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From Hartree–Fock to Electron Correlation: Application to Magnetic Systems

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1.1

Introduction

At the beginning of last century, quantum mechanics broke out and the famous Schrödinger's and Dirac's equations were derived and constituted tremendously important milestones. Even though they aim at describing the nanoscopic correlated world, it is known that the analytical solution is limited to the two-particle system, a prototype of which being the H atom. In particular, the description of a simple system as H₂ necessarily relies on approximations. One may first consider electrons as independent particles moving in the field of fixed nuclei. The appealing strategy of a mean field approximation was thus suggested along with the important picture of screened nuclei. How much the fluctuation with respect to this description dominates the physical properties has been a widely debated challenging issue.

This review will be organized as follows. First, the different methods traditionally used in quantum chemistry are briefly recalled starting from the Hartree–Fock description to the introduction of correlation effects. Since quantum chemistry aims at describing the interactions between atomic partners, the one-electron functions (so-called molecular orbitals, MOs) are derived from one-electron atomic basis sets localized on the atoms (atomic orbitals, AOs). However, it is known that a major drawback in this single determinantal description of the wavefunction is its inability to properly account for bond breaking. The H₂ case is used as a pedagogical example in Section 1.2.2.2 to exemplify the need for multireference SCF algorithms. For the study of homolytic breaking of such a single bond, it is recalled that both bonding and antibonding MOs must be introduced to incorporate the so-called nondynamical correlation effects. In this hierarchical construction of the wavefunction, the *Complete Active Space Self-Consistent Field* (CASSCF) [1, 2] procedure is described (see Section 1.2.3.1). Such methodology is particularly efficient since along bond stretching, two electrons become strongly correlated and the CASSCF treatment tends to localize one electron in each atom. The important dynamical correlation effects are then exemplified deriving the H₂–H₂ interactions,

and the short distance behavior ($1/R^6$) of the van der Waals potential is recovered (see Section 1.3.1).

In the last section, the machinery and efficiency of *ab initio* techniques are demonstrated over selected examples. A prime family is represented by magnetic systems which have attracted much attention over the last decades considering their intrinsic fundamental behaviors and possible applications in nanoscale devices. Chemists have put much effort to design and fully characterize new families of systems which may exhibit unusual and fascinating properties arising from the strongly correlated character of their electronic structures. From a fundamental point of view, high- T_c superconducting copper oxides [3–5], and colossal magnetoresistant manganite oxides [6–11] are such families which cannot be ignored in the field of two- and three-dimensional materials. One-dimensional chains [12–15] as well as molecular systems mimicking biological active centers [16,17] have more recently been considered as promising targets in the understanding of dominant electronic interactions. In such materials, a rather limited number of electrons are responsible for the observed intriguing properties. Reasonably satisfactory energetics description of such systems can be obtained by the elegant broken-symmetry (BS) method [18–21]. Let us mention that, in particular, BS *density functional theory* (DFT) calculations have turned out to be very efficient in the determination of magnetic coupling constants and EPR parameters (see [22–29] and references therein). On the other hand, the DFT methodology has been extensively used in surface science to follow at a microscopic level the reactant transformation leading to products. Nevertheless, this description has shown to suffer from an unrealistic description of physisorption [30]. Thus, a combined approach based on the periodic DFT method with MP₂ correction has been proposed to overcome this intrinsically methodological drawback [31, 32].

These examples aim at shedding light over a selected number of systems in materials science, catalysis, and enzymatic activity which may call for explicitly correlated calculations.

1.2 Methodological Aspects of the Electronic Problem

1.2.1 The Electronic Problem

Physical properties of molecules take their origin in electron assembly phenomena. To understand these properties, one has to investigate the electron distributions and interactions. This information is contained in the electronic wavefunction governed by Schrödinger's equation:

$$\hat{H}\Psi = E\Psi, \quad (1.1)$$

which is to be solved, defining the N -electron eigenfunction Ψ and eigenvalue E of the Hamiltonian $\hat{H}$. The nonrelativistic Hamiltonian is written as a sum of

different kinetic and potential contributions arising from interacting electrons and nuclei:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}. \quad (1.2)$$

Since the nuclei are much heavier than the electrons, their kinetic energy is much smaller and, consequently, can be considered as motionless. In the study of the electronic problem, the nuclei positions are parameters for the motion of the electrons, and the problem is solved by considering only the electronic part of the Hamiltonian (so-called the Born–Oppenheimer approximation [33]). Thus, the electronic Hamiltonian using atomic units reads

$$\hat{H}_{\text{elec}} = \sum_i -\frac{1}{2} \Delta_i - \sum_i \sum_A \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}}. \quad (1.3)$$

While the first two terms are monoelectronic in nature, the third one is the electron–electron repulsion which excludes any analytical resolution of the many-body problem.

Traditionally, one looks for a step-by-step procedure to incorporate the important physical contributions in a hierarchical way. A reasonable zeroth-order wavefunction is accessible within the Hartree–Fock scheme. Such treatment relies on a meanfield approximation where each electron moves in the field generated by the nuclei and the average electronic distribution arising from the $N - 1$ other electrons (see Section 1.2.2.1). It was rapidly understood that such single determinantal strategy fails to properly describe bond breakings. As a matter of fact, as a bond is stretched, the independent electron approximation breaks down as the electrons tend to localize in a concerted way one on each nuclei. To overcome this failure and incorporate the so-called static correlation, the CASSCF procedure has been proposed [1, 2]. Along this procedure, the wavefunction becomes intrinsically multireference (see Section 1.2.3.1). Finally, contributions which tend to reduce the electron–electron repulsion account for the dynamical correlation. Its main effect is the digging of the Coulomb hole to increase the probability of finding two electrons in different regions of space, distinguishing radial and angular correlations. This concept has been widely used in the understanding of DFT approaches.

