJWEZ								
QWABHAC								
YETYOL					-421	-145	194	143
PEMPEC10					35	79	104	72
HEWMAX								

^a The values have been calculated using the coupling function $f = (p_r p_s)^{3/4}$.

^b The values have been calculated using the coupling function $f = (p_r p_s)^{(1 - \frac{1}{2p_r p_s} + \frac{\delta}{1+\delta})}$.

tion.^{163,243} This led Ko *et al.* to propose that a fixed scaling factor could be used to improve the overall performance of the B3LYP functional.²⁹⁷ This approach is justified by assuming that B3LYP introduces a systematic error, due to SIE, that can be eliminated by a scaling factor. To further study this approach, a linear fit of $y = Ax + B$ was made to a data set of experimental vs. calculated magnetic coupling constants for various functionals and formalisms. The results are presented in Table 6. Most methods show very high linear correlation indicated by the high R^2 values. The worst correlation is observed with the values calculated with M06 and M06-HF using the UKS formalism, B3LYP using the REKS formalism with the older coupling function and M06-HF with the SF-TDDFT formalism. All other methods show $R^2 > 0.9$. It should be noted that M06-2X and M06-HF are designed for main-group chemistry and are thus expected to perform poorly for transition-metal systems. An optimal linear fit should have $A = 1.0$ and $B = 0.0$. The best gradient A is obtained with the LC- ω PBE method, followed closely by B2-PLYP, M06 and B3LYP with REKS formalism and the older coupling function. M06 yields a very large constant term B and a poor correlation as discussed above. Regardless of the negligible spin contamination in the SF-TDDFT results, all the functionals studied herein fail with this formalism. REKS is able to produce reasonable gradients with the older coupling function but the constant term is very large with both coupling functions.

Table 6: The mean absolute error, its standard deviation and the R^2 , A and B parameters of a linear fit made to a data set of experimental vs. calculated coupling constants.

Method	Projected		w/o projection		R^2	A	B
	MAE ^a	SDV ^b	MAE ^a	SDV ^b			
B3LYP	88.7	96.1	29.8	30.6	0.993	1.609	0.995
PBE0	42.8	41.9	48.8	59.7	0.995	1.299	6.42
M06	85.2	88.8	64.3	105.5	0.747	1.103	40.833
M06-2X	67.7	85.4	100.1	124.7	0.985	0.495	3.442
M06-HF	118.0	132.1	124.7	148.6	0.770	0.138	9.323
HSE	48.5	49.9	46.3	55.1	0.995	1.332	4.221
LC- ω PBE	16.8	15.9	67.0	84.2	0.986	1.007	7.944
B2-PLYP	28.0	18.8	72.8	88.8	0.981	0.968	19.227
B2GP-PLYP	54.8	64.3	93.0	112.8	0.969	0.663	17.624
REKS ^c /B3LYP			124.3	91.4	0.799	0.944	118.798
REKS ^d /B3LYP			62.9	70.5	0.954	1.328	79.253
SF-TDDFT/B3LYP	271.8	300.8			0.910	2.379	-137.363
SF-TDDFT/M06	137.3	147.7			0.957	1.684	-70.636
SF-TDDFT/M06-2X	71.3	85.9			0.988	0.473	0.306
SF-TDDFT/M06-HF	113.2	146.8			0.733	0.212	29.336

^a Mean absolute error between the calculated and experimental values.

^b Standard deviation of the mean absolute error.

^c Coupling function $f = (p_r p_s)^{3/4}$ has been used.

^d Coupling function $f = (p_r p_s)^{(1 - \frac{1}{2p_r p_s} + \frac{\delta}{1+\delta})}$ has been used.

To summarize the discussion above, the best systematic results can be obtained with the LC- ω PBE functional followed closely by B2-PLYP. Attempts to circumvent the broken symmetry problem with REKS or SF-TDDFT are unable to improve the results. Of the traditional hybrids, PBE0 performs the best. This is most likely a result of the non-empirical design of the functional. B3LYP and the M06 family are both fitted to thermochemical data, and while this assures good performance in thermochemical problems it does not guarantee that the functional performs well in unrelated problems such as calculation of magnetic coupling constants. The excellent performance of the LC- ω PBE model can be explained by the lack of SIE in the long-range part of the exchange potential which is treated as 100% HF exchange. This is in good agreement with the results on the H–He–H system where the one-electron SIE free SIC-B3LYP performed the best. B2-PLYP performs very well but its re-parametrized version B2GP-PLYP performs roughly as well as PBE0. This would suggest that double-hybrids do not, in general, offer a clear improvement over traditional hybrids especially considering the increased computational costs.

The good performance of the LC- ω PBE model has been demonstrated by studies on other magnetic systems as well.²⁶⁶ Bandeira and Le Guenic have applied a variety of DFT methods to hydrogen-bonded Cu complexes and have come to the conclusion that B2-PLYP and LC- ω PBE (as well as CAM-B3LYP) offer the best description with spin projected methods.¹⁸⁰ They also noted that the improvement offered by double-hybrid functionals is not worth the increased computational cost. A recent study of Saito *et al.* showed that for a nitroxide dimer model system, LC- ω PBE can nearly reproduce the results of multireference coupled cluster calculations.¹⁵ Considering the tremendous difference in computational cost between the two models, this achievement is truly remarkable.

A much discussed aspect in the field of magnetic coupling constants and traditional hybrid functionals is the specific amount of exact exchange included in the functional parametrization. Various authors have suggested that improved values of magnetic coupling constants can be obtained by increasing the amount of exact exchange.^{298–301} There is some theoretical justification for this as increasing the percentage of exact exchange does reduce the amount of SIE present in the functional approximation and improves the long-range decay of the exchange potential. The results in Table 6 however do not show any clear validation for this reasoning. The M06 family of functionals shows decreasing performance with increasing percentage of exact exchange (27% in M06, 54% in M06-

2X and 100% in M06-HF). The percentage in the best performing traditional hybrid, PBE0, is only 25%. Also, of the two double-hybrids studied the one that performs better, B2-PLYP, has 53% of exact exchange whereas the worse performing B2GP-PLYP has 65%. The best approximation, LC- ω PBE, does include 100% of exact exchange, but only in the long range part of the exchange potential whereas at short-range there is only GGA exchange. In a study of various DFT methods on six binuclear complexes Ruiz has shown that CAM-B3LYP, which includes 60% of exact exchange in the long-range part, performs only slightly worse than LC- ω PBE.²⁶⁷ Thus, it can be concluded that increasing the overall percentage of exact exchange does not improve the approximation but improving the long-range behavior of the exchange potential does.

As a final remark, it should also be mentioned that the above discussion has considered only binuclear Cu complexes. The results most likely show qualitative trends of the overall performance of these methods but there is no guarantee that they could be generalized to other categories of magnetic coupling problems. This is evident in the study of Ko *et al.*²⁹⁷ on a set of organic diradicals. Their data set produced a gradient of 2.632 for B3LYP. This is very different from the gradient of 1.609 for the Cu complexes. A thorough validation study of DFT methods on magnetic coupling problems would require a wide range of magnetic compounds including organic diradicals, organic molecular magnet systems, first row transition-metal complexes as well as heavier paramagnetic centers.

8 Conclusions

The currently available density functional methods for the calculation of magnetic coupling constants have been reviewed. Magnetic coupling problems expose many of the deficiencies of practical KS theory such as description of multireference systems and the lack of clear definition for $\langle \hat{S}^2 \rangle$. It is commonplace to use the spin state of the KS reference wave function as an approximation to the spin state of the true wave function although there is little theoretical validation for this. No consensus exists as to how the broken symmetry problem of the UKS method is best treated although spin projection schemes are routinely employed. In order to enforce the correct spin symmetry of the KS reference wave function and avert the projection process, alternative methods to the standard UKS approach such as the REKS method have been developed. These do not, however, show great improvement over UKS. Another problem is choosing the right XC functional as no universally valid approximation exists. Even the much used and very successful B3LYP fails in magnetic coupling problems as does the highly parametrized M06 family of functionals. Combining a functional with an inappropriate projection scheme can produce numerically good results due to error cancellation, but this approach can hardly be theoretically justified. This is most evident in applications of the B3LYP functional without spin projection. Despite all these problems, good results can be obtained without the need to completely abandon theoretical rigor. The LC- ω PBE and B2-PLYP functionals show very good performance when coupled with a spin-projected approach. The former approach can nearly reproduce results of much higher level coupled cluster calculations for certain systems.

The success of LC- ω PBE suggests that the key to improving functional approximations to better suit magnetic coupling problems is the correct treatment of self-interaction error. The one-electron self-interaction error can be routinely corrected, but the much more mathematically complicated N -electron self-interaction error is a more difficult problem for future functional design. At present, the best approach to SIE-free functionals seems to be that of LC- ω PBE, where the long-range part of the exchange potential is treated as 100% exact exchange. The good performance of the Perdew–Zunger self-interaction-corrected SIC-B3LYP on the H–He–H model system suggests that removing the one-electron self-interaction error in the short range part of LC- ω PBE could further improve its performance.

