How to determine model Hamiltonians for strongly correlated materials

Marie-Bernadette Lepetit

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Marie-Bernadette LEPETIT
Laboratoire de Physique Quantique
Unité Mixte de Recherche 5626 du CNRS
IRSAMC
Université Paul Sabatier
118 route de Narbonne
F-31062 Toulouse
France

Abstract

The present paper reviews recent achievements on the ab initio determination of effective model Hamiltonians aimed at the description of strongly correlated materials. These models (Heisenberg, $t-J$, extended Hubbard, Kondo, etc) are crucial to solid state physicists for the description and understanding of the electronic remarkable properties such as magnetic orders, photo-induced magnetism, transport properties, high t_c super conductivity, etc. We will see how the association and the control of embedding techniques, fragment spectroscopy, effective or intermediate Hamiltonian theories, provides a systematic and well controlled method for the determination of trustworthy models Hamiltonians.

1. Introduction

Since the synthesis of the first organic conductors in the late 70s with the TCNQ-based compounds[1] and later the Bechgaard salts[2], the chemists have synthesized a large number of materials presenting new and remarkable electronic properties. Besides the organic and organometallic metals, to cite only a few among the most attractive systems of the last decades, one can remember the spin chains[3] and ladders[4], the copper-oxide high T_c super-conductors[5], manganites with giant magneto-resistance[6], photo-induced magnets[7], etc... These materials span a very large variety of structural arrangements, phases and physical properties. Indeed one can find among them molecular crystals, transition metals oxides, Prussian blue analogs, etc. They can be isotropic as well as present large anisotropies both in their properties and structural arrangement, from the cubic, 3D, isotropic photo-induced magnets, to the 2D, layered copper oxides or manganites, up to the quasi-1D stacks of the Bechgaard salts or oxides spin chains and ladders. These compounds present a wide variety of phases going from metals and super-conductors to semi-conductors, Peierls or spin-Peierls insulators, Mott insulators, charge or spin density wave insulators, they may present long range order such as anti-ferromagnetic ordering, have exponentially vanishing correlation functions, etc.

In view of this very large spectra of chemical compositions, structural arrangements and physical properties one may wonder what all these compounds have in common. In fact all these materials have in common an essential characteristic : the electrons responsible for their low energy physics are few (per unit cell) and localized both spatially and energetically. The spatial localisation of these, from now on called, *active* electrons induces a strong correlation between their relative positions ($\rho_2\left(\vec{r}_1,\vec{r}_2\,;\,\vec{r}'_1,\vec{r}'_2\right) \neq$

$\rho_1(\vec{r}_1\,;\,\vec{r}'_1)\,\rho_1(\vec{r}_2\,;\,\vec{r}'_2) - \rho_1(\vec{r}_1\,;\,\vec{r}'_2)\,\rho_1(\vec{r}_2\,;\,\vec{r}'_1)$, where ρ_2 is the two electrons density matrix and ρ_1 is the one electron density matrix) and the impossibility to describe their movement — even in a qualitative manner or at the zeroth order — by an independent electrons representation. These systems belong to the strongly correlated universality class and essentially mono-electronic methods such as tight-binding, mean-field approximations or even density functional methods fail to describe their electronic structure[8]. The *active* electrons are energetically localized close to the Fermi level and are thus responsible for the low energy properties of the materials. It is thus convenient to partition the electrons of these strongly correlated materials in a similar way as the usual core-valence separation in atoms. On can define 2 classes, the *core* electrons, essentially localized on the energetically deep, closed-shell orbitals of the basic entities (atoms or molecules according to the chemical nature of the crystal), and the previously cited *active* electrons supported by localized, partially-filled orbitals, presenting charge and/or spin fluctuations in the ground and low energy-excited states.

While in finite, small systems, the treatment at the ab-initio level of strong electron-correlation effects can be achieved in a satisfactory manner, in infinite systems this is still an essentially unsolved question. The difficulty is even larger when excited states are involved or thermodynamic properties seeked. In order to by-pass this problem and to understand the microscopic mechanisms underlying the spectacular properties of these materials, physicists have developed the usage of model Hamiltonians on the same bases than the semi-empirical models used by quantum chemists in the 50's and 60's[9] — Zero Differential Overlap (ZDO) approximation[10] and reduction to the dominant interactions — but with somewhat simpler expressions. Among the most famous models one can cite the spin models such as the Heisenberg-Dirac-Van Vleck models[11,12] for magnetic half-filled systems, the $t-J$ models[13] for doped magnetic systems, the Hubbard[14] and extended Hubbard models — simplified versions of the Pariser-Parr-Pople[9] approximation — that can describe metal-insulator phase transitions. A simple description of these models is given in the appendix.

The description and understanding of the electronic structure, low energy physics and the associated macroscopic properties of these materials is therefore achieved within a three steps procedure.

- The first step is the determination of an appropriate model. Such a model, aimed at describing the low energy physics of the material, must define the *active* electrons, the *active* orbitals and the form of the dominant interactions between them.
- The second step consists in the evaluation of the amplitude of these interactions. This evaluation can, in some well conditioned cases, be extracted from experimental data, however in most cases there is no unique and unambiguous way to determine such parameters from spectroscopy or thermodynamic properties measurements.
- The last step is devoted to the determination of the collective properties of an assembly of electrons on a lattice, described by the previously-defined, effective, local interactions .

We will see in this paper how it is possible to construct, step by step, a coherent procedure for the determination of trustworthy models describing the low energy physics of strongly correlated materials. We will also see how quantum chemistry can play a major role, both in the determination and validation of a model and in reliable evaluations of the effective interactions amplitudes. The last step is usually devoted to physicists since it requires the usage of specific analytical methods such as renormalisation theories-bosonisation[15], Bethe ansatz[16], etc as well as specific numerical methods such as Density Matrix Renormalisation Group (DMRG) methods[17], exact diagonalisations, Monte-Carlo, etc. It aims at the determination of the macroscopic order from the microscopic effective model. It is however fascinating to follow the whole process and understand the intrinsic link between the local chemical structure of the materials and their macroscopic properties.

2. Requirements for a *good* model

Before any discussion on how to built an accurate and reliable model for strongly correlated materials one should examine what means *good*, *accurate* and *reliable*, that is what do we expect from such a model. The model is supposed to fulfill several properties that can be ordered into three

sets : the formal properties, the physics we would like to reproduce and the transferability of the interactions.