As both static and dynamical correlations are turned on top of a Hartree–Fock solution, electrons are allowed to occupy arbitrarily (respecting spin and space symmetries!) all the MOs, introducing other electronic configurations which may be necessary to describe the physical state of interest. In a sense, the expansion of the wavefunction as a linear combination of Slater determinants (*configuration interaction*, CI) tends to recover the physical effects absent in the initial orbital approximation.

1.2.2

Finding a Solution

Let us start from an infinite set of MOs, ϕ_i , and a zeroth-order approximation to the N -electron problem. The MOs are split into two sets, either doubly occupied

Figure 1.1 (a) $|\Psi_0\rangle$, (b) single, and (c) double excited determinants.

or empty (referenced as $(a, b, c, \dots)$ and $(r, s, t, \dots)$, respectively), defining $|\Psi_0\rangle$ as $|a\bar{a}b\bar{b}c\bar{c}\rangle$. The wavefunction can be developed upon $|\Psi_0\rangle$ and the electronic configurations built from $|\Psi_0\rangle$ by successive excitations (see Figure 1.1),

$$|\Psi\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots, \quad (1.4)$$

where $|\Psi_a^r\rangle$ represents single excited determinants, $|\Psi_{ab}^{rs}\rangle$ double excited, and so on.

Solving the electronic problem consists in the determination of (i) the MOs, and (ii) the amplitudes of different electronic configurations (c_0 , $\{c_a^r\}$, $\{c_{ab}^{rs}\}$, $\dots$). The first task is achieved along the Hartree–Fock procedure, while the second calls for numerical demanding methods which are constantly under intense investigations.

1.2.2.1 Hartree–Fock Approximation

The goal is to find a set of MOs sustaining the reference determinant $|\Psi_0\rangle$. These orbitals should form an orthonormal basis of one-electron functions. Under these constraints, the Hartree–Fock equations are easily derived by minimizing the expectation value of $\hat{H}$ and $|\Psi_0\rangle$:

$$\left[\hat{h} + \sum_{a, \text{occ}} (J_a - K_a) \right] \phi_i = E_i \phi_i, \quad (1.5)$$

where J_a and K_a represent the Coulomb and the exchange operators, respectively.

The eigenfunction problem(s) must be solved iteratively (self-consistent field procedure, SCF) since the Fock operator $\hat{f} = \hat{h} + \sum_{a, \text{occ}} (J_a - K_a)$ is constructed on the occupations of its own eigenvectors. $\hat{h}$ is the sum of the kinetic energy and nuclei–electron interactions, while the sum defines the Hartree–Fock potential that averages the interelectronic repulsion so as to give a monoelectronic operator.

1.2.2.2 Example

In order to clarify the Hartree–Fock SCF framework, let us concentrate on the quantum chemist’s “swiss army knife” system, namely H_2 in a minimal AO basis

set $\{a, b\}$. From symmetry consideration, one can build two MOs, symmetric (g)

$$g = \frac{1}{\sqrt{2}}(a + b) \quad (1.6)$$

and antisymmetric (u)

$$u = \frac{1}{\sqrt{2}}(a - b). \quad (1.7)$$

Evidently, the Hartree–Fock solution for the ground state is

$$|\Psi_0\rangle = |g\bar{g}| \quad (1.8)$$

or returning to the AOs,

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} \left(\frac{|a\bar{a}| + |b\bar{b}|}{\sqrt{2}} + \frac{|a\bar{b}| + |b\bar{a}|}{\sqrt{2}} \right) = \frac{1}{\sqrt{2}} (|\Psi_{\text{ion}}\rangle + |\Psi_{\text{neutral}}\rangle).$$

$|a\bar{a}|$ and $|b\bar{b}|$ are referred to as the ionic forms since the two electrons are localized on the same atomic center. This is to be contrasted with the combination $\frac{1}{\sqrt{2}}(|a\bar{b}| + |b\bar{a}|)$ which is the neutral singlet. Thus, $|\Psi_0\rangle$ consists of an equal weight of ionic and neutral forms. While the H_2 molecule should clearly dissociate into $\text{H}^\bullet + \text{H}^\bullet$ (see Figure 1.2), the Hartree–Fock procedure overestimates the weight of the ionic forms. As a matter of fact, the latter should physically become vanishingly small as the bond is stretched. This is a major pitfall of the Hartree–Fock theory which is being taken care of in a multireference approach.

Figure 1.2 H_2 potential curve calculated by various methods.