Overall, hybrid density functional theory can offer the means to predict accurate values of magnetic coupling constants at a fraction of the computational cost of quantitative *ab initio* methods. In order to maintain at least some theoretical rigor in the calculations, one must be careful in choosing functionals and projection methods. Simply relying on good numerical results, that can arise from error cancellation, might lead to validation of a combination of methods that does not necessarily work on other types of magnetic coupling problems.

References

- [1] J. S. Miller. Organometallic- and Organic-Based Magnets: New Chemistry and New Materials for the New Millennium. *Inorg. Chem.* **2000**, *39*, 4392–4408.
- [2] S. J. Blundell, F. L. Pratt. Organic and molecular magnets. *J. Phys.: Condens. Matter* **2004**, *16*, R771.
- [3] I. Ratera, J. Veciana. Playing with organic radicals as building blocks for functional molecular materials. *Chem. Soc. Rev.* **2012**, *41*, 303–349.
- [4] M. N. Leunberger, D. Loss. Quantum computing in molecular magnets. *Nature* **2001**, *410*, 789–793.
- [5] L. Bogani, W. Wernsdorfer. Molecular spintronics using single-model magnets. *Nat. Mater.* **2008**, *7*, 179–186.
- [6] K. V. Raman, A. M. Kamerbeek, A. Mukherjee, N. Atodiresei, T. K. Sen, P. Lazic, V. Caciuc, R. Michel, D. Stalke, S. K. Mandal, S. Blugel, M. Munzenberg, J. S. Moodera. Interface-engineered templates for molecular spin memory devices. *Nature* **2013**, *493*, 509–513.
- [7] J. P. Malrieu, R. Caballol, C. J. Calzado, C. de Graaf, N. Guihery. Magnetic Interactions in Molecules and Highly Correlated Materials: Physical Content, Analytical Derivation, and Rigorous Extraction of Magnetic Hamiltonians. *Chem. Rev.* **2013**, in press, DOI:10.1021/cr300500z.
- [8] I. d. P. R. Moreira, F. Illas. A unified view of the theoretical description of magnetic coupling in molecular chemistry and solid state physics. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1645–1659.
- [9] R. J. Bartlett, M. Musiał. Coupled-cluster theory in quantum chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.
- [10] F. Jensen, *Introduction to Computational Chemistry 2nd ed.*, Wiley, The Atrium, Southern Gate, Chichester, West Sussex, UK, **2007**.
- [11] J. Pople, R. Seeger, R. Krishnan. Variational Configuration Interaction Methods and Comparison with Perturbation Theory. *Int. J. Quant. Chem.* **1977**, *Suppl. Y-11*, 149–163.

- [12] A. Szabo, N. Ostlund, *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory 1st ed.*, Dover, Mineola, NY, USA, **1996**.
- [13] M. Musial, R. J. Bartlett. Critical comparison of various connected quadruple excitation approximations in the coupled-cluster treatment of bond breaking. *J. Chem. Phys.* **2005**, *122*, 224102.
- [14] K. R. Yang, A. Jalan, W. H. Green, D. G. Truhlar. Which *Ab Initio* Wave Function Methods Are Adequate for Quantitative Calculations of the Energies of Biradicals? The Performance of Coupled-Cluster and Multi-Reference Methods Along a Single-Bond Dissociation Coordinate. *J. Chem. Theor. Comp.* **2013**, *9*, 418–431.
- [15] T. Saito, A. Ito, T. Watanabe, T. Kawakami, M. Okumura, K. Yamaguchi. Performance of the coupled cluster and DFT methods for through-space magnetic interactions of nitroxide dimer. *Chem. Phys. Letters* **2012**, *542*, 19–25.
- [16] G. Das, A. C. Wahl. New Techniques for the Computation of Multiconfiguration Self-Consistent Field (MCSCF) Wavefunctions. *J. Chem. Phys.* **1972**, *56*, 1769–1775.
- [17] B. O. Roos, P. R. Taylor, P. E. Sigbahn. A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chem. Phys.* **1980**, *48*, 157 – 173.
- [18] K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski. Second-order perturbation theory with a CASSCF reference function. *J. Phys. Chem.* **1990**, *94*, 5483–5488.
- [19] K. Andersson, P.-A. Malmqvist, B. O. Roos. Second-order perturbation theory with a complete active space self-consistent field reference function. *J. Chem. Phys.* **1992**, *96*, 1218–1226.
- [20] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory 2nd ed.*, Wiley, Weinheim, Germany, **2001**.
- [21] C. Fiolhais, F. Nogueira, M. A. Marques (Eds.), *A Primer in Density Functional Theory 1st ed.*, Springer, Germany, **2003**.
- [22] T. Ziegler. Approximate density functional theory as a practical tool in molecular energetics and dynamics. *Chem. Rev.* **1991**, *91*, 651–667.

- [23] S. F. Sousa, P. A. Fernandes, M. J. Ramos. General Performance of Density Functionals. *J. Phys. Chem. A* **2007**, *111*, 10439–10452.
- [24] K. Capelle. A bird's-eye view of density-functional theory. *Braz. J. Phys.* **2006**, *36*, 1318–1343.
- [25] C. J. Cramer, D. G. Truhlar. Density functional theory for transition metal and transition metal chemistry. *Physical Chemistry Chem. Phys.* **2009**, *11*, 10757–10816.
- [26] W. Kohn, L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.
- [27] A. D. Becke. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [28] A. D. Becke. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [29] C. Lee, W. Yang, R. G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
- [30] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch. *Ab Initio* Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- [31] A. J. Cohen, P. Mori-Sánchez, W. Yang. Challenges for Density Functional Theory. *Chem. Rev.* **2012**, *112*, 289–320.
- [32] F. Illas, I. de P. R. Moreira, J. M. Bofill, M. Filatov. Extent and limitations of density-functional theory in describing magnetic systems. *Phys. Rev. B* **2004**, *70*, 132414.
- [33] F. Illas, I. Moreira, J. Bofill, M. Filatov. Spin Symmetry Requirements in Density Functional Theory: The Proper Way to Predict Magnetic Coupling Constants in Molecules and Solids. *Theor. Chem. Acc.* **2006**, *116*, 587–597.
- [34] R. Caballol, O. Castell, F. Illas, I. de P. R. Moreira, J. P. Malrieu. Remarks on the Proper Use of the Broken Symmetry Approach to Magnetic Coupling. *J. Phys. Chem. A* **1997**, *101*, 7860–7866.

- [35] J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun, G. I. Csonka. Some Fundamental Issues in Ground-State Density Functional Theory: A Guide for the Perplexed. *J. Chem. Theor. Comp.* **2009**, *5*, 902–908.
- [36] M. Reiher. On the definition of local spin in relativistic and nonrelativistic quantum chemistry. *Farad. Discuss.* **2007**, *135*, 97–124.
- [37] E. Ruiz, S. Alvarez, J. Cano, V. Polo. About the calculation of exchange coupling constants using density-functional theory: The role of the self-interaction error. *J. Chem. Phys.* **2005**, *123*, 164110.
- [38] J. Coey. Magnetism in future. *J. Magn. Magn. Mater.* **2001**, *226–230*, Part 2, 2107–2112.
- [39] W. Heisenberg. Zur Theorie des Ferromagnetismus. *Z. Physik* **1928**, *49*, 619–636.
- [40] S. Elliott, *The Physics and Chemistry of Solids 1st ed.*, Wiley, The Atrium, Southern Gate, Chichester, West Sussex, UK, **1998**, Reprinted with corrections in 2006.
- [41] J. V. Vleck, *The Theory of Electric and Magnetic Susceptibilities 1st ed.*, Oxford University Press, Amen House, London, UK, **1932**, Reprinted in 1948.
- [42] C. E. Housecroft, A. G. Sharpe, *Inorg. Chem. 3rd ed.*, Pearson, Edinburg Gate, Harlow, Essex, UK, **2008**.
- [43] W. Heitler, F. London. Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik. *Z. Physik.* **1927**, *44*, 455–472.
- [44] L. Pauling, J. E. Bright Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry 1st ed.*, McGraw-Hill, NY, USA, **1935**, Reprinted in 1985 by Dover, NY, USA.
- [45] P. W. Anderson. Antiferromagnetism. Theory of Superexchange Interaction. *Phys. Rev.* **1950**, *79*, 350–356.
- [46] D. Reid. The chemistry of the phenalenes. *Q. Rev. Chem. Soc.* **1965**, *19*, 274–302.