2-A. Formal properties

These requirements are quite obvious and have already been mentioned. They can be summarized as

- Hermiticity of the model Hamiltonian.
- Small number of electrons and basis set orbitals per unit cell.
- Small number of basic interactions.

2-B. Modeling the low energy physics

The final aim of the model is to be able to produce a reliable representation of the low energy physics and the properties of the material, that is to be able to described and interpret not only phase transitions but also experimental results such as low energy spectroscopy, low energy photo-emission or photo-absorption, NMR, X-ray or neutron diffraction, magnetic susceptibility, conductivity, etc. We therefore need not only an accurate reproduction of the first excitation energies but also accurate reproduction of the associated wave-functions. In particular it is crucial to well reproduce the charge and spin arrangements as well as the relative weight of the major configurations in the ground and low energy excited states. This means for instance, to reproduce accurately the ratio between the coefficients of the Valence-Bond (VB) neutral and ionic configurations, of the different spin arrangements within the neutral configurations, etc. Such requirements on the wave function suppose that

- the low energy states we would like to reproduce (let us call them the target states $|\Psi_i\rangle,\ i = 1 \cdots m_t$) are clearly defined (for instance states essentially based on neutral Valence Bond configurations) and based on a small set of common active orbitals,
- the projection of the exact target states wave functions onto the vector space supporting the model Hamiltonian (called the active space from now on, P being its projector operator) should be large (one should notice that there is no requirement for the active space to be complete)
- the exact target states excitation energies ($\varepsilon_i,\ i = 1 \cdots m_t$) should be well reproduced by the model hamiltonian eigenvalues (ϵ_i) or a convenient subset of them,
- the model Hamiltonian eigenstates (noted $|\xi_i\rangle,\ i = 1 \cdots m_a,\ m_a \geq m_t$), or a subset of them should mimic the projection of the target states onto the active space, that is in the ideal situation

$$\forall i = 1 \cdots m_t, \quad |\xi_i\rangle = P|\Psi_i\rangle / \sqrt{\langle \Psi_i | P | \Psi_i \rangle}$$

2-C. Locality of the interactions

As already mentioned, the model Hamiltonians are defined on a basis set of local active orbitals and thus the microscopic interactions are local, involve only a small number of electrons and a small number of centers, usually one or two. Let us cite for instance, the one-electron, two-centers hopping integral (as in the $t - J$ or extended Hubbard models) or the two-electrons, two-centers super-exchange integral (as in the $t - J$ or Heisenberg Hamiltonians). One should however point out that the concepts of *center* or *site* are not necessarily synonymous of *atom*, but rather the expression of the basic building block participating to the low energy physics of the system. For supraconducting copper oxides for instance, a center will be a copper atom, the oxygens and other atoms being excluded from an explicit representation in the model. For molecular crystal a center will be the whole building molecule (such as TMTSF[36], TCNQ[37], etc) and its HOMO and/or LUMO will be the localized active orbitals supporting the low energy physics of the materials. The concept of locality can thus refer to fairly large units from the molecular point of view but of size always inferior to the unit cell and therefore localized from the crystal point of view. The locality assumption has the immediate and important consequence that the interactions do not depend of the number of explicit active centers and that, provide a set of orbitals and associated energies, a n-centers interaction will act in a finite system in the same way as in an infinite one. This property is usually called transferability. The hopping or the exchange integrals can, for instance, be defined from the low excitation energies of a two centers system. The exchange integral is the singlet triplet energy difference in a two active electrons system and the hopping integral is half the symmetric versus an-

tisymmetric doublet energy difference, in a single active particle system.

The exchange integral J_{ab}
2 $\bar{e}$ - 2 orb. - 2 sites

$$\begin{array}{cc} \uparrow & \downarrow \\ \bullet & \bullet \\ a & b \end{array}$$

$$\mathbf{J_{ab}} = E(sg) - E(tp)$$

Hopping integral t_{ab}
1 $\bar{e}$ - 2 orb. - 2 sites

$$\begin{array}{cc} \uparrow & \\ \bullet & \bullet \\ a & b \end{array}$$

$$\mathbf{t_{ab}} = \left(E(db_+) - E(db_-)\right)/2$$

Despite their local definition in the model Hamiltonians scheme, it is clear that these interactions are *effective* and one should wonder whether they are truly local or whether they do involve in an effective manner non local mechanisms. This is the question behind the transferability problem. Its answer is crucial for the determination of reliable models. Indeed, without the assurance of a true locality of the interactions the whole model hamiltonian scheme fails. The derivation of the macroscopic properties of an infinite lattice is based on the idea that this infinite system is the limit of increasing large size finite systems. The implicit hypotheses behind it are that the interactions involve a finite and small number of bodies and that their nature and amplitude do not change when the system size increases, i.e. they are perfectly transferable. The effective inclusion of non local mechanism is incompatible with these hypotheses since it would render the effective integrals dependent on the system size.

One should however remember that the exact Hamiltonian can always be expressed in an atomic basis set where all interactions are local and transferable. The non locality of a model Hamiltonian can therefore always be fixed by an appropriate modification of the model, usually consisting in the addition of longer range interactions, interactions involving a larger number of centers or an enlarged definition of the active space. The transferability property is therefore an useful tool for the verification of the model pertinence. A model which is not transferable usually neglects the explicit treatment of an important physical effect and the transferability is restored by the inclusion of the omited mechanism within the model Hamiltonian. The whole process is however limited by the complexity of the final model, the number of basic interactions and the number of bodies involved in it.

3. Locality of effective interactions

In this section we will investigate the locality problem for the major types of effective interactions found in model Hamiltonians, namely hopping, exchange and repulsion. In this analysis we will suppose that the orbital space has been partitioned into the

core orbitals , these orbitals are essentially doubly-occupied in the target states and support the inactive electrons, explicit reference to them is usually omitted in the model Hamiltonian,

active orbitals , they support the active electrons responsible for the low energy physics, these orbitals are supporting the model Hamiltonian and have fluctuating occupation and/or spins in the target states,

virtual orbitals , these orbitals are essentially empty in the target states and omitted in the model.

The above orbital basis set will be supposed to be local, orthogonal and the orbitals composition (as can be given by their expansion on the atomic orbitals basis set) and energies already defined. We will come back later on the problem of these orbital and orbital energies definitions and analyze the non-locality contained in it. This partition of the all electrons basis set is crucial and will be refered at all over this paper.