1.2.2.3 Beyond Hartree–Fock Treatment: Electronic Correlation

As mentioned previously, the main effort is to calculate the coefficients in the wavefunction expansion. This calculation gives a correlated wavefunction, the energy of which defines the correlation energy as

$$E_{\text{corr}} = E - E_{\text{Hartree–Fock}}.$$

Practically the expansion cannot be carried out upon an infinity of excitations and a selection of excited determinants must be made in the configuration interaction treatment. In practice, this procedure cannot lead to the exact solution of the many-electron problem for two main reasons:

- It is impossible to handle infinite one-electron basis sets. Therefore, the constructed determinants $\{|\Psi_i\rangle\}$ cannot form a complete N -electron function basis set.
- Even for relatively small basis sets, the number of determinants to be considered may become extremely large. Thus, in practice, one will not take into account all determinants (*full*-CI procedure) but only a small part of these (*truncated*-CI), in single and/or double (CIS, CISD) calculations.

Traditionally, one distinguishes static and dynamical correlations in the CI approach. In the next section, we will clarify these notions using the H_2 example.

1.2.3

Correlation Energy

1.2.3.1 Static Correlation: CASSCF Approach

Let us concentrate on the problem of bond breaking of H_2 . In the g orbital, the maximum of electronic density is in the middle of the bond. Conversely, the u function displays a nodal plane and the maximum of density is concentrated on the nuclei.

To overcome the major failure of the Hartree–Fock description, one may introduce in a multireference expansion other determinants. Clearly, g and u become quasidegenerate in the long-distance regime. Thus, $|u\bar{u}\rangle$ may as well significantly participate in the two-electron wavefunction. By allowing the occupations of two MOs by two electrons, leaving all the other orbitals either doubly occupied (inactive) or vacant (virtual), one performs a Complete Active Space Self-Consistent Field CAS(2,2)SCF calculation (see Figure 1.3). From a physical point of view, this procedure consists in treating exactly the correlation in the active space and let the inactive orbitals react to the field generated by different configurations built in the active space. This point constitutes the major difficulty of the CASSCF calculation. Indeed, since the active space is the only part of the system where the correlation is treated with fine accuracy, it has to include the necessary configurations to describe the property of interest.

One defines the best set of MOs under this constraint. The inactive MOs respond to the occupations of the active MOs, treating democratically the $|g\bar{g}\rangle$ and $|u\bar{u}\rangle$

Figure 1.3 CASSCF configurations.

configurations. The comparison between H_2 and F_2 systems is instructive since the latter holds such inactive shells. The CAS(2,2) inactive MOs of F_2 will be the best compromise between the double occupancy of g and u .

For H_2 in a minimal basis set, the correlation energy is analytical from the 2×2 matrix diagonalization (see Ref. [34] for derivations). Writing $|\Psi\rangle = |g\bar{g}\rangle + c|u\bar{u}\rangle$ and $\Delta = \langle u\bar{u}|\hat{H}|u\bar{u}\rangle - \langle g\bar{g}|\hat{H}|g\bar{g}\rangle$

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{gu}^2} \quad (1.9)$$

$$c = \frac{K_{gu}}{-\Delta - \sqrt{\Delta^2 + K_{gu}^2}}. \quad (1.10)$$

These results call for two important comments. First the correlation energy is negative as a result of the flexibility offered to the wavefunction. Then, the amplitude c of $|u\bar{u}\rangle$ being negative reduces the weight of the ionic forms. Eventually, as $R \rightarrow \infty$, it can be shown that $c \rightarrow -1$ and the wavefunction reduces to $\frac{1}{\sqrt{2}}(|a\bar{b}| + |b\bar{a}|)$. The electrons are no longer independent, they are said to be correlated. The reduction of the ionic forms stresses the demand of atoms to recover their neutral character. The nondynamical correlation strikes back again the delocalization preference arising from the Hartree–Fock scheme. Along the CASSCF procedure one introduces the leading physical contributions in a multireference wavefunction. This allows one to treat on the same footing quasidegenerated electronic configurations given in a predefined active space (so-called CAS). Typically, the dissociation of H_2 can be properly discussed using a CAS(2,2)SCF calculation (see Figure 1.2).

1.2.3.2 Dynamical Correlation

In the light of the previous considerations, let us again concentrate on H_2 close to the equilibrium distance. Consequently, the Δ value is large whilst c is almost negligible. Ψ is almost monoreference. A statistical analysis of the wavefunction shows that the electrons spend much time in the g orbital and sometimes explore the u one. In this case, the correlation is a fluctuation of the electronic density around an average value. This is part of the origin for dynamical terminology. The dynamical correlation brings a correction to the energy and wavefunction, but the qualitative results of the Hartree–Fock approach are not deeply changed.

More generally, on top of the CASSCF wavefunction one traditionally performs either second-order perturbation theory treatment (CASPT2) [35, 36] or variational CI such as the so-called first-order CI which incorporates in a variational way all the single excitations on the CAS determinants. These contributions account for the electronic relaxations which respond to the instantaneous field modifications or spin polarization in the active space.