- [47] Y. Morita, S. Suzuki, K. Sato, T. Takui. Synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments. *Nature Chem.* **2011**, *3*, 197–204.
- [48] A. E. Clark, E. R. Davidson. Local spin. *J. Chem. Phys.* **2001**, *115*, 7382–7392.
- [49] E. R. Davidson, A. E. Clark. Local spin II. *Mol. Phys.* **2002**, *100*, 373–383.
- [50] A. E. Clark, E. R. Davidson. Local Spin III: Wave Function Analysis along a Reaction Coordinate, H Atom Abstraction, and Addition Processes of Benzyne. *J. Phys. Chem. A* **2002**, *106*, 6890–6896.
- [51] E. Ramos-Cordoba, E. Matito, I. Mayer, P. Salvador. Toward a Unique Definition of the Local Spin. *J. Chem. Theor. Comp.* **2012**, *8*, 1270–1279.
- [52] E. Ramos-Cordoba, E. Matito, P. Salvador, I. Mayer. Local spins: improved Hilbert-space analysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 15291–15298.
- [53] P. A. M. Dirac. The Quantum Theory of the Electron. *Proc. R. Soc. Lond. A* **1928**, *117*, 610–624.
- [54] C. R. Jacob, M. Reiher. Spin in density-functional theory. *Int. J. Quant. Chem.* **2012**, *112*, 3661–3684.
- [55] A. I. M. Rae, *Quantum Mechanics 5th ed.*, Talyor & Francis, Boca Raton, FL, USA, **2008**.
- [56] P. Dirac. Quantum Mechanics of Many-Electron Systems. *Proc. R. Soc. Lond. A* **1929**, *123*, 714–713.
- [57] J. H. Van Vleck. A Survey of the Theory of Ferromagnetism. *Rev. Mod. Phys.* **1945**, *17*, 27–47.
- [58] J. C. Slater. Ferromagnetism and the Band Theory. *Rev. Mod. Phys.* **1953**, *25*, 199–210.
- [59] G. Nicolas, P. Durand. A new general methodology for deriving effective Hamiltonians for atoms and molecules. Application to the transferability of atomic potentials in the hydrocarbon series. *J. Chem. Phys.* **1980**, *72*, 453–463.

- [60] J. P. Malrieu, D. Maynau. A valence bond effective Hamiltonian for neutral states of π systems. 1. Method. *J. Am. Chem. Soc* **1982**, *104*, 3021–3029.
- [61] D. Maynau, J. P. Malrieu. A valence bond effective Hamiltonian for the neutral states of π systems. 2. Results. *J. Am. Chem. Soc* **1982**, *104*, 3029–3034.
- [62] D. Maynau, M. Said, J. P. Malrieu. Looking at chemistry as a spin ordering problem. *J. Am. Chem. Soc* **1983**, *105*, 5244–5252.
- [63] C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol. Analysis of the magnetic coupling in binuclear complexes. II. Derivation of valence effective Hamiltonians from *ab initio* CI and DFT calculations. *J. Chem. Phys.* **2002**, *116*, 3985–4000.
- [64] R. Maurice, R. Bastardis, C. d. Graaf, N. Suaud, T. Mallah, N. Guihéry. Universal Theoretical Approach to Extract Anisotropic Spin Hamiltonians. *J. Chem. Theor. Comp.* **2009**, *5*, 2977–2984.
- [65] I. d. P. R. Moreira, N. Suaud, N. Guihéry, J. P. Malrieu, R. Caballol, J. M. Bofill, F. Illas. Derivation of spin Hamiltonians from the exact Hamiltonian: Application to systems with two unpaired electrons per magnetic site. *Phys. Rev. B* **2002**, *66*, 134430.
- [66] R. K. Nesbet. Antiferromagnetic Superexchange Effect. *Phys. Rev.* **1960**, *119*, 658–662.
- [67] R. K. Nesbet. Molecular Model of the Heisenberg Exchange Interaction. *Phys. Rev.* **1961**, *122*, 1497–1508.
- [68] F. Neese. Prediction of molecular properties and molecular spectroscopy with density functional theory: From fundamental theory to exchange-coupling. *Coord. Chem. Rev.* **2009**, *253*, 526–563.
- [69] I. Ciofini, C. A. Daul. DFT calculations of molecular magnetic properties of coordination compounds. *Coord. Chem. Rev.* **2003**, *238–239*, 187–209.
- [70] J. Huang, M. Kertesz. Theoretical Analysis of Intermolecular Covalent π - π Bonding and Magnetic Properties of Phenalenyl and spiro-Biphenalenyl Radical π -Dimers. *J. Phys. Chem. A* **2007**, *111*, 6304–6315.

- [71] T. Ukai, K. Nakata, S. Yamanaka, T. Kubo, Y. Morita, T. Takada, K. Yamaguchi. CASCI-DFT study of the phenalenyl radical system. *Polyhedron* **2007**, *26*, 2313–2319.
- [72] H. M. McConnell. Ferromagnetism in Solid Free Radicals. *J. Chem. Phys.* **1963**, *39*, 1910–1910.
- [73] M. Deumal, J. J. Novoa, M. J. Bearpark, P. Celani, M. Olivucci, M. A. Robb. On the Validity of the McConnell-I Model of Ferromagnetic Interactions: The [2.2]Paracyclophane Example. *J. Phys. Chem. A* **1998**, *102*, 8404–8412.
- [74] S. Paul, A. Misra. Interpretation and Quantification of Magnetic Interaction through Spin Topology. *J. Chem. Theor. Comp.* **2012**, *8*, 843–853.
- [75] D. J. Griffiths, *Introduction to Quantum Mechanics 2nd ed.*, Pearson, Upper Saddle River, NJ, USA, **2005**.
- [76] A. Landé. Termstruktur und Zeemaneffekt der Multipletts. *Zeitschrift für Physik* **1923**, *15*, 189–205.
- [77] F. Illas, J. Casanovas, M. A. García-Bach, R. Caballol, O. Castell. Towards an *ab initio* description of magnetism in ionic solids. *Phys. Rev. Lett.* **1993**, *71*, 3549–3552.
- [78] J. Casanovas, F. Illas. An *ab initio* cluster model study of the magnetic coupling in KNiF₃. *J. Chem. Phys.* **1994**, *100*, 8257–8264.
- [79] I. Ciofini, C. Adamo, V. Barone, G. Berthier, A. Rassat. Mapping the many-electron generalised spin-exchange Hamiltonian to accurate post-HF calculations. *Chem. Phys.* **2005**, *309*, 133–141.
- [80] P. Atkins, R. Friedman, *Molecular Quantum Mechanics 5th ed.*, Oxford University Press, Oxford, UK, **2011**.
- [81] C. Roothaan. New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.* **1951**, *23*, 69–89.
- [82] G. Hall. The Molecular Orbital Theory of Chemical Valency. VIII. A Method of Calculating Ionization Potentials. *Proc. R. Soc. Lond.* **1951**, *A205*, 541–552.

- [83] J. A. Pople, R. K. Nesbet. Self-Consistent Orbitals for Radicals. *J. Chem. Phys.* **1954**, *22*, 571–572.
- [84] J. Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- [85] J. Olsen, P. Jorgensen, H. Koch, A. Balkova, R. J. Bartlett. Full configuration–interaction and state of the art correlation calculations on water in a valence double-zeta basis with polarization functions. *J. Chem. Phys.* **1996**, *104*, 8007–8015.
- [86] C. Møller, M. S. Plesset. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.
- [87] M. Head-Gordon, J. Pople, M. Frisch. MP2 energy evaluation by direct methods. *Chem. Phys. Letters* **1988**, *153*, 503–506.
- [88] J. Moilanen, C. Ganesamoorthy, M. S. Balakrishna, H. M. Tuononen. Weak Interactions between Trivalent Pnictogen Centers: Computational Analysis of Bonding in Dimers $X_3E \cdots EX_3$ (E = Pnictogen, X = Halogen). *Inorg. Chem.* **2009**, *48*, 6740–6747.
- [89] G. D. P. III, R. J. Bartlett. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
- [90] Y. J. Bomble, J. F. Stanton, M. Kallay, J. Gauss. Coupled-cluster methods including noniterative corrections for quadruple excitations. *J. Chem. Phys.* **2005**, *123*, 054101.
- [91] M. Musial, S. A. Kucharski, R. J. Bartlett. Formulation and implementation of the full coupled-cluster method through pentuple excitations. *J. Chem. Phys.* **2002**, *116*, 4382–4388.
- [92] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon. A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Letters* **1989**, *157*, 479–483.
- [93] D. Feller, D. A. Dixon. Extended benchmark studies of coupled cluster theory through triple excitations. *J. Chem. Phys.* **2001**, *115*, 3484–3496.