The effective integrals can be decomposed (using the above partition of the orbitals basis set) into a *zeroth-order* part corresponding to the exact Hamiltonian integrals within the active space, and a higher order part that takes effectively into account the effect of the configurations out of the active space. It is in this higher order part that non local mechanisms may be introduced through long-range dynamical polarisation or correlation effects.

We will start by the analysis of the effective bi-electronic integrals since their case is somewhat simpler than for the mono-electronic ones.

3-A. The effective exchange integrals

The effective exchange integrals appear in magnetic models such as the Heisenberg or $t-J$ Hamiltonians. These models are suited for the description of very strongly correlated systems where the on-site bi-electronic repulsion is so high that the explicit reference to configurations where an active orbital is doubly occupied can be excluded from the model. The essential role of the effective exchange integrals is therefore to take into account the effects of these double occupancies on the interactions between neutral Valence-Bond configurations, that is to position properly the local singlet to triplet excitation energy between two nearby centers.

Within the complete configurations space defined from the active orbitals (CAS), Anderson[18] has clearly detailed this mechanism and provided a perturbative expression of the effective super-exchange integral J_{ab} (see figure 1)

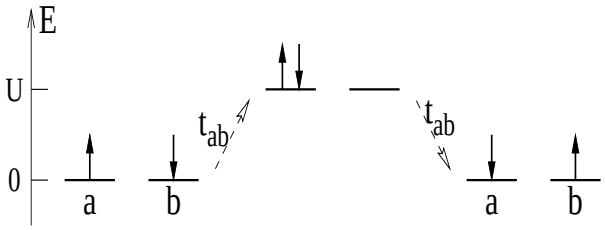

FIG. 1: Anderson super-exchange mechanism

$$\begin{aligned} J_{ab} &= -4\frac{\langle a\bar{b}|H|a\bar{a}\rangle^2}{E\left(|a\bar{a}\rangle\right) - E\left(|b\bar{b}\rangle\right)} \\ &= -4\frac{t_{ab}^2}{U} \end{aligned}$$

where t_{ab} is the hopping between the magnetic orbitals a and b and U is the Coulomb repulsion integral when a magnetic orbital is doubly-occupied.

Things are a little more complicated when the exchange mechanism is not direct but through a chemical bridge. This is for instance the case in most transition metal oxides where the super-exchange interaction between two d orbitals of nearby metal atoms is mediated through the oxygen atom(s). In this case the leading perturbative term comes at the fourth order and two different mechanisms add (see figure 2).

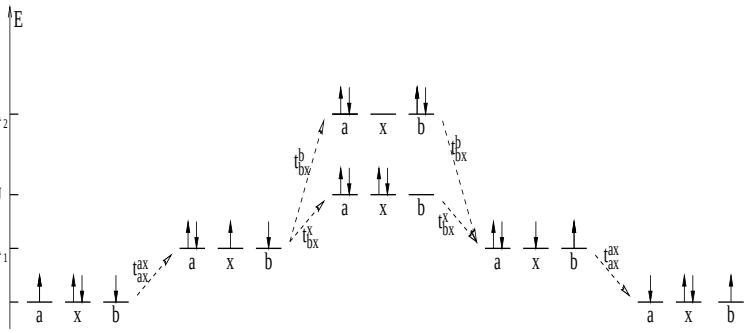

FIG. 2: Through-bridge super-exchange mechanism. In this example we supposed that the process goes through the occupied orbitals of the bridge, represented by x. It may also go through the unoccupied orbitals or both.

$$J_{ab} = -4\frac{\left(t_{ax}^{ax}\right)^2\left(t_{bx}^{x}\right)^2}{\left(\Delta_1\right)^2 U} - 8\frac{\left(t_{ax}^{ax}\right)^2\left(t_{bx}^{b}\right)^2}{\left(\Delta_1\right)^2 \Delta_2}$$

where

$$\begin{aligned} t_{bx}^{x} &= \langle x\bar{x}|H|x\bar{b}\rangle \text{ is the hopping between orbitals } b \text{ and } x \text{ with a spectator electron on } x \\ t_{bx}^{b} &= \langle b\bar{x}|H|b\bar{b}\rangle \text{ is the hopping between orbitals } b \text{ and } x \text{ with a spectator electron on } b \\ t_{ax}^{ax} &= \langle ax\bar{x}|H|ax\bar{a}\rangle \text{ is the hopping between orbitals } a \text{ and } x \text{ with two spectators electron on } a \text{ and } x \\ \Delta_1 &= E\left(|ax^2\bar{b}\rangle\right) - E\left(|a^2x\bar{b}\rangle\right) \\ U &= E\left(|ax^2\bar{b}\rangle\right) - E\left(|a^2x^2\rangle\right) \\ \Delta_2 &= E\left(|ax^2\bar{b}\rangle\right) - E\left(|a^2b^2\rangle\right) \end{aligned}$$

It should be noted that the second path goes through a configuration where the doubly-occupied orbital of the bridge has been totally emptied (or totally doubly-occupied if the process goes through the unoccupied orbitals of the bridge). Such a configuration is usually very energetic and its contribution negligible in front of the first path. In that case the through-bridge super exchange integral can again be written in an Anderson's form $J_{ab} = 4t_{ab}^2/U$ provided that an effective, through-bridge, hopping integral t_{ab} between the two magnetic orbitals is defined as (see figure 3)

$$t_{ab} = \frac{t_{ax}^{ax} t_{bx}^{x}}{\Delta_1}$$

It is clear that all these processes included in the effective exchange integral are totally local. Dynamical polarisation or correlation processes that

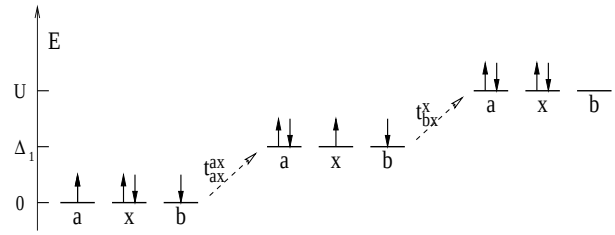

FIG. 3: Through-bridge hopping mechanism. In this example we supposed that the process goes through the occupied orbitals of the bridge, represented by x. It may also go through the unoccupied orbitals or both.

may act on top of the them (for a review of all diagrams contributing to the unbridged super-exchange mechanisms at the second order of perturbation see ref.[19]) remain local as long as they involve only orbitals located on the magnetic or neighboring atoms, including the possible bridge. The only possibility to include non-local contributions is therefore the dynamical polarisation and correlation processes where the excitations take place on a center far from the magnetic orbitals. The leading contributions of such terms (second order of perturbation) correspond to the super-exchange plus polarisation diagrams in the DeLoth denomination[19] (see figure 4)

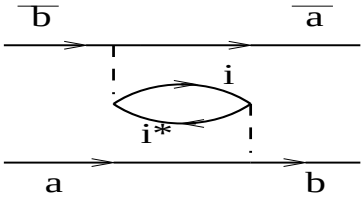

FIG. 4: Leading non local contributions to the exchange effective integral. i and i^* are respectively occupied and vacant orbitals on a distant site.