In this respect, the *Difference Dedicated* CI (DDCI) methodology [37–39] has shown to provide impressive results in magnetically coupled systems [40–42]. The conceptual guideline is the quasidegenerated perturbation theory (QDPT) developed by Bloch [43]. For a two-electron/two-MO system one looks for the singlet–triplet energy difference $2J$, J being the one-parameter model Heisenberg Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ($S_1 = S_2 = 1/2$). The model space consists of two neutral forms $|a\bar{b}|$ and $|b\bar{a}|$ upon which the QDPT defines an effective Hamiltonian $\hat{H}_{\text{eff}}$. At the second order of perturbation theory, the off-diagonal element of $\hat{H}_{\text{eff}}$ is precisely J and reads

$$\langle a\bar{b} | \hat{H}_{\text{eff}}^2 | b\bar{a} \rangle = K_{ab} + \sum_{\alpha} \frac{\langle a\bar{b} | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | b\bar{a} \rangle}{E_0^{(0)} - E_{\alpha}^{(0)}},$$

$|\alpha\rangle$ being outer-space determinants, including ionic forms $|a\bar{a}|$ and $|b\bar{b}|$. If the sum is restricted to $\alpha = a\bar{a}, b\bar{b}$, then J reads

$$J = K_{ab} + \frac{\langle a\bar{b} | \hat{H} | a\bar{a} \rangle \langle a\bar{a} | \hat{H} | b\bar{a} \rangle}{E_0^{(0)} - E_{a\bar{a}}^{(0)}} + \frac{\langle a\bar{b} | \hat{H} | b\bar{b} \rangle \langle b\bar{b} | \hat{H} | b\bar{a} \rangle}{E_0^{(0)} - E_{b\bar{b}}^{(0)}}$$

$$J = K_{ab} + 2 \frac{t^2}{-U}$$

with $t = \langle a\bar{a} | \hat{H} | a\bar{b} \rangle$ and $U = E_0^{(0)} - E_{a\bar{a}}^{(0)}$. One recovers the famous competition between ferromagnetic and antiferromagnetic contributions. For $|\alpha\rangle$ to be simultaneously coupled to $|a\bar{b}|$ and $|b\bar{a}|$, it should not defer by more than two spin orbitals (Slater's rule). Thus, the determinants are traditionally listed according to the number of holes (h) and particles (p) generated on the model space. As soon as this space is enlarged to the full valence space (i.e., including the ionic forms), it can be shown that $1h, 1p, 1h+1p, 2h, 2p, 2h+1p$, and $2p+1h$ participate in the hierarchical organization of the singlet and triplet.

Figure 1.4 Successive determinants considered in the DDCI approach.

Indeed the purely inactive excitations $2h + 2p$ simply shift the diagonal matrix elements. As shown in Figure 1.4, the selection gives rise to DDCI-1, -2, and -3 levels of calculations. Being a truncated-CI methodology, DDCI suffers from intrinsic size-consistency issue which has been elegantly corrected in the so-called *Size-Consistent Self-Consistent* (SC)² framework [44]. The physical effects (spin polarization, dynamical correlation) have been clarified by considering different levels of calculations [45–47].

In order to remedy to this size-consistency problem, alternative approaches have been proposed and coupled pairs methodology turned out to be very efficient [48]. Unfortunately, the cost of such calculations does not allow one to handle even moderate size systems. Nevertheless, the CASPT2 method [35, 36] offers a remarkable compromise, introducing at second-order of perturbation theory the correlation effects. The corresponding atomic effects are properly incorporated in this contracted treatment of correlation effects. Such methodology has proven to be remarkably efficient in the inspection of magnetic properties of molecular and extended systems.

1.3

Correlation at Work

Over the past decades, a huge amount of experimental data carried out on a wide panel of systems has received much attention from both CI- and DFT-based

frameworks. For the present purpose, we limit our inspection to a selection of architectures of various dimensionalities. Over the years, the possibilities of generating magnetic systems using versatile ligands coordinated to different metallic centers have been much considered in the light of the porphyrin-like molecules activity. Thus, the traditional scenario involving open- d shells in the environment of closed-shell magnetic couplers (see Section 1.3.3) has been revisited based on both experimental and theoretical works (see Section 1.3.2). Nevertheless, we shall first investigate prototypes of weak interactions arising in the $(\text{H}_2)_2$ dimer (see Section 1.3.1). The van der Waals forces are of prime importance in physisorption phenomena which are likely to control catalyzed reactions. These effects have a purely quantum origin as they correspond to instantaneous charge fluctuations.

1.3.1

Dipoles Interactions: Example of $(\text{H}_2)_2$

Let us consider two H_2 molecules well separated in space ($l \ll L$, see Figure 1.5).

If a, b, c , and d refer to the AOs, one can build the g and u MOs on each H_2 fragment (see Figure 1.6).

Figure 1.5 Schematic representation of the $(\text{H}_2)_2$ dimer.

Figure 1.6 $|\Psi_0\rangle$ for $(\text{H}_2)_2$.

Figure 1.7 $|\Psi_{g_1 g_2}^{u_1 u_2}\rangle$ for $(H_2)_2$.

Thus, a zeroth-order wavefunction is given by

$$|\Psi_0\rangle = |g_1 \bar{g}_1 g_2 \bar{g}_2| = \frac{1}{4} \left| (a\bar{b} + b\bar{a} + a\bar{a} + b\bar{b}) (c\bar{d} + d\bar{c} + c\bar{c} + d\bar{d}) \right|.$$

One can observe in the development of $|\Psi_0\rangle$ that the doubly ionic structures “ $H^+H^-H^+H^-$ ” and “ $H^-H^+H^-H^+$ ” hold equal weights, in disagreement with naive electrostatic argument. However, the double excitation $g_1 g_2 \rightarrow u_1 u_2$ (see Figure 1.7) enhances the former and reduces the latter thanks to configurations interaction:

$$\begin{aligned} \langle \Psi_0 | \hat{H} | \Psi_{g_1 g_2}^{u_1 u_2} \rangle &= \langle g_1 g_2 | \hat{H} | u_1 u_2 \rangle = \frac{1}{4} (a^2 - b^2, c^2 - d^2) \\ &= \frac{1}{4} (J_{ac} + J_{bd} - J_{bc} - J_{ad}). \end{aligned}$$