- [94] F. B. Brown, I. Shavitt, R. Shepard. Multireference configuration interaction treatment of potential energy surfaces: symmetric dissociation of H₂O in a double-zeta basis. *Chem. Phys. Letters* **1984**, *105*, 363–369.
- [95] H.-J. Werner, P. J. Knowles. An efficient internally contracted multiconfiguration–reference configuration interaction method. *J. Chem. Phys.* **1988**, *89*, 5803–5814.
- [96] P. J. Knowles, H.-J. Werner. An efficient method for the evaluation of coupling coefficients in configuration interaction calculations. *Chem. Phys. Letters* **1988**, *145*, 514–522.
- [97] R. J. Gdanitz, R. Ahlrichs. The averaged coupled-pair functional (ACPF): A size-extensive modification of MR CI(SD). *Chem. Phys. Letters* **1988**, *143*, 413–420.
- [98] P. G. Szalay, R. J. Bartlett. Multi-reference averaged quadratic coupled-cluster method: a size-extensive modification of multi-reference CI. *Chem. Phys. Letters* **1993**, *214*, 481–488.
- [99] P. G. Szalay, R. J. Bartlett. Multi-reference averaged quadratic coupled-cluster method: a size-extensive modification of multi-reference CI. *Chem. Phys. Letters* **1993**, *214*, 481–488.
- [100] R. L. Martin, F. Illas. Antiferromagnetic Exchange Interactions from Hybrid Density Functional Theory. *Phys. Rev. Lett.* **1997**, *79*, 1539–1542.
- [101] E. Fermi. Un Metodo Statistico per la Determinazione di Alcune Proprieta dell'Atomo. *Rend. Accad. Lincei* **1927**, *24*, 602–607.
- [102] L. H. Thomas. The calculation of atomic fields. *Proc. Cambridge Phil. Soc.* **1927**, *23*, 542–548.
- [103] F. Bloch. Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfähigkeit. *Zeitschrift für Physik* **1929**, *57*, 545–555.
- [104] P. A. M. Dirac. Note on Exchange Phenomena in the Thomas Atom. *Proc. Cambridge Phil. Soc.* **1930**, *26*, 376–385.

- [105] P. Hohenberg, W. Kohn. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.
- [106] P. Dirac. On Theory of Quantum Mechanics. *Proc. R. Soc. Lond. A* **1926**, *112*, 661–677.
- [107] T. Kato. On the eigenfunctions of many-particle systems in quantum mechanics. *Comm. Pure Appl. Math.* **1957**, *10*, 151–177.
- [108] M. Levy. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v -representability problem. *Proc. Natl. Acad. Sci.* **1979**, *76*, 6062–6065.
- [109] E. J. Baerends, O. V. Gritsenko. A Quantum Chemical View of Density Functional Theory. *J. Phys. Chem. A* **1997**, *101*, 5383–5403.
- [110] A. D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [111] C. Lee, W. Yang, R. G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
- [112] B. Miehlich, A. Savin, H. Stoll, H. Preuss. Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Letters* **1989**, *157*, 200–206.
- [113] J. P. Perdew, K. Burke, M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [114] J. P. Perdew, W. Yue. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Phys. Rev. B* **1986**, *33*, 8800–8802.
- [115] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46*, 6671–6687.
- [116] C. J. Umrigar, X. Gonze. Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series. *Phys. Rev. A* **1994**, *50*, 3827–3837.

- [117] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- [118] Y. Zhao, D. G. Truhlar. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- [119] O. V. Gritsenko, E. J. Baerends. Electron correlation effects on the shape of the Kohn-Sham molecular orbital. *Theor. Chem. Acc.* **1997**, *96*, 44–50.
- [120] J. Gräfenstein, E. Kraka, M. Filatov, D. Cremer. Can Unrestricted Density-Functional Theory Describe Open Shell Singlet Biradicals? *Int. J. Mol. Sci.* **2002**, *3*, 360–394.
- [121] F. Neese. Definition of corresponding orbitals and the diradical character in broken symmetry DFT calculations on spin coupled systems. *J. Phys. Chem. Solids* **2004**, *65*, 781–785.
- [122] O. Gunnarsson, B. I. Lundqvist. Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B* **1976**, *13*, 4274–4298.
- [123] J. P. Perdew, A. Savin, K. Burke. Escaping the symmetry dilemma through a pair-density interpretation of spin-density functional theory. *Phys. Rev. A* **1995**, *51*, 4531–4541.
- [124] K. Burke, M. Ernzerhof, J. P. Perdew. The adiabatic connection method: a non-empirical hybrid. *Chem. Phys. Letters* **1997**, *265*, 115–120.
- [125] D. C. Langreth, J. P. Perdew. Exchange-correlation energy of a metallic surface: Wave-vector analysis. *Phys. Rev. B* **1977**, *15*, 2884–2901.
- [126] A. D. Becke. Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys.* **1996**, *104*, 1040–1046.

- [127] J. P. Perdew, M. Ernzerhof, K. Burke. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- [128] C. Adamo, V. Barone. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- [129] M. Ernzerhof, G. E. Scuseria. Assessment of the Perdew–Burke–Ernzerhof exchange–correlation functional. *J. Chem. Phys.* **1999**, *110*, 5029–5036.
- [130] C. Adamo, V. Barone. Toward reliable adiabatic connection models free from adjustable parameters. *Chem. Phys. Letters* **1997**, *274*, 242–250.
- [131] Y. Zhao, D. Truhlar. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [132] Y. Zhao, D. G. Truhlar. Comparative DFT Study of van der Waals Complexes: Rare-Gas Dimers, Alkaline-Earth Dimers, Zinc Dimer, and Zinc-Rare-Gas Dimers. *J. Phys. Chem. A* **2006**, *110*, 5121–5129, PMID: 16610834.
- [133] Y. Zhao, D. G. Truhlar. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2006**, *110*, 13126–13130, PMID: 17149824.
- [134] Y. Zhao, N. E. Schultz, D. G. Truhlar. Exchange–correlation functional with broad accuracy for metallic and nonmetallic compounds, kinetics, and noncovalent interactions. *J. Chem. Phys.* **2005**, *123*, 161103.
- [135] Y. Zhao, N. E. Schultz, D. G. Truhlar. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theor. Comp.* **2006**, *2*, 364–382.

- [136] Y. Zhao, D. G. Truhlar. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theor. Comp.* **2008**, *4*, 1849–1868.
- [137] M. Reiher, O. Salomon, B. Artur Hess. Reparameterization of hybrid functionals based on energy differences of states of different multiplicity. *Theor. Chem. Acc.* **2001**, *107*, 48–55.
- [138] X. Xu, W. A. Goddard. The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 2673–2677.
- [139] A. J. Cohen, N. C. Handy. Dynamic correlation. *Mol. Phys.* **2001**, *99*, 607–615.
- [140] M. Swart, A. W. Ehlers, K. Lammertsma. Performance of the OPBE exchange-correlation functional. *Mol. Phys.* **2004**, *102*, 2467–2474.
- [141] A. D. Boese, J. M. L. Martin. Development of density functionals for thermochemical kinetics. *J. Chem. Phys.* **2004**, *121*, 3405–3416.
- [142] M. D. Wodrich, C. Corminboeuf, P. R. Schreiner, A. A. Fokin, P. v. R. Schleyer. How Accurate Are DFT Treatments of Organic Energies? *Org. Lett.* **2007**, *9*, 1851–1854.
- [143] P. Schreiner. Relative Energy Computations with Approximate Density Functional Theory—A Caveat! *Angew. Chem. Int. Ed.* **2007**, *46*, 4217–4219.
- [144] F. Della Sala, A. Görling. Asymptotic Behavior of the Kohn-Sham Exchange Potential. *Phys. Rev. Lett.* **2002**, *89*, 033003.
- [145] C.-O. Almbladh, U. von Barth. Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues. *Phys. Rev. B* **1985**, *31*, 3231–3244.
- [146] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao. A long-range-corrected time-dependent density functional theory. *J. Chem. Phys.* **2004**, *120*, 8425–8433.

- [147] T. M. Henderson, A. F. Izmaylov, G. E. Scuseria, A. Savin. The importance of middle-range Hartree-Fock-type exchange for hybrid density functionals. *J. Chem. Phys.* **2007**, *127*, 221103.
- [148] T. Leininger, H. Stoll, H.-J. Werner, A. Savin. Combining long-range configuration interaction with short-range density functionals. *Chem. Phys. Letters* **1997**, *275*, 151–160.
- [149] I. C. Gerber, J. G. Ángyán. Hybrid functional with separated range. *Chem. Phys. Letters* **2005**, *415*, 100–105.
- [150] H. Iikura, T. Tsuneda, T. Yanai, K. Hirao. A long-range correction scheme for generalized-gradient-approximation exchange functionals. *J. Chem. Phys.* **2001**, *115*, 3540–3544.
- [151] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao. A long-range-corrected time-dependent density functional theory. *J. Chem. Phys.* **2004**, *120*, 8425–8433.
- [152] M. Seth, T. Ziegler. Range-Separated Exchange Functionals with Slater-Type Functions. *J. Chem. Theor. Comp.* **2012**, *8*, 901–907.
- [153] J. Heyd, G. E. Scuseria, M. Ernzerhof. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.
- [154] J. Heyd, G. E. Scuseria. Assessment and validation of a screened Coulomb hybrid density functional. *J. Chem. Phys.* **2004**, *120*, 7274–7280.
- [155] J. Heyd, G. E. Scuseria. Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional. *J. Chem. Phys.* **2004**, *121*, 1187–1192.
- [156] O. A. Vydrov, G. E. Scuseria. Assessment of a long-range corrected hybrid functional. *J. Chem. Phys.* **2006**, *125*, 234109.
- [157] O. A. Vydrov, J. Heyd, A. V. Krukau, G. E. Scuseria. Importance of short-range versus long-range Hartree-Fock exchange for the performance of hybrid density functionals. *J. Chem. Phys.* **2006**, *125*, 074106.