The corresponding perturbative contribution is

$$-\frac{\langle i\bar{b}|\frac{1}{r_{12}}|i^*\bar{a}\rangle\langle i^*a|\frac{1}{r_{12}}|ib\rangle}{\Delta E}$$

which varies as a function of the distance R between the magnetic distribution ab and the distant local excitation ii^* as a dipole-dipole interaction, that is as $1/\left(R^3\right)^2 = 1/R^6$.

One can therefore reasonably consider that these non-local contributions are negligible and that the exchange effective integral is really local. This locality property has been numerically verified by Illas and coworkers[20] from ab-initio calculations on a variety of compounds such as the KMF_3 and K_2MF_4 (M = Cu, Ni) family or hight T_c perovskites.

3-B. The effective coulomb repulsion integrals

The effective coulomb repulsion terms act on the diagonal of the effective Hamiltonian. They correspond to screened bi-electronic repulsions. This is through this screening that non local effects may occur.

The screening that may come from the active electrons is treated explicitly in the model Hamiltonian, for instance through hybridisation and delocalisation processes, and therefore do not contribute to the effective repulsion integral. It remains the dynamical polarisation and correlation effects.

The main non-local contributions come from dynamical correlation effects through double-excitations from two core orbitals towards two virtual ones. However, these excitations yield equal contributions (at the second order of perturbation) to all VB configurations in the active space and give only a shift in the definition of the model Hamiltonian zero of energy. Thus they are non pertinent and can be omitted.

The remaining leading non-local contributions come from distant single-excitations. For the sake of simplicity, we will suppose that the core (i) and virtual (i^*) orbitals are eigenvectors of the core Fock operator (as defined from the antisymmetrized product of all doubly-occupied core orbitals). The leading term comes therefore from the coupling between the ($i\,i^*$) distant distribution and the local ($a\,\bar{a}$) distribution (if the two electrons are on the same orbital), ($a\,\bar{b}$) or ($a\,b$) distributions (if the two electrons are on different orbitals). See figure 5).

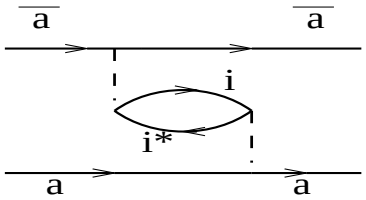

FIG. 5: Leading non local contribution to the on-site effective repulsion integral between two electrons in the same orbital. i and i^* are respectively occupied and vacant orbitals of the distant excitation

In the case where the effective repulsion integral acts between two electrons in the same orbital, the leading non-local contributions are at the second

order contribution

$$-\frac{\langle i\bar{a}|\frac{1}{r_{12}}|i^*\bar{a}\rangle\langle i^*a|\frac{1}{r_{12}}|ia\rangle}{\Delta E}$$

This terms vary as a function of the distance R between the $a\bar{a}$ distribution and the distant excitations ii^* as a charge to dipole interaction, that is as $1/\left(R^2\right)^2 = 1/R^4$.

When the repulsion integral acts between two electrons in different orbitals, this dominant non-local contributions vary as a dipole-dipole interactions, that is as $1/\left(R^3\right)^2 = 1/R^6$.

The non-local contributions to the repulsion integrals vary therefore either as $1/R^4$ or as $1/R^6$, that is fast enough to consider that these effective integrals are essentially local.

3-C. The effective hopping integrals

The case of hopping integrals or other mono-electronic integrals (such as orbital energies for instance) is somewhat more complicated. Indeed in their zeroth-order description (projected exact Hamiltonian in the active space) these integrals are coupled to the Fock operator, that is both to the nuclear and the electronic charge repartition on the entire system. It is clear that, through this coupling, the mono-electronic integrals are non local. However, once provided the definition of the orbitals (core, active and virtual), their composition in terms of the atomic orbitals and their energies, the other contributions to the hopping integrals can be analyzed as was done for the super-exchange or repulsion integrals. Let us decompose the problem into three terms, the first term is the coupling with the core orbitals (and the corresponding charge density of the entire system) through the Fock operator, the second term is contributions from the active orbitals, the third term is the excitations out of the active space that are included in an effective manner.

The first term is totally defined by the Fock operator. The problem intrinsically depends upon the average charge repartition on the entire system and is solved by the definition of the orbitals themselves through a self-consistent, mean-field approximation. This is the major non local contribution and its consequences is that the infinite system is never really treated as the limit of *true* large but finite system — since the edge effects should not be taken into account in the orbitals and orbital energies definitions. A proper definition of the orbitals therefore suppose that the finite systems are in fact embedded in a mean field approximation of the rest of the crystal.

The second term reminds us that the hopping integrals are dependent on the specific configurations they act upon. For instance the transfer of an electron on a bond depend on the number and the nature of the spectators (active) electrons on it.

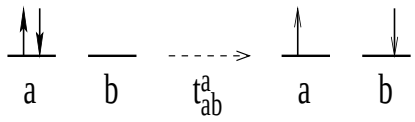

FIG. 6: t^a_{ab} hopping with a spectator electron in a.

$$\begin{aligned} t^a_{ab} &= \langle a\bar{a}|H|a\bar{b}\rangle \\ &= \langle \bar{a}|H|\bar{b}\rangle + \langle a\bar{a}|1/r_{12}|a\bar{b}\rangle \end{aligned}$$

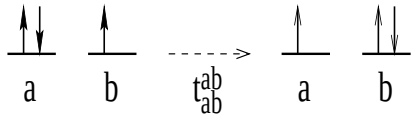

FIG. 7: t^{ab}_{ab} hopping with two spectator electrons in a and b.

$$\begin{aligned} t^{ab}_{ab} &= \langle ab\bar{a}|H|ab\bar{b}\rangle \\ &= \langle \bar{a}|H|\bar{b}\rangle + \langle a\bar{a}|1/r_{12}|a\bar{b}\rangle + \langle b\bar{a}|1/r_{12}|b\bar{b}\rangle \end{aligned}$$

The hopping integrals therefore depend upon the distant active space charge distribution of the configurations they act on. The corresponding contributions vary as $\langle xa|1/r_{12} - xb\rangle$, that is as $1/R^2$ if R is the distance between the (ab) and the distant (xx) distributions. This dependence should be explicitly include in the model hamiltonian definition. However, despite its rather slow decrease with R, it is usually ignored, except may be for the dependence to the occupation of the orbitals localized on the same sites as a and b.