The bielectronic Coulomb integrals can be approximated as the inverse of interatomic distances,

$$\begin{aligned} J_{ac} = J_{bd} &\approx \frac{1}{L} \\ J_{ad} &\approx \frac{1}{L+l}, \quad J_{bc} \approx \frac{1}{L-l}. \end{aligned}$$

Thus, a second-order development ($l \ll L$) gives

$$\langle g_1 g_2 | H | u_1 u_2 \rangle \approx -\frac{l^2}{2L^3}.$$

Using second-order perturbation theory to evaluate the correlation energy, the L^{-6} dependence of the dispersion energy is recovered.

Figure 1.8 Head-to-tail dipole interactions are favored from correlation effects.

The origin of the dispersion energy is clear in this procedure. Indeed, the development of the doubly excited determinant $|\Psi_{g_1g_2}^{u_1u_2}\rangle$ on the atomic orbitals a , b , c , and d (see Figure 1.8) exhibits the role of correlation between the fluctuations of the positions of the electrons in the two bonds. When the electrons move from b to a , then the probability of a concerted displacement from d to c is larger than the one of a movement from c to d .

1.3.2

Open-Shell Ligands: Noninnocence Concept

Considering the possibility of generating high oxidation states ions (in iron chemistry for instance, let us mention notable examples of Fe(IV) [49, 50], Fe(V) [51–53] and Fe(VI) [54]), much synthetic effort has been devoted to the preparation of specific multidentate ligands. The use of such ligands, known as *noninnocent*, has opened up the route to original synthetic materials, involving open shells on both metal and ligands partners [55–61]. The spectacular *excited-state coordination* chemistry concept in which a ligand coordinates in an excited electronic state to a metal center has emerged from this class of compounds [62]. The generation of radical ligands in coordination compounds has given rise to a promising route to magnetic materials.

From the theoretical point of view, DFT as well as CI calculations have been undertaken to scrutinize the electronic structures of such *noninnocent* ligand-based systems [58–60, 62, 63]. In particular, the comparison between experimental and calculated exchange-coupling constants and the analysis of the magnetic interactions has been the subject of intense work. While DFT has sometimes failed to fully account for the low-energy spectroscopy, the wavefunction-based DDCI method has elucidated the unusual behavior of several complexes [58, 62]. Among those, a striking example is given by the Fe(gma)CN complex containing the glyoxalbis(mercaptoanil) (gma) ligand (see Figure 1.9) [22]. Even though the *noninnocent* character of the gma ligand was clearly demonstrated both experimentally and theoretically, DFT calculations were only partially successful in the description of the electronic structure of the full complex [62]. The magnetic susceptibility and zero-field Mössbauer measurements clearly favored a doublet ground state. Nevertheless, DFT calculations did not provide any clear evidence in that sense, the $M_s = 1/2$ solution exhibiting a low-spin Fe(III) ($S_{\text{Fe}} = 1/2$) coupled to a closed shell gma ligand ($S_{\text{gma}} = 0$). Clearly, for a good

Figure 1.9 Structure of Fe(gma)CN. Fe, S, N, C, and H are represented in purple, yellow, blue, gray, and white, respectively.

description of the electronic structure of such system, DFT and its monodeterminantal character is not appropriate and correlated *ab initio* calculations might be desirable.

Based on this statement, correlated *ab initio* calculations on this particular system by means of DDCI-2 calculations on the top of the CAS(5,5)SCF wavefunction were performed [22]. Interestingly, the active orbitals consist of three metal-centered and two ligand-centered MOs (see Figure 1.10) [62]. The calculations showed that the low-energy spectrum exhibits a 200 cm^{-1} quartet–doublet gap, in agreement with different experiments, and that the observed strong antiferromagnetic is due to important ligand-to-metal charge transfer (LMCT). The resulting ground-state wavefunction which exhibits an intermediate magnetic/covalent character is rather strongly correlated and is dominated by local ($S_{\text{Fe}} = 3/2$ and $S_{\text{gma}} = 1$) electronic configuration. Finally, whereas the gma ligand is clearly a closed-shell singlet

Figure 1.10 Optimized active average MOs for the lowest doublet and quartet state of Fe(gma)CN.

when considered alone, it is likely to be a triplet when coordinated to the iron center. The multiconfigurational nature of the wavefunction has been identified in this example and makes this class of compounds still very challenging for theoreticians. It has been recently suggested that the energetics of low-lying states of coordination complexes based on porphyrins and related entities may not be accessible by means of DFT methodology (see Ref. [23] and references therein). More troublesome is the dependence of the spin density maps on the functional choice.

1.3.3

Growing 1D Materials: Ni-Azido Chains

With the generation of magnetic properties goal in mind, experimentalists have prepared higher dimensionality materials. One of the main challenges in the synthesis of extended 1D systems is to prevent the local magnetic moments from canceling out. In the presence of most frequent antiferromagnetic interactions, pioneer approaches were devoted to regular heterospin ferrimagnetic chains [12] holding alternating spin carriers, coupled through a unique exchange constant. Another strategy consists in varying the magnetic exchange constants between homospin carriers [64, 65]. Finally, the use of strong anisotropic metal ions to reduce the magnetization relaxation has generated the promising field of the single-chain magnet (SCM) [13–15].