- [158] O. A. Vydrov, G. E. Scuseria, J. P. Perdew. Tests of functionals for systems with fractional electron number. *J. Chem. Phys.* **2007**, *126*, 154109.
- [159] T. Yanai, D. P. Tew, N. C. Handy. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Letters* **2004**, *393*, 51–57.
- [160] Y. Akinaga, S. Ten-no. Range-separation by the Yukawa potential in long-range corrected density functional theory with Gaussian-type basis functions. *Chem. Phys. Letters* **2008**, *462*, 348–351.
- [161] M. Seth, T. Ziegler, M. Steinmetz, S. Grimme. Modeling Transition Metal Reactions with Range-Separated Functionals. *J. Chem. Theor. Comp.* **2013**, *9*, 2286–2299.
- [162] I. C. Gerber, J. G. Ángyán. Hybrid functional with separated range. *Chem. Phys. Letters* **2005**, *415*, 100–105.
- [163] P. Rivero, I. de P. R. Moreira, F. Illas, G. E. Scuseria. Reliability of range-separated hybrid functionals for describing magnetic coupling in molecular systems. *J. Chem. Phys.* **2008**, *129*, 184110.
- [164] K. A. Nguyen, P. N. Day, R. Pachter. The performance and relationship among range-separated schemes for density functional theory. *J. Chem. Phys.* **2011**, *135*, 074109.
- [165] A. Görling, M. Levy. Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion. *Phys. Rev. B* **1993**, *47*, 13105–13113.
- [166] A. Görling, M. Levy. Exact Kohn-Sham scheme based on perturbation theory. *Phys. Rev. A* **1994**, *50*, 196–204.
- [167] P. Mori-Sanchez, Q. Wu, W. Yang. Orbital-dependent correlation energy in density-functional theory based on a second-order perturbation approach: Success and failure. *J. Chem. Phys.* **2005**, *123*, 062204.
- [168] R. J. Bartlett, V. F. Lotrich, I. V. Schweigert. *Ab initio* density functional theory: The best of both worlds? *J. Chem. Phys.* **2005**, *123*, 062205.

- [169] S. Grimme. Semiempirical hybrid density functional with perturbative second-order correlation. *J. Chem. Phys.* **2006**, *124*, 034108.
- [170] C. Adamo, V. Barone. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models. *J. Chem. Phys.* **1998**, *108*, 664–675.
- [171] A. Karton, A. Tarnopolsky, J.-F. Lamere, G. C. Schatz, J. M. L. Martin. Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical Kinetics†. *J. Phys. Chem. A* **2008**, *112*, 12868–12886, PMID: 18714947.
- [172] J.-D. Chai, M. Head-Gordon. Long-range corrected double-hybrid density functionals. *J. Chem. Phys.* **2009**, *131*, 174105.
- [173] J.-D. Chai, M. Head-Gordon. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
- [174] J.-D. Chai, M. Head-Gordon. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* **2008**, *128*, 084106.
- [175] K. Sharkas, J. Toulouse, A. Savin. Double-hybrid density-functional theory made rigorous. *J. Chem. Phys.* **2011**, *134*, 064113.
- [176] E. Bremond, C. Adamo. Seeking for parameter-free double-hybrid functionals: The PBE0-DH model. *J. Chem. Phys.* **2011**, *135*, 024106.
- [177] J. Toulouse, K. Sharkas, E. Bremond, C. Adamo. Communication: Rationale for a new class of double-hybrid approximations in density-functional theory. *J. Chem. Phys.* **2011**, *135*, 101102.
- [178] J. C. Sancho-Garcia, C. Adamo. Double-hybrid density functionals: merging wavefunction and density approaches to get the best of both worlds. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14581–14594.

- [179] T. Schwabe, S. Grimme. Calculation of Magnetic Couplings with Double-Hybrid Density Functionals. *J. Phys. Chem. Lett.* **2010**, *1*, 1201–1204.
- [180] N. A. G. Bandeira, B. L. Guennic. Calculation of Magnetic Couplings in Hydrogen-Bonded Cu(II) Complexes Using Density Functional Theory. *J. Phys. Chem. A* **2012**, *116*, 3465–3473.
- [181] V. Polo, J. Gräfenstein, E. Kraka, D. Cremer. Influence of the self-interaction error on the structure of the DFT exchange hole. *Chem. Phys. Letters* **2002**, *352*, 469–478.
- [182] V. Polo, E. Kraka, D. Cremer. Some thoughts about the stability and reliability of commonly used exchange–correlation functionals – coverage of dynamic and nondynamic correlation effects. *Theor. Chem. Acc.* **2002**, *107*, 291–303.
- [183] V. Polo, J. Gräfenstein, E. Kraka, D. Cremer. Long-range and short-range Coulomb correlation effects as simulated by Hartree–Fock, local density approximation, and generalized gradient approximation exchange functionals. *Theor. Chem. Acc.* **2003**, *109*, 22–35.
- [184] Y. Zhang, W. Yang. A challenge for density functionals: Self-interaction error increases for systems with a noninteger number of electrons. *J. Chem. Phys.* **1998**, *109*, 2604–2608.
- [185] P. Mori-Sanchez, A. J. Cohen, W. Yang. Many-electron self-interaction error in approximate density functionals. *J. Chem. Phys.* **2006**, *125*, 201102.
- [186] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, G. E. Scuse-ria. Density functionals that are one- and two- are not always many-electron self-interaction-free, as shown for H_2^+ , He_2^+ , LiH^+ , and Ne_2^+ . *J. Chem. Phys.* **2007**, *126*, 104102.
- [187] P. Mori-Sánchez, A. J. Cohen, W. Yang. Localization and Delocalization Errors in Density Functional Theory and Implications for Band-Gap Prediction. *Phys. Rev. Lett.* **2008**, *100*, 146401.
- [188] J. P. Perdew, A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.

- [189] O. A. Vydrov, G. E. Scuseria. A simple method to selectively scale down the self-interaction correction. *J. Chem. Phys.* **2006**, *124*, 191101.
- [190] O. A. Vydrov, G. E. Scuseria, J. P. Perdew, A. Ruzsinszky, G. I. Csonka. Scaling down the Perdew-Zunger self-interaction correction in many-electron regions. *J. Chem. Phys.* **2006**, *124*, 094108.
- [191] A. D. Becke. Real-space post-Hartree-Fock correlation models. *J. Chem. Phys.* **2005**, *122*, 064101.
- [192] P. Mori-Sanchez, A. J. Cohen, W. Yang. Self-interaction-free exchange-correlation functional for thermochemistry and kinetics. *J. Chem. Phys.* **2006**, *124*, 091102.
- [193] O. A. Vydrov, G. E. Scuseria. Effect of the Perdew-Zunger self-interaction correction on the thermochemical performance of approximate density functionals. *J. Chem. Phys.* **2004**, *121*, 8187-8193.
- [194] A. J. Cohen, P. Mori-Sanchez, W. Yang. Development of exchange-correlation functionals with minimal many-electron self-interaction error. *J. Chem. Phys.* **2007**, *126*, 191109.
- [195] C. Adamo, V. Barone, A. Bencini, R. Broer, M. Filatov, N. M. Harrison, F. Illas, J. P. Malrieu, I. de P. R. Moreira. Comment on "About the calculation of exchange coupling constants using density-functional theory: The role of the self-interaction error" [*J. Chem. Phys.* *123*, 164110 (2005)]. *J. Chem. Phys.* **2006**, *124*, 107101.
- [196] E. Ruiz, J. Cano, S. Alvarez, V. Polo. Reply to "Comment on 'About the calculation of exchange coupling constants using density-functional theory: The role of the self-interaction error'" [*J. Chem. Phys.* *123*, 164110 (2005)]. *J. Chem. Phys.* **2006**, *124*, 107102.
- [197] J. M. Wittbrodt, H. B. Schlegel. Some reasons not to use spin projected density functional theory. *J. Chem. Phys.* **1996**, *105*, 6574-6577.
- [198] E. Ruiz, P. Alemany, S. Alvarez, J. Cano. Toward the Prediction of Magnetic Coupling in Molecular Systems: Hydroxo- and Alkoxo-Bridged Cu(II) Binuclear Complexes. *J. Am. Chem. Soc.* **1997**, *119*, 1297-1303.