The third term contributions are included in an effective manner. Their leading non-local processes come from distant single-excitations acting on the transfer, as shown in figure 8.

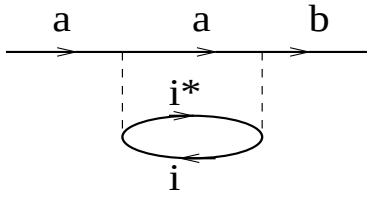

FIG. 8: Leading non local dynamical contribution to the effective hopping t_{ab}.

The Fock operator being defined as previously, the perturbative expression of the dominant is

$$- \frac{\langle ai|1/r_{12}|ai^*\rangle\langle ai^*|1/r_{12}|bi\rangle}{\Delta E_a}$$
$$- \frac{\langle ai|1/r_{12}|bi^*\rangle\langle bi^*|1/r_{12}|bi\rangle}{\Delta E_b}$$

which varies as $1/R^2 \times 1/R^3 = 1/R^5$, that is fast enough to be considered as a non-significant source of effective non-local processes.

As a summary the major types of interactions encountered in model Hamiltonians are essentially local in nature, provided that the coupling to the average charge repartition of the entire crystal (which is the major non-local mechanisms) is treated through a proper definition of the orbitals and orbital energies. It is therefore pertinent to evaluate the interactions amplitudes and check a model validity by ab-initio calculations on properly embedded fragments. Such a technique presents a lot of advantages.

- All short range effects can be explicit and accurate treated by the inclusion of the active sites local environment in the computed fragment.
- The dynamical processes that strongly affect the values of the effective interactions can be accurately evaluated. Indeed, it is possible to use large atomic basis set and up-to-date quantum chemical methods for the fragment spectroscopy.
- One has access not only to the local excitation energies but also to the associated wave functions. In particular the knowledge of the relative contributions of the major active space VB configurations is determinant for the good reproduction of the material properties by the model.

The question of the embedding is therefore crucial, as it determines the composition of the orbitals (core, active and virtuals) as well as their energies.

4. How to built a *good* bath

According to the previous analysis a *good* embedding should be such that the fragment orbitals and their energies are similar to what they would be in the crystal. Reaching this goal necessitates that the effects of the rest of the crystal on the fragment are properly reproduced. These effects may be partitioned into long range effects and short range effects.

The previous analysis showed us that the major long range effects are mono-electronic, comes through the Fock operator definition and more specifically through the coupling to the entire system average charge repartition. Considering that these strongly correlated systems are most of the time ionic, this term is large and corresponds to the Madelung potential. It can be easily reproduced by a set of positive and negative charges respectively positioned at the location of the cations and anions of the rest of the crystal. The volume involved should be large enough and centered on the fragment. Border charges can be adapted according to the Evjen procedure in order to increase the potential convergence.

The short range effects of the rest of the crystal on the fragment are essentially exclusion effects. They come from the orthogonality requirement of the fragment orbitals to the orbitals of the rest of the crystal. This effect is crucial since in the vacuum the orbitals of the fragment — which is often highly negatively charged — have a tendency to extend far out of the fragment volume, in region of space where the other electrons of the crystal should be located. It is therefore necessary to forbid these domains of $\mathcal{R}^3$ by a repulsive potential mimicking the electronic volume of the atoms of the rest of the crystal. This aim can be reached by the usage of total ions pseudo-potentials[21] at the location of the first shells neighboring atoms of the fragment.

Since all these embedding effects are mono-electronic they can be easily checked. Indeed, they are included in a simple Hartree-Fock (HF) calculation thus a good embedding should reproduce the HF density of states of the entire crystal, projected onto the fragment atomic orbitals.

4-A. Example : the $\alpha' NaV_2O_5$ compound

As an example of the importance of the embedding on the orbitals definitions and orbitals energies[22] we will discuss the case of the $\alpha' NaV_2O_5$ compound. $\alpha' NaV_2O_5$ is a ionic layered compound built from VO_5 square-pyramids arranged in (a, b) planes (see figure 9) and doped by sodium ions located between the layers.

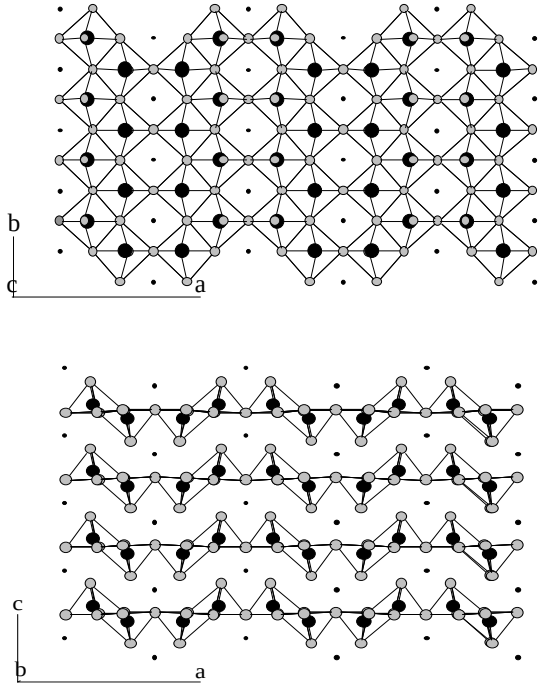

FIG. 9: Schematic structure of $\alpha' NaV_2O_5$, along the a-b and the a-c planes. The oxygen atoms are denoted by open circles, the vanadium atoms by filled circles and the sodium atoms by dots.

The compound is strongly ionic and the formal charge transfer yields a formula of $Na^+ (V_2)^{9+} (O^{2-})_5$. The vanadium atoms support therefore one unpaired electron for two magnetic sites. It has been shown that the different layers are very weakly coupled and that the electronic structure can be considered as two dimensional[23]. In fact most authors see the compound as coupled, quarter-filled (one active electron for two active orbitals), magnetic ladders (see figure 10).