In this respect, the azido ligand turned out to be extremely appealing in linking metal ions and a remarkable magnetic coupler for propagating interactions between paramagnetic ions. The structural variety of the azido complexes ranges from molecular clusters to extended 1D to 3D materials [66–71]. An interesting prototype of such a system has been recently synthesized where a single azido unit bridges in an alternating End-On (EO) and End-to-End (EE) way the Ni(II) ions (see Figure 1.11) [72]. The system can be considered from the chemical point of view as a quasi-1D chain. However, based on magnetic susceptibility measurements, it was suggested that the system should be described from the magnetic point of view as isolated dimers. Indeed, the introduction of a second magnetic interaction was shown to be irrelevant. Therefore, the question of the nature and amplitude of the magnetic interactions between the nearest Ni(II) ions deserved special attention. The alternation of EO and EE units strongly suggested the presence of two magnetic exchange pathways which can be accessible through Ni₂ dimers spectroscopy analysis. Thus, CAS(5,6)SCF/DDCI-2 calculations were performed on the molecular EE and EO fragments extracted from the available crystal structure.

Figure 1.11 Nickel(II) chain $\{\text{Ni}_2(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-N}_3)(\text{L})_2(\text{MeOH})_2\}_n$ with alternating End-On/End-to-End single azido bridges.

Figure 1.12 Molecular EE (a) and EO (b) fragments and in-phase active metallic MOs. For the sake of simplicity, the out-of-phase combinations are not shown.

Figure 1.13 Energy spectrum of a two-center Heisenberg $S = 1$ Hamiltonian.

The active orbitals consist of the in-phase and out-of-phase linear combinations of the d_{z^2} and $d_{x^2-y^2}$ metallic AOs (see Figure 1.12) and the nonbonding MO of the N_3^- bridge.

Since the Ni(II) ion is formally d^8 , it is expected that exchange interactions between $S = 1$ ions should give rise to three spin states in the Ni_2 units, namely singlet (S), triplet (T), and quintet (Q) states. In a Heisenberg picture $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ($S_1 = S_2 = 1$), the energy separations are $6|J|$ and $4|J|$ between the quintet and singlet, quintet and triplet states, respectively (see Figure 1.13). Within the EE unit, a relatively large antiferromagnetic exchange constant ($J_{EE} \sim -50 \text{ cm}^{-1}$) was calculated in good agreement with the unique value extracted from experiment

Figure 1.14 Schematic representation of the Ni-azido chain resulting from the isolated EE dimer picture.

($\sim -40 \text{ cm}^{-1}$). This is to be contrasted with the EO Ni_2 unit, which exhibits a negligibly small magnetic interaction ($\alpha = J_{\text{EO}}/|J_{\text{EE}}|$ ratio ~ 0.02) (see Figure 1.14).

The correlated calculations not only confirmed the isolated dimers picture, but also associated the leading antiferromagnetic exchange pathway with the EE bridging mode. In the light of the calculated $(E_Q - E_S)/(E_Q - E_T)$ ratio, let us mention that the deviation from a pure Heisenberg picture is negligible (less than 2%) ruling out the speculated participation of quadratic terms. The attempt to generate high-enough ferromagnetic interactions between $S = 1$ sites looked very promising since the antiferromagnetic coupling between the resulting $S = 2$ units through EE bridges might have resulted in a Haldane chain with vanishingly small spin gap [73, 74]. The versatility of the azido magnetic coupler should still be considered to generate synthetic models for theoretical physics analysis.

1.4

Discussion and Concluding Remarks

Quantum chemical calculations have become valuable means of investigation which cannot be ignored. As spectroscopy accuracy can be reached down to several tens of wavenumbers, *ab initio* techniques have the ability to rationalize interactions in magnetic materials. Interestingly, the different contributions to energy splitting are accessible and the underlying physical phenomena can be interpreted. The information which is conveyed by the wavefunction is crucial in the characterization of model Hamiltonians. Undoubtedly, significant efforts must be devoted to extract the relevant parameters in a “boil down” procedure of the *ab initio* information. Even though certain CI methodologies might be very demanding when dealing with large systems such as enzyme active sites, they allow one to manipulate symmetry and spin-adapted eigenstates of the exact Hamiltonian. The impressive demand for catalyzed reactions interpretation has led to a spectacular developments of DFT-based tools dedicated to surface-type issues. Popular codes take advantage of the crystal periodicity by introducing plane waves rather than localized atomic orbitals. It is noteworthy that some recent works have suggested that *a posteriori* corrections should be performed on the reaction site cluster embedded in a periodic environment. Such methodology has opened up new routes to important issues involving biological systems. Nevertheless, some specific systems including open-shell compounds are the concern of explicitly

correlated calculations which allow an efficient treatment of both nondynamical and dynamical correlations.