- [199] J. Cano, P. Alemany, S. Alvarez, M. Verdaguer, E. Ruiz. Exchange Coupling in Oxalato-Bridged Copper(II) Binuclear Compounds: A Density Functional Study. *Chemistry – A European Journal* **1998**, *4*, 476–484.
- [200] E. Ruiz, J. Cano, S. Alvarez, P. Alemany. Broken symmetry approach to calculation of exchange coupling constants for homobinuclear and heterobinuclear transition metal complexes. *J. Comp. Chem.* **1999**, *20*, 1391–1400.
- [201] L. Noodleman. Valence bond description of antiferromagnetic coupling in transition metal dimers. *J. Chem. Phys.* **1981**, *74*, 5737–5743.
- [202] L. Noodleman, E. R. Davidson. Ligand spin polarization and antiferromagnetic coupling in transition metal dimers. *Chem. Phys.* **1986**, *109*, 131–143.
- [203] L. Noodleman, D. A. Case. Density-Functional Theory of Spin Polarization and Spin Coupling in Iron—Sulfur Clusters. *Adv. Inorg. Chem.* **1992**, *38*, 423–470.
- [204] L. Noodleman, C. Peng, D. Case, J.-M. Mouesca. Orbital interactions, electron delocalization and spin coupling in iron-sulfur clusters. *Coord. Chem. Rev.* **1995**, *144*, 199–244.
- [205] A. J. Cohen, D. J. Tozer, N. C. Handy. Evaluation of $\langle \hat{S}^2 \rangle$ in density functional theory. *J. Chem. Phys.* **2007**, *126*, 214104.
- [206] J. Wang, A. D. Becke, J. Vedene H. Smith. Evaluation of $\langle \hat{S}^2 \rangle$ in restricted, unrestricted Hartree–Fock, and density functional based theories. *J. Chem. Phys.* **1995**, *102*, 3477–3480.
- [207] A. P. Ginsberg. Magnetic exchange in transition metal complexes. 12. Calculation of cluster exchange coupling constants with the X.alpha.-scattered wave method. *J. Am. Chem. Soc* **1980**, *102*, 111–117.
- [208] E. Ruiz, J. Cano, S. Alvarez, P. Alemany. Broken symmetry approach to calculation of exchange coupling constants for homobinuclear and heterobinuclear transition metal complexes. *J. Comp. Chem.* **1999**, *20*, 1391–1400.

- [209] K. Yamaguchi, F. Jensen, A. Dorigo, K. Houk. A spin correction procedure for unrestricted Hartree-Fock and Møller-Plesset wavefunctions for singlet diradicals and polyradicals. *Chem. Phys. Letters* **1988**, *149*, 537–542.
- [210] K. Yamaguchi, T. Tsunekawa, Y. Toyoda, T. Fueno. *Ab initio* molecular orbital calculations of effective exchange integrals between transition metal ions. *Chem. Phys. Letters* **1988**, *143*, 371–376.
- [211] S. Yamanaka, T. Kawakami, H. Nagao, K. Yamaguchi. Effective exchange integrals for open-shell species by density functional methods. *Chem. Phys. Letters* **1994**, *231*, 25–33.
- [212] T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, K. Yamaguchi. *Ab initio* computations of effective exchange integrals for H–H, H–He–H and Mn₂O₂ complex: comparison of broken-symmetry approaches. *Chem. Phys. Letters* **2000**, *319*, 223–230.
- [213] M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, K. Yamaguchi. A general algorithm for calculation of Heisenberg exchange integrals J in multispin systems. *Chem. Phys. Letters* **2006**, *432*, 343–347.
- [214] C. A. Jimenez-Hoyos, T. M. Henderson, T. Tsuchimochi, G. E. Scuseria. Projected Hartree–Fock theory. *J. Chem. Phys.* **2012**, *136*, 164109.
- [215] P. Rivero, C. A. Jiménez-Hoyos, G. E. Scuseria. Predicting Singlet–Triplet Energy Splittings with Projected Hartree–Fock Methods. *J. Phys. Chem. A* **2013**, *117*, 8073–8080.
- [216] A. J. Garza, C. A. Jimenez-Hoyos, G. E. Scuseria. Capturing static and dynamic correlations by a combination of projected Hartree-Fock and density functional theories. *J. Chem. Phys.* **2013**, *138*, 134102.
- [217] T. Saito, W. Thiel. Analytical Gradients for Density Functional Calculations with Approximate Spin Projection. *J. Phys. Chem. A* **2012**, *116*, 10864–10869.
- [218] J. M. Ricart, R. Dovesi, C. Roetti, V. R. Saunders. Electronic and magnetic structure of KNiF₃ perovskite. *Phys. Rev. B* **1995**, *52*, 2381–2389.

- [219] R. Dovesi, J. M. Ricart, V. R. Saunders, R. Orlando. Superexchange interaction in K_2NiF_4 : an *ab initio* Hartree-Fock study. *J. Phys.: Condens. Matter* **1995**, *7*, 7997.
- [220] I. de P. R. Moreira, F. Illas. *Ab initio* theoretical comparative study of magnetic coupling in $KNiF_3$ and K_2NiF_4 . *Phys. Rev. B* **1997**, *55*, 4129–4137.
- [221] F. Illas, I. P. R. Moreira, C. de Graaf, V. Barone. Magnetic coupling in biradicals, binuclear complexes and wide-gap insulators: a survey of *ab initio* wave function and density functional theory approaches. *Theor. Chem. Acc.* **2000**, *104*, 265–272.
- [222] D. Dai, M.-H. Whangbo. Spin-Hamiltonian and density functional theory descriptions of spin exchange interactions. *The Journal of Chemical Physics* **2001**, *114*, 2887–2893.
- [223] D. Dai, M.-H. Whangbo. Spin exchange interactions of a spin dimer: Analysis of broken-symmetry spin states in terms of the eigenstates of Heisenberg and Ising spin Hamiltonians. *The Journal of Chemical Physics* **2003**, *118*, 29–39.
- [224] B. B. Miehlich, H. Stoll, A. Savin. A correlation-energy density functional for multideterminantal wavefunctions. *Mol. Phys.* **1997**, *91*, 527–536.
- [225] J. Gräfenstein, D. Cremer. The combination of density functional theory with multi-configuration methods — CAS-DFT. *Chem. Phys. Letters* **2000**, *316*, 569–577.
- [226] J. Gräfenstein, D. Cremer. Development of a CAS-DFT method covering non-dynamical and dynamical electron correlation in a balanced way. *Mol. Phys.* **2005**, *103*, 279–308.
- [227] R. Takeda, S. Yamanaka, K. Yamaguchi. CAS-DFT based on odd-electron density and radical density. *Chem. Phys. Letters* **2002**, *366*, 321–328.
- [228] S. Yamanaka, T. Ohsaku, D. Yamaki, K. Yamaguchi. Generalized spin density functional study of radical reactions. *Int. J. Quant. Chem.* **2003**, *91*, 376–383.

- [229] R. Takeda, S. Yamanaka, K. Yamaguchi. Approximate on-top pair density into one-body functions for CAS-DFT. *Int. J. Quant. Chem.* **2004**, *96*, 463–473.
- [230] S. Yamanaka, K. Nakata, T. Ukai, T. Takada, K. Yamaguchi. Multireference density functional theory with orbital-dependent correlation corrections. *Int. J. Quant. Chem.* **2006**, *106*, 3312–3324.
- [231] T. Leininger, H. Stoll, H.-J. Werner, A. Savin. Combining long-range configuration interaction with short-range density functionals. *Chem. Phys. Letters* **1997**, *275*, 151–160.
- [232] R. Pollet, A. Savin, T. Leininger, H. Stoll. Combining multideterminantal wave functions with density functionals to handle near-degeneracy in atoms and molecules. *J. Chem. Phys.* **2002**, *116*, 1250–1258.
- [233] J. Toulouse, F. Colonna, A. Savin. Long-range–short-range separation of the electron-electron interaction in density-functional theory. *Phys. Rev. A* **2004**, *70*, 062505.
- [234] E. Fromager, J. Toulouse, H. J. A. Jensen. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. *J. Chem. Phys.* **2007**, *126*, 074111.
- [235] E. Fromager, F. Real, P. Wahlin, U. Wahlgren, H. J. A. Jensen. On the universality of the long-/short-range separation in multiconfigurational density-functional theory. II. Investigating f^0 actinide species. *J. Chem. Phys.* **2009**, *131*, 054107.
- [236] S. Gusarov, P.-Å. Malmqvist, R. Lindh, B. O. Roos. Correlation potentials for a multiconfigurational-based density functional theory with exact exchange. *Theor. Chem. Acc.* **2004**, *112*, 84–94.
- [237] K. Nakata, T. Ukai, S. Yamanaka, T. Takada, K. Yamaguchi. CASSCF version of density functional theory. *Int. J. Quant. Chem.* **2006**, *106*, 3325–3333.
- [238] K. Sharkas, A. Savin, H. J. A. Jensen, J. Toulouse. A multiconfigurational hybrid density-functional theory. *J. Chem. Phys.* **2012**, *137*, 044104.