Let us concentrate, for instance, on the interactions of the magnetic electrons on a rung of the ladders (for an ab initio evaluation of the different interactions in the high temperature phase see ref.[24], in the low temperature phase see ref.[25] and for an ab-initio evaluation of the charge ordering ref.[26]). They are of two types, hopping and superexchange. They can be evaluated by the spectroscopy of an embedded fragment composed of two VO_5 pyramids sharing a corner oxygen (see figures 11 and 12).

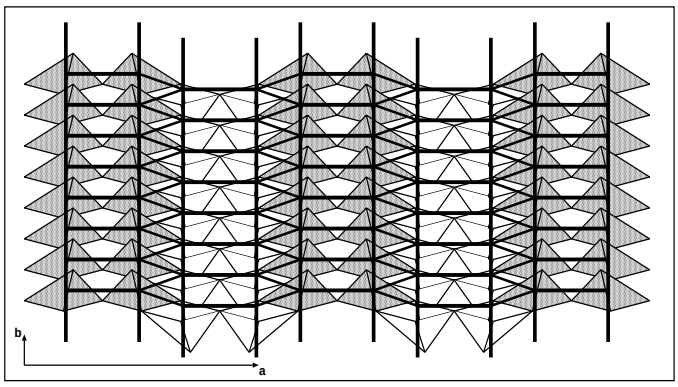

FIG. 10: Schematic structure of the coupled magnetic ladders in the (a,b) plane.

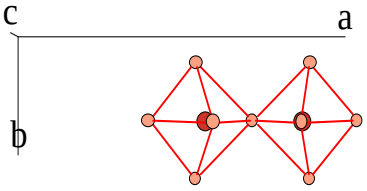

FIG. 11: Fragment of the crystal used for the cluster calculations of the interactions along a rung seen in the (a, b) plane.

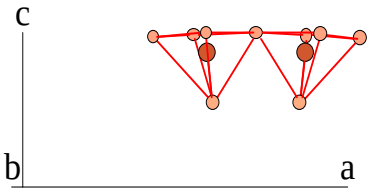

FIG. 12: Fragment of the crystal used for the cluster calculations of the interactions along a rung seen in the (a, c) plane.

We can therefore check the importance of the embedding on the orbitals definitions and orbitals energies by the comparison of the density of states (DOS) of the entire crystal (as computed from periodic HF techniques[27]), the density of states of the isolate fragment and the density of states of the fragment embedded in different baths. For sake of clarity we will project the DOS on the most important orbitals for the effective hopping and exchange interactions, namely the magnetic orbitals of the vanadium atoms ($3d_{xy}$ if x, y, z refer respectively to the crystallographic orthogonal a, b, c directions) and the $2p_y$ orbital of the bridging oxygen that mediate the interactions. Figure 13

and figure 14 report respectively the different projected DOS on the magnetic and bridging orbitals. One can see immediately that the isolated fragment DOS is very different from the infinite crystal one. In fact, while the highest occupied crystalline bands are built from the d_{xy} atomic orbitals of the vanadium atoms, in accordance with the magnetic character of this orbital, in the isolated fragment the molecular orbital based on the vanadium $3d_{xy}$ is far above the Fermi level, the unpaired Highest Occupied Molecular orbital being a delocalized orbital on the $3p$ orbitals of the vanadium and the $2p$ orbitals of different oxygen atoms. The embedding built from atomic formal charges ($V^{4.5+}$, O^{2-} and Na^{+}) is properly reproducing the DOS projected on the oxygen $2p_y$ bridging orbital, however it is unable to reproduce the crystal DOS projected on the magnetic orbitals. An orbital analysis of the different embedded fragments and crystal calculations shows that the apical oxygen is not linked to the vanadium by an ionic bond but that a strong, dative, triple bond is taking place between these two atoms. The consequence is a strong deviation of the Madelung potential from the one defined by formal charges. A redefinition of the bath using approximate self-consistent Mülliken charges on the vanadyle, that is V^{3+} and $O^{0.5-}$ finally yield a proper reproduction of the DOS projected on all the orbitals of the fragment, insuring a reliable taking into account of the non-local crystal effects.

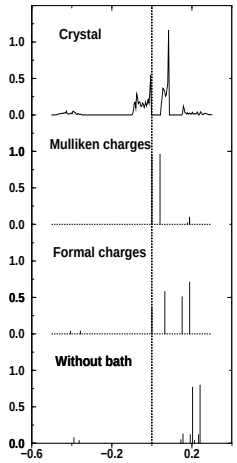

FIG. 13: Density of states projected on the magnetic d_{xy} orbitals of the rung vanadium atoms[22].

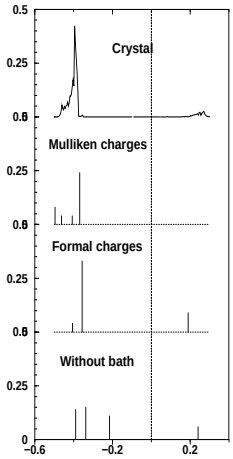

FIG. 14: Density of states projected on the $2p_y$ orbital of the rung bridging oxygen atom[22].

Let us now take a look at the importance of these embedding problems on the effective integrals amplitudes, namely the hopping $t_\perp$ integral of a magnetic electron between the two vanadium atoms of the rung, and the super-exchange $J_\perp$ integral of two magnetic electrons on the rung. As seen previously, these integrals can be defined from the fragment spectroscopy as half the symmetric versus antisymmetric doublet excitation energy for the hopping ($t_\perp = 1/2\,[E(D_g) - E(D_u)]$), and as the singlet versus triplet excitation energy for the exchange ($J_\perp = E(Sg) - E(Tp)$). We shall not describe here the computational technique used for these spectroscopic calculations since the next section will be devoted to this problem. Table 1 integrals both for the formal charges and the Madelung charges embeddings. One can see immediately that a small change in the dipole moment of the vanadyle fragment ($V^{4.5+}O^{2-}$ in the formal charges bath, $V^{3+}O^{0.5-}$ in the so-called Mülliken charges bath) can considerably modify the effective integrals amplitudes, since $J_\perp$ is multiplied by a 1.73 factor between the two calculations.