References

- 1 Roos, B. O. *Adv. Chem. Phys.* **1987**, *LXIX*, 399.
- 2 Olsen, J., Roos, B. O., Jorgensen, P., Jensen, H. J. A. *J. Chem. Phys.* **1988**, *89*, 2185.
- 3 Bednorz, J. G., Müller, K. A. *Z. Phys. B: Condens. Matter* **1986**, *64*, 189.
- 4 Dagotto, E. *Rev. Mod. Phys.* **1994**, *66*, 763.
- 5 Nagaosa, N. *Science* **1997**, *275*, 1078.
- 6 Kiryukhin, V., Casa, D., Hill, J. P., Kelmer, B., Vigliante, A., Tomioka, Y., Tokura, Y. *Nature* **1997**, *386*, 813.
- 7 Asamitsu, A., Tomioka, Y., Kuwahara, H., Tokura, Y. *Nature* **1997**, *388*, 50.
- 8 Fäth, M., Freisem, S., Menovsky, A. A., Tomioka, Y., Aarts, J., Mydosh, J. A. *Science* **1999**, *285*, 1540.
- 9 Kimura, T., Tokura, Y. *Annu. Rev. Mater. Sci.* **2000**, *30*, 451.
- 10 Yoo, Y. K., Duewer, F., Yang, H., Yi, D., Li, J.-W., Xiang, X.-D. *Nature* **2000**, *406*, 704.
- 11 Dagotto, E., Hotta, T., Moreo, A. *Phys. Rep.* **2001**, *344*, 1.
- 12 Kahn, O. *Molecular Magnetism*; New York, Wiley-VCH, **1993**.
- 13 Caneschi, A., Gatteschi, D., Lalioti, N., Sangregorio, C., Sessoli, R., Venturi, G., Vindigni, A., Rettori, A., Pini, M. G., Novak, M. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 1760.
- 14 Coulon, C., Miyasaka, H., Clérac, R. Single-Chain Magnets: Theoretical Approach and Experimental Systems. In *Single-Molecule Magnets and Related Phenomena*, Vol. 122; Winpenny, R., Ed.; Springer: Berlin, Heidelberg, **2006**.
- 15 Lescouëzec, R., Toma, L. M., Vaissermann, J., Verdager, M., Delgado, F. S., Ruiz-Pérez, C., Lloret, F., Julve, M. *Coord. Chem. Rev.* **2005**, *249*, 2691.
- 16 Yoon, J., Mirica, L. M., Stack, T. D. P., Solomon, E. I. *J. Am. Chem. Soc.* **2004**, *126*, 12586.
- 17 Yoon, J., Solomon, E. I. *Coord. Chem. Rev.* **2007**, *251*, 379.
- 18 Noodleman, L., Norman, J. G. *J. Chem. Phys.* **1979**, *70*, 4903.
- 19 Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.
- 20 Noodleman, L., Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423.
- 21 Noodleman, L., Peng, C. Y., Case, D. A., Mouesca, J.-M. *Coord. Chem. Rev.* **1995**, *144*, 199.
- 22 Messaoudi, S., Robert, V., Guihéry, N., Maynaud, D. *Inorg. Chem.* **2006**, *45*, 3212.
- 23 Ghosh, A. *J. Biol. Inorg. Chem.* **2006**, *11*, 712.
- 24 Pierloot, K., Vancoillie, S. *J. Chem. Phys.* **2006**, *125*, 124303.
- 25 Caballol, R., Castell, O., Illas, F., de P. R. Moreira, I., Malrieu, J. P. *J. Phys. Chem. A* **1997**, *101*, 7860.
- 26 Kahn, O., Martinez, C. J. *Science* **1998**, *279*, 44.
- 27 Christou, G., Gatteschi, D., Hendrickson, D. N., Sessoli, R. *MRS Bull.* **2000**, *25*, 66.
- 28 Gatteschi, G., Sessoli, R. *Angew. Chem. Int. Ed.* **2003**, *42*, 268.
- 29 Bogani, L., Sangregorio, C., Sessoli, R., Gatteschi, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 5817.
- 30 Ruzsinszky, A., Perdew, J. P., Csonka, G. I. *J. Phys. Chem. A* **2005**, *109*, 11015.
- 31 Tuma, C., Sauer, J. *Chem. Phys. Lett.* **2004**, *387*, 388.
- 32 Tuma, C., Sauer, J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3955.
- 33 Born, M., Oppenheimer, R. *Ann. Phys.* **1927**, *84*, 457.
- 34 Szabo, A., Attila, N. S. *Modern Quantum Chemistry*; New York, Dover, **1982**.