- [239] A. J. Perez-Jimenez, J. M. Perez-Jorda, I. d. P. R. Moreira, F. Illas. Merging multiconfigurational wavefunctions and correlation functionals to predict magnetic coupling constants. *J. Comp. Chem.* **2007**, *28*, 2559–2568.
- [240] E. H. Lieb. Density functionals for coulomb systems. *Int. J. Quant. Chem.* **1983**, *24*, 243–277.
- [241] H. Englisch, R. Englisch. Exact Density Functionals for Ground-State Energies II. Details and Remarks. *Phys. Status Solidi B* **1984**, *124*, 373–379.
- [242] H. Englisch, R. Englisch. Exact Density Functionals for Ground-State Energies. I. General Results. *Phys. Status Solidi B* **1984**, *123*, 711–721.
- [243] I. d. P. R. Moreira, R. Costa, M. Filatov, F. Illas. Restricted Ensemble-Referenced Kohn–Sham versus Broken Symmetry Approaches in Density Functional Theory: Magnetic Coupling in Cu Binuclear Complexes. *J. Chem. Theor. Comp.* **2007**, *3*, 764–774.
- [244] A. Savin, *On degeneracy, near-degeneracy and density functional theory in Recent Developments and Applications of Modern Density Functional Theory*, Vol. 4 of *Comp. Theor. Chem.*, J. Seminario (Ed.), Elsevier, **1996**, pp. 327–357.
- [245] M. Filatov, S. Shaik. Spin-restricted density functional approach to the open-shell problem. *Chem. Phys. Letters* **1998**, *288*, 689–697.
- [246] M. Filatov, S. Shaik. A spin-restricted ensemble-referenced Kohn–Sham method and its application to diradicaloid situations. *Chem. Phys. Letters* **1999**, *304*, 429–437.
- [247] S. G. Wang, W. H. E. Schwarz. Simulation of nondynamical correlation in density functional calculations by the optimized fractional orbital occupation approach: Application to the potential energy surfaces of O₃ and SO₂. *J. Chem. Phys.* **1996**, *105*, 4641–4648.
- [248] M. Filatov, S. Shaik. Diradicaloids: Description by the Spin-Restricted, Ensemble-Referenced Kohn–Sham Density Functional Method. *J. Phys. Chem. A* **2000**, *104*, 6628–6636.

- [249] Y. Shao, M. Head-Gordon, A. I. Krylov. The spin-flip approach within time-dependent density functional theory: Theory and applications to diradicals. *J. Chem. Phys.* **2003**, *118*, 4807–4818.
- [250] F. Wang, T. Ziegler. Time-dependent density functional theory based on a noncollinear formulation of the exchange-correlation potential. *J. Chem. Phys.* **2004**, *121*, 12191–12196.
- [251] A. I. Krylov. Triradicals. *J. Phys. Chem. A* **2005**, *109*, 10638–10645.
- [252] Y. A. Bernard, Y. Shao, A. I. Krylov. General formulation of spin-flip time-dependent density functional theory using non-collinear kernels: Theory, implementation, and benchmarks. *J. Chem. Phys.* **2012**, *136*, 204103.
- [253] E. Runge, E. K. U. Gross. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- [254] M. Petersilka, U. J. Gossmann, E. K. U. Gross. Excitation Energies from Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **1996**, *76*, 1212–1215.
- [255] R. Bauernschmitt, R. Ahlrichs. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Letters* **1996**, *256*, 454–464.
- [256] R. E. Stratmann, G. E. Scuseria, M. J. Frisch. An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules. *J. Chem. Phys.* **1998**, *109*, 8218–8224.
- [257] A. Dreuw, M. Head-Gordon. Single-Reference *ab Initio* Methods for the Calculation of Excited States of Large Molecules. *Chem. Rev.* **2005**, *105*, 4009–4037.
- [258] S. Hirata, M. Head-Gordon. Time-dependent density functional theory within the Tamm–Dancoff approximation. *Chem. Phys. Letters* **1999**, *314*, 291–299.
- [259] M. Huix-Rotllant, B. Natarajan, A. Ipatov, C. Muhavini Wawire, T. Deutsch, M. E. Casida. Assessment of noncollinear spin-flip Tamm–Dancoff approximation time-dependent density-functional

- theory for the photochemical ring-opening of oxirane. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12811–12825.
- [260] T. Ziegler, M. Seth, M. Krykunov, J. Autschbach, F. Wang. On the relation between time-dependent and variational density functional theory approaches for the determination of excitation energies and transition moments. *J. Chem. Phys.* **2009**, *130*, 154102.
- [261] H. Zhekova, M. Seth, T. Ziegler. Introduction of a New Theory for the Calculation of Magnetic Coupling Based on Spin-Flip Constricted Variational Density Functional Theory. Application to Trinuclear Copper Complexes which Model the Native Intermediate in Multicopper Oxidases. *J. Chem. Theor. Comp.* **2011**, *7*, 1858–1866.
- [262] R. Valero, F. Illas, D. G. Truhlar. Magnetic Coupling in Transition-Metal Binuclear Complexes by Spin-Flip Time-Dependent Density Functional Theory. *J. Chem. Theor. Comp.* **2011**, *7*, 3523–3531.
- [263] H. R. Zhekova, M. Seth, T. Ziegler. Calculation of the exchange coupling constants of copper binuclear systems based on spin-flip constricted variational density functional theory. *J. Chem. Phys.* **2011**, *135*, 184105.
- [264] I. Seidu, H. R. Zhekova, M. Seth, T. Ziegler. Calculation of Exchange Coupling Constants in Triply-Bridged Dinuclear Cu(II) Compounds Based on Spin-Flip Constricted Variational Density Functional Theory. *J. Phys. Chem. A* **2012**, *116*, 2268–2277.
- [265] R. Valero, R. Costa, I. de P. R. Moreira, D. G. Truhlar, F. Illas. Performance of the M06 family of exchange-correlation functionals for predicting magnetic coupling in organic and inorganic molecules. *J. Chem. Phys.* **2008**, *128*, 114103.
- [266] J. E. Peralta, J. I. Melo. Magnetic Exchange Couplings with Range-Separated Hybrid Density Functionals. *J. Chem. Theor. Comp.* **2010**, *6*, 1894–1899.
- [267] E. Ruiz. Exchange coupling constants using density functional theory: Long-range corrected functionals. *J. Comp. Chem.* **2011**, *32*, 1998–2004.

- [268] J. J. Phillips, J. E. Peralta. The role of range-separated Hartree–Fock exchange in the calculation of magnetic exchange couplings in transition metal complexes. *J. Chem. Phys.* **2011**, *134*, 034108.
- [269] I. Rudra, Q. Wu, T. Van Voorhis. Accurate magnetic exchange couplings in transition-metal complexes from constrained density-functional theory. *J. Chem. Phys.* **2006**, *124*, 024103.
- [270] A. Bencini, F. Totti, C. A. Daul, K. Doclo, P. Fantucci, V. Barone. Density Functional Calculations of Magnetic Exchange Interactions in Polynuclear Transition Metal Complexes. *Inorg. Chem.* **1997**, *36*, 5022–5030.
- [271] E. Ruiz, J. Cano, S. Alvarez, P. Alemany. Broken symmetry approach to calculation of exchange coupling constants for homobinuclear and heterobinuclear transition metal complexes. *J. Comp. Chem.* **1999**, *20*, 1391–1400.
- [272] F. H. Allen. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Cryst. B* **2002**, *58*, 380–388.
- [273] J. Cabrero, N. Ben-Amor, R. Caballol. Singlet-Triplet Gap in α -n-Dehydrotoluene and Related Biradicals: An *ab Initio* Configuration Interaction Study. *J. Phys. Chem. A* **1999**, *103*, 6220–6224.
- [274] D. J. R. Brook, H. H. Fox, V. Lynch, M. A. Fox. Structural Indicators of Electronic Interaction in the 1,1',5,5'-Tetramethyl-6,6'-dioxo-3,3'-biverdazyl Diradical. *J. Phys. Chem.* **1996**, *100*, 2066–2071.
- [275] R. D. Willett, C. Dwiggin, R. F. Kruh, R. E. Rundle. Crystal Structures of KCuCl_3 and NH_4CuCl_3 . *J. Chem. Phys.* **1963**, *38*, 2429–2436.
- [276] T. Tokii, N. Hamamura, M. Nakashima, Y. Muto. Crystal Structures and Magnetic Properties of Novel μ -Carboxylato- μ -Hydroxo-Bridged Binuclear Copper(II) Complexes with 1,10-Phenanthroline. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1214–1219.
- [277] C. Lopez, R. Costa, F. Illas, E. Molins, E. Espinosa. Ferromagnetic Copper(II) Complex Containing Ferrocenecarboxylato Bridging Ligands. *Inorg. Chem.* **2000**, *39*, 4560–4565.