Integral	Mulliken charges	Formal charges
$J_\perp$	-293.5 meV	-509.7 meV
$t_\perp$	-538.2 meV	-581.2 meV

TABLE 1. Hopping and super-exchange effective integrals of magnetic electrons between the two vanadium sites of the rung according to the nature of the embedding[22].

5. Fragment spectroscopy

The fragment embedding being properly defined, the question is now how to computed accurate excitation energies and related wave-functions. The question is far from trivial since the total energies of the computed states are usually of the order of $10^3 eV$ while the seeked transition energies are of the order of a few tenth up to a few tens of meV, that is from 5 to 7 orders of magnitude smaller. Even the correlation part of the energies are of the order of a few tens of eV which is still between 3 to 5 orders of magnitude larger than the seeked excitations energies. Reliable results therefore necessitate procedures that calculate identically the major part of the total energies. This can only be achieved if a common set of unbiased orbitals is used for the different states involved in the excitation, whether they do belong to the same irreducible symmetry representation (space and spin) or they do not.

A zeroth-order description of these seeked target states can be obtained using a CASCI[38] calculation. The main question is the choice of the

set of orbitals supporting the CAS space. While it is obvious that the active orbitals (as defined in sections 3 and 1) should belong to this set, one may wonder whether it should be restricted to them. The question is specially crucial in the case of bridged systems where the interactions are mediated by a ligand and the question of including in the active space the mediating orbitals of the bridge (denoted as x) should be asked. The answer depends on the weight — in the target states — of the configurations involving a partial occupation of x ; that is different from 2 if x is a core orbital and different from 0 if x is a virtual one. If large, the mediating orbitals x should be included into the set supporting the CAS. In such cases, one may wonder whether the definition of the active orbitals supporting the model shouldn't be enlarged accordingly. Independently of the definition of the CAS for the ab-initio calculations, the answer to this question and accordingly the validity of the model and related active orbital space definitions, can be checked using a simple criterium : the norm of the projection onto the active space supporting the model Hamiltonian, of the computed target states wave functions. A large value (≥ 0.7) of this projection insures a correct definition of the model while a small value is the sign that an important physical effect have been omitted.

While the CAS is a good reference description, it is well known that a CASCI calculation is far from yielding accurate excitation energies. Indeed it is missing not only the dynamical correlation effects, but also the space and spin repolarisation effects specific to the different VB configurations (dynamical polarisation), which are known to be crucial both for a proper treatment of charge delocalisation[28] and for correct relative weights of the different VB configurations (in particular the ionic ones) in the active space[29]. This last point is of great interest since it discards all computational methods which do not allow a revision of the relative weights of the different VB configurations within the CAS, in perspective of the dynamical polarisation effects. This is the case for instance of the perturbative methods after a CAS zeroth order. They necessitate large CAS including the major part of the repolarisation effects in the zeroth order wave function in order to give accurate results[30].

As a matter of illustration table 2 reports the evaluation of the effective exchange and hopping integrals on the rung of the $\alpha' NaV_2O_5$ compound computed both at the CASCI (the CAS being supported by the magnetic orbitals and the mediating orbital of the bridging oxygen) and the CASCI + all single excitations on all CAS determinants (zeroth-order + dynamical polarisation) levels. One notices immediately that the effective integrals are dramatically modified by the inclusion of the dynamical polarisation effects. Indeed their inclusion increases the super-exchange integral by a factor $\simeq 5.3$ and the effective hopping by a factor of $\simeq 1.3$. One may however wonder why this repolarisation effect is so much stronger on the exchange integral than on the hopping. At the simplest level of description, the hopping involves a charge fluctuation between the two magnetic sites, thus strong changes in the electrostatic potential. An accordingly strong dynamical polarisation response can be expected. On the contrary the exchange integrals involves only spin field modifications which is usually expected to yields much smaller repolarisation effects. This apparent contradiction can be levelled if one remembers the through-bridge super-exchange mechanism shown in figure 2. While the through-bridge hopping mechanism involves only paths going through configurations with a $1\bar{e}$ occupation change (relative to the references) of the bridging orbital x, the exchange mechanism involves not only similar paths, but also paths where the bridging orbital occupation is modified by $2\bar{e}$. This is these paths that induce extremely strong specific repolarisation effects. Indeed, in the present case this last path carries half of the effective exchange amplitude explaining the observed much stronger repolarisation effects than on the hopping integral.

Integrals	CASCI	CASCI + singles	CASCI + singles + diff. doubles
$J_\perp$	-60.6	-321.1	-293.5
$t_\perp$	-420.6	-542.7	-538.2

TABLE 2. $\alpha' NaV_2O_5$. Effective exchange and hopping integrals between the magnetic d_{xy} orbitals of the two vanadium atoms of the rungs[24]. The calculations have been performed using the IDDCI$_n$ approach.

Comparatively the dynamical correlation effects due to the double-excitations on the CAS determinants have much smaller contributions (in general of the order of 10% to 20%[31] and much smaller in the present example). I would like to point out that while the large majority of the double-

excitations on the CAS involve excitations from two core orbitals towards two virtual orbitals, these excitations do not significantly contribute to the excitation energies between two CAS-based states. In fact they exactly cancel out in a second order perturbative approach. It can therefore be a wise solution to consider only the differential double-excitations, that is only the double-excitations that contribute to the energy differences at the second order of perturbation. This is what is done in the Difference Dedicated Configuration Interactions method of Malrieu *et al*[32].

One should however notice that in the presented results the bridging orbital have been included in the CAS and that the crucial bridge polarisation and correlation effects are included in the single and double-excitations to the CAS. Whether the CAS should be restricted to the only magnetic orbitals, than triple-excitations to the CAS should be considered in order to treat these effects.

6. From the ab initio wave function to the model Hamiltonian

In the simplest cases — which are the most numerous — the knowledge of the excitation energies is necessary and sufficient to determine the integrals amplitudes of the model hamiltonian. This is for instance the case for the effective exchange integral between 1/2 effective spins (as was largely discussed in section 2) or for the effective hopping between sites, if they are not equivalent by the space symmetry operations. However things can be sometimes more complicated. Typically one may encounter two types of difficulties.