- 35 Neese, F. ORCA – An *Ab Initio*, Density Functional and Semi-Empirical Program Package, Max-Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr, Germany, 2005.
- 36 Cabrero, J., Ben Amor, N., de Graaf, C., Illas, F., Caballol, R. *J. Phys. Chem. A* **2000**, 104, 9983.
- 37 Miralles, J., Daudey, J.-P., Caballol, R. *Chem. Phys. Lett.* **1992**, 198, 555.
- 38 Cabrero, J., de Graaf, C., Bordas, E., Caballol, R., Malrieu, J.-P. *Chem. Eur. J.* **2003**, 9, 2307.
- 39 de P. R. Moreira, I., Illas, F., Calzado, C. J., Sanz, J. F., Malrieu, J.-P., Ben Amor, N., Maynau, D. *Phys. Rev. B* **1999**, 59, R6593.
- 40 Suaud, N., Lepetit, M.-B. *Phys. Rev. B* **2000**, 62, 402.
- 41 Munoz, D., Illas, F., de P. R. Moreira, I. *Phys. Rev. Lett.* **2000**, 84, 1579.
- 42 Petit, S., Borshch, S. A., Robert, V. *J. Am. Chem. Soc.* **2002**, 124, 1744.
- 43 Lindgren, I., Morrison, J. *Atomic Many-Body Theory*; Berlin, Springer-Verlag, 1982.
- 44 Daudey, J.-P., Heully, J.-L., Malrieu, J.-P. *J. Chem. Phys.* **1993**, 99, 1240.
- 45 de Loth, P., Cassoux, P., Daudey, J.-P., Malrieu, J.-P. *J. Am. Chem. Soc.* **1981**, 103, 4007.
- 46 Calzado, C. J., Cabredo, J., Malrieu, J. P., Caballol, R. *J. Chem. Phys.* **2002**, 116, 2728.
- 47 Calzado, C. J., Cabredo, J., Malrieu, J. P., Caballol, R. *J. Chem. Phys.* **2002**, 116, 3985.
- 48 Bartlett, R. J., Musial, M. *Rev. Mod. Phys.* **2007**, 79, 291.
- 49 Collins, T. J., Uffelman, E. S. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 1509.
- 50 Kostka, K. L., Fox, B. G., Hendrich, M. P., Collins, T. J., Rickard, C. E. F., Wright, L. J., Munck, E. J. *Am. Chem. Soc.* **1993**, 115, 6746.
- 51 Meyer, K., Bill, E., Mienert, B., Weyhermüller, T., Wieghardt, K. *J. Am. Chem. Soc.* **1999**, 121, 4859.
- 52 Grapperhaus, C. A., Mienert, B., Bill, E., Weyhermüller, T., Wieghardt, K. *Inorg. Chem.* **2000**, 39, 5306.
- 53 Wasbotten, I., Ghosh, A. *Inorg. Chem.* **2006**, 45, 4910.
- 54 Berry, J. F., Bill, E., Bothe, E., George, S. D., Mienert, B., Neese, F., Wieghardt, K. *Science* **2006**, 312, 1937.
- 55 Dutta, S. K., Beckmann, U., Bill, E., Weyhermüller, T., Wieghardt, K. *Inorg. Chem.* **2000**, 39, 3355.
- 56 Chaudhuri, P., Verani, C. N., Bill, E., Bothe, E., Weyhermüller, T., Wieghardt, K. *J. Am. Chem. Soc.* **2001**, 123, 2213.
- 57 Herebian, D., Bothe, E., Bill, E., Weyhermüller, T., Wieghardt, K. *J. Am. Chem. Soc.* **2001**, 123, 10012.
- 58 Herebian, D., Wieghardt, K. E., Neese, F. *J. Am. Chem. Soc.* **2003**, 125, 10997.
- 59 Bachler, V., Olbrich, G., Neese, F., Wieghardt, K. *Inorg. Chem.* **2002**, 41, 4179.
- 60 Sun, X., Chun, H., Hildenbrand, K., Bothe, E., Weyhermüller, T., Neese, F., Wieghardt, K. *Inorg. Chem.* **2002**, 41, 4295.
- 61 Beckmann, U., Bill, E., Weyhermüller, T., Wieghardt, K. *Inorg. Chem.* **2003**, 42, 1045.
- 62 Ghosh, P., Bill, E., Weyhermüller, T., Neese, F., Wieghardt, K. *J. Am. Chem. Soc.* **2003**, 125, 1293.
- 63 Ray, K., Petrenko, T., Wieghardt, K., Neese, F. *Dalton Trans.* **2007**, 1552.
- 64 Vicente, R., Escuer, A., Ribas, J., Solans, X. *Inorg. Chem.* **1992**, 31, 1726.
- 65 Julve, M., Lloret, F., Faus, J., De Munno, G., Verdaguer, M., Caneschi, A. *Angew. Chem. Int. Ed.* **1993**, 32, 1046.
- 66 Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortés, R., Lezama, L., Rojo, T. *Coord. Chem. Rev.* **1999**, 193–195, 1027.
- 67 Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortes, R., Lezama, L., Rojo, T., Goher, M. A. S. In *Magnetism: Molecules to Materials II: Molecule-Based Materials*; S., M. J., Drillon, M., Eds.; Wiley-VCH: Weinheim, 2002.
- 68 Manson, J. L., Arif, A. M., Miller, J. S. *Chem. Commun.* **1999**, 1479.

- 69 Liu, F.-C., Zeng, Y.-F., Jiao, J., Bu, X.-H., Ribas, J., Batten, S. R. *Inorg. Chem.* **2006**, 45, 2776.
- 70 Monfort, M., Resino, I., Ribas, J., Stoeckli-Evans, H. *Angew. Chem. Int. Ed.* **2000**, 39, 191.
- 71 Mautner, F. A., Cortes, R., Lezema, L., Rojo, T. *Angew. Chem. Int. Ed.* **1996**, 35, 96.
- 72 Bonnet, M.-L., Aronica, C., Chastanet, G., Pilet, G., Luneau, D., Mathonière, C., Clérac, R., Robert, V. *Inorg. Chem.* **2008**, 47, 1127.
- 73 Haldane, F. D. M. *Phys. Rev. Lett.* **1983**, 50, 1153.
- 74 Yamashita, M., Ishii, T., Matsuzaka, H. *Coord. Chem. Rev.* **2000**, 198, 347.