- [278] C. Lopez, R. Costa, F. Illas, C. de Graaf, M. M. Turnbull, C. P. Landee, E. Espinosa, I. Mata, E. Molins. Magneto-structural correlations in binuclear copper(II) compounds bridged by a ferrocenecarboxylato(-1) and an hydroxo- or methoxo-ligands. *Dalton Trans.* **2005**, 2322–2330.
- [279] M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalles, O. Kahn. Design of μ -oxalato copper(II) binuclear complexes exhibiting expected magnetic properties. *Inorg. Chem.* **1984**, 23, 3808–3818.
- [280] J. Sletten. The Structures of Two Oxalato-bridged Cu Dimers; $[\text{Cu}_2(\text{Me}_4\text{en})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{Et}_5\text{dien})_2(\text{C}_2\text{O}_4)]$. *Acta Chem. Scand.* **1983**, 37A, 569–578.
- [281] P. de Meester, S. R. Fletcher, A. C. Skapski. Refined crystal structure of tetra- μ -acetato-bis-aquodicopper(II). *J. Chem. Soc., Dalton Trans.* **1973**, 2575–2578.
- [282] O. Castillo, I. Muga, A. Luque, J. M. Gutierrez-Zorrilla, J. Sertucha, P. Vitoria, P. Roman. Synthesis, chemical characterization, X-ray crystal structure and magnetic properties of oxalato-bridged copper(II) binuclear complexes with 2,2'-bipyridine and diethylenetriamine as peripheral ligands. *Polyhedron* **1999**, 18, 1235–1245.
- [283] H.-H. Song, L.-M. Zheng, Y.-J. Liu, X.-Q. Xin, A. J. Jacobson, S. Decurtins. Syntheses, structures and magnetic properties of two copper(II) diphosphonates: $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_2[\text{Cu}_2(\text{hedp})_2] \cdot \text{H}_2\text{O}$ and $[\text{NH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_3]_2[\text{Cu}_2(\text{hedp})_2]$ (hedp = 1-hydroxyethylidenediphosphonate). *J. Chem. Soc., Dalton Trans.* **2001**, 3274–3278.
- [284] T. R. Felthouse, E. J. Laskowski, D. N. Hendrickson. Magnetic exchange interactions in transition metal dimers. 10. Structural and magnetic characterization of oxalate-bridged, bis(1,1,4,7,7-pentaethyldiethylene triamine)oxalatodicopper tetraphenylborate and related dimers. Effects of nonbridging ligands and counterions on exchange interactions. *Inorg. Chem.* **1977**, 16, 1077–1089.
- [285] C. Mathoniere, O. Kahn, J. C. Daran, H. Hilbig, F. H. Koehler. Complementarity and internal consistency between magnetic and optical properties for the manganese(II) copper(II) heterodinuclear compound $[\text{Mn}(\text{Me}_6\text{-[14]ane-N}_4)\text{Cu}(\text{oxpn})](\text{CF}_3\text{SO}_3)_2$ ($\text{Me}_6\text{-[14]ane-N}_4$

- = (\pm)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; oxpn = *N,N'*-bis(3-aminopropyl)oxamide). *Inorg. Chem.* **1993**, *32*, 4057–4062.
- [286] Y. Sun, M. Melchior, D. A. Summers, R. C. Thompson, S. J. Rettig, C. Orvig. $[(\mu\text{-OCH}_3)\text{VO}(\text{ma})]_2$, a Strongly Antiferromagnetic Oxovanadium(IV) Dimer. *Inorg. Chem.* **1998**, *37*, 3119–3121.
- [287] G. Haselhorst, K. Wieghardt, S. Keller, B. Schrader. The $(\mu\text{-oxo})\text{bis}[\text{trichloroferrate(III)}]$ dianion revisited. *Inorg. Chem.* **1993**, *32*, 520–525.
- [288] K.-O. Schäfer, R. Bittl, W. Zweggart, F. Lendzian, G. Haselhorst, T. Weyhermüller, K. Wieghardt, W. Lubitz. Electronic Structure of Antiferromagnetically Coupled Dinuclear Manganese (Mn(III)Mn(IV)) Complexes Studied by Magnetic Resonance Techniques. *J. Am. Chem. Soc.* **1998**, *120*, 13104–13120.
- [289] S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson. Magnetostructural Correlations in $\mu_2\text{-1,1-N}_3$ Bridged, Dinuclear Copper(II) Complexes. 1. Ferromagnetic and Antiferromagnetic Coupling Associated with the Azide Bridge. X-ray Crystal Structures of $[\text{Cu}_2(\text{DMPTD})(\mu_2\text{-N}_3)(\mu_2\text{-Cl})\text{Cl}_2]\cdot\text{CH}_3\text{CN}$, $[\text{Cu}_2(\text{DMPTD})(\mu_2\text{-N}_3)_2(\text{N}_3)_2]$, $[\text{Cu}_2(\text{DIP})(\mu_2\text{-N}_3)(\mu_2\text{-Cl})\text{Cl}_2]\cdot 0.5\text{CH}_3\text{OH}$, $[\text{Cu}_2(\text{PAP}_{46}\text{Me-H})(\mu_2\text{-N}_3)(\text{N}_3)_2]\cdot 0.33\text{H}_2\text{O}$, $[\text{Cu}_2(\text{PAP})(\mu_2\text{-N}_3)\text{Cl}_3]\cdot\text{CH}_2\text{Cl}_2$, $[\text{Cu}_2(\text{PAP})(\mu_2\text{-N}_3)(\text{N}_3)(\text{NO}_3)(\text{CH}_3\text{OH})](\text{NO}_3)\cdot\text{CH}_3\text{OH}$, $[\text{Cu}_2(\text{PPD}_3\text{Me})(\mu_2\text{-N}_3)\text{Cl}_3(\text{H}_2\text{O})_{1.5}]$, and $[\text{Cu}_2(\text{PPD})(\mu_2\text{-N}_3)(\text{NO}_3)_3(\text{H}_2\text{O})_{1.6}]$. *Inorg. Chem.* **1994**, *33*, 5555–5570.
- [290] G. De Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi. Alternating Ferro- and Antiferromagnetic Interactions in Unusual Copper(II) Chains. *Inorg. Chem.* **1995**, *34*, 157–165.
- [291] F. Birkelbach, M. Winter, U. Floerke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A. X. Trautwein, K. Wieghardt, P. Chaudhuri. Exchange Coupling in Homo- and Heterodinuclear Complexes Cu(II)M [$\text{M} = \text{Cr(III)}, \text{Mn(III)}, \text{Mn(II)}, \text{Fe(III)}, \text{Co(III)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$]. Synthesis, Structures, and Spectroscopic Properties. *Inorg. Chem.* **1994**, *33*, 3990–4001.

- [292] A. Schäfer, H. Horn, R. Ahlrichs. Fully optimized contracted Gaussian basis sets for atoms Li to Kr. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- [293] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs. RI-MP2: optimized auxiliary basis sets and demonstration of efficiency. *Chem. Phys. Letters* **1998**, *294*, 143–152.
- [294] F. Weigend. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
- [295] A. Hellweg, C. Hättig, S. Höfener, W. Klopper. Optimized accurate auxiliary basis sets for RI-MP2 and RI-CC2 calculations for the atoms Rb to Rn. *Theor. Chem. Acc.* **2007**, *117*, 587–597.
- [296] A. Schäfer, C. Huber, R. Ahlrichs. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835.
- [297] K. C. Ko, D. Cho, J. Y. Lee. Scaling Approach for Intramolecular Magnetic Coupling Constants of Organic Diradicals. *J. Phys. Chem. A* **2013**, *117*, 3561–3568.
- [298] R. L. Martin, F. Illas. Antiferromagnetic Exchange Interactions from Hybrid Density Functional Theory. *Phys. Rev. Lett.* **1997**, *79*, 1539–1542.
- [299] F. Illas, R. L. Martin. Magnetic coupling in ionic solids studied by density functional theory. *J. Chem. Phys.* **1998**, *108*, 2519–2527.
- [300] I. de P. R. Moreira, F. Illas, R. L. Martin. Effect of Fock exchange on the electronic structure and magnetic coupling in NiO. *Phys. Rev. B* **2002**, *65*, 155102.
- [301] X. Feng, N. M. Harrison. Magnetic coupling constants from a hybrid density functional with 35% Hartree-Fock exchange. *Phys. Rev. B* **2004**, *70*, 092402.