- The problem may be over-determined.
  This is for instance the case for an effective spin-1 Heisenberg model. Such models are particularly adequate for the description of magnetic systems where the magnetic sites support two unpaired electrons in (quasi-) degenerate, strongly correlated, orbitals. The Hund's rule imposes a triplet coupling of these two electrons and, under certain conditions[33], they can be modeled by an effective spin-1. The interaction between two such spin-1 yields a set of singlet, triplet and quintet states, which wave functions are totally defined by the spin symmetry, and energy differences by the effective exchange parameter J. One therefore has *two* computed target states excitation energies (singlet to triplet, $\Delta E_{sg\to tp}$, and singlet to quintet, $\Delta E_{sg\to qt}$) that have no reasons to strictly follow the spin-1 Heisenberg hamiltonian eigenvalues relationships ($\Delta E_{sg\to tp} = J$, $\Delta E_{sg\to qt} = 3J$), and only *one* parameter (J).

- The problem may be under-determined.
  This is for instance the case for a hopping problem between non-equivalent sites : the excitation energy between the two doublet states is not sufficient to determine both the inter-site hopping and the energy difference between the two active orbitals. In such cases, it is necessary to use the wave functions information.

- More generally in systems for which the states are not totally determined by the space or spin symmetry, the energy differences are not sufficient for the complete and accurate determination of the effective model. Since the excitation energies cannot provide the necessary wave function information, it is impossible to meet the requirement of a good reproduction of the wave-functions physical content.

According to the types of difficulties encountered, several solutions can be proposed that will be detailed in the next sections.

6-A. Least square fit

In the case of an over-determined problem, one may choose to abandon the reproduction of some target states and to reduce the objectives of the model to the accurate description of a smaller set of selected states. Part of the model hamiltonian eigenstates will thus be present in the model only as a purpose of completion or in order to allow the sufficient flexibility to reach the seeked accuracy on the selected states. A detailed analysis of this option will be given later on.

An alternative choice can be to abandon the exact reproduction of the ab initio data and rather to model them *at the best* using a least square fit technique. This method has the advantages to describe equally well (or bad) the whole set of target states. The aim is to fit, simultaneously and on an equal footing, the computed energies and target states projections. One will thus apply the least square fit on the eigen-equations of the model

hamiltonian (H_{mod}). In a first approximation the Lagrangian can be defined as

$$\mathcal{L} = \sum_i |H_{mod}P|\Psi_i\rangle - \varepsilon_i P|\Psi_i\rangle|^2$$

or equivalently

$$\mathcal{L} = \sum_i \sum_\alpha (\langle\Phi_\alpha|H_{mod}P|\Psi_i\rangle/\langle\Phi_\alpha|P|\Psi_i\rangle - \varepsilon_i)^2$$

where $|\Psi_i\rangle$ and ε_i are respectively the computed target states wave functions and energies, $P = \sum_\alpha |\Phi_\alpha\rangle\langle\Phi_\alpha|$ is the active space projector and $|\Phi_\alpha\rangle$ are the VB configurations acting as basis set of the active space. The minimisation of $\mathcal{L}$ runs on the parameters of H_{mod}. The strict usage of the above formulation presents however some drawbacks.

- The total energies have no real signification and only the excitation energies have a physical meaning. One should therefore use only eigen-equations differences in the Lagrangian.
- The weight devoted in the Lagrangian to the very small components of the wave function is much too large compared to the weight devoted to the large components. Specially since the relative error made on these small coefficient is much larger and their physical importance much less. One should therefore ponderate their contribution in $\mathcal{L}$ so that small variations of their amplitude (but that may be large in relative variations) do not significantly affect the result.

Finally, as in all least square fit method, the accuracy of the procedure is measured by amplitude of $\sqrt{\mathcal{L}}$ which should be much smaller than the typical scale of the fitted effective interactions.

6-B. Using the wave function information

The usage of the computed target states wave functions raises the question of the reduction of the information contained in a wave function spanned over several hundred thousands to millions of determinants onto a model state described by a few VB configurations.

For this purpose it is possible to use the guidelines of the effective hamiltonian theory[34], that is to define the model hamiltonian by its eigenvalues and eigenvectors.

- The model hamiltonian eigenvalues (ϵ_i) should be set to the target states excitation energies computed from the ab-initio spectroscopy of the embedded fragments (ε_i).
- The model hamiltonian eigenvectors (ξ_i) should be set to the projection onto the active space of the computed target states wave functions (Ψ_i).

These conditions — that suppose the equality between the active space and the target space dimensions ($m_a = m_t$) — totally define the model hamiltonian in a unique manner. However the procedure can be strictly used only in few special cases since it is often incompatible with some the of formal requirements demanded from the model.

- Typically when the target states projections onto the active space ($P|\Psi_i\rangle$) are not fully defined by the symmetry of the system, there is no reason for them to form an orthogonal set. The direct corollary of this non-orthogonality is the lost of the hermiticity property of the model hamiltonian. Going back to the example of the effective hopping between two non equivalent sites a and b, the two computed target doublets ($|\Psi_1\rangle$ of energy ε_1 and $|\Psi_2\rangle$ of energy ε_2) can be written as

$$\frac{P|\Psi_1\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} = \cos\alpha\,|a\rangle + \sin\alpha\,|b\rangle$$

$$\frac{P|\Psi_2\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} = -\sin\beta\,|a\rangle + \cos\beta\,|b\rangle$$

which yield a model hamiltonian

$$H_{mod} = \begin{array}{c} \\ \\ \end{array} \begin{array}{c} |a\rangle \\ \\ \end{array} \begin{array}{c} |b\rangle \\ \\ \end{array} \left(\begin{array}{cc} \frac{\varepsilon_1\cos\alpha\cos\beta+\varepsilon_2\sin\alpha\sin\beta}{\cos(\alpha-\beta)} & \frac{(\varepsilon_1-\varepsilon_2)\cos\alpha\sin\beta}{\cos(\alpha-\beta)} \\ \\ \frac{(\varepsilon_1-\varepsilon_2)\sin\alpha\cos\beta}{\cos(\alpha-\beta)} & \frac{\varepsilon_1\sin\alpha\sin\beta+\varepsilon_2\cos\alpha\cos\beta}{\cos(\alpha-\beta)} \end{array} \right)$$

One sees immediately that when $\alpha \neq \beta$ the hermiticity is not verified.

- In addition, the above procedure yields a priori independent and non-zero matrix elements between all VB configurations in the same irreducible representation. In consequence, the number of independent parameters of the effective model is equal to the number of matrix elements not directly imposed by the symmetry. The goal of the modelisation, in terms of the reduction of the physics to a small number of physically readable, dominant interactions, is therefore totally lost.

The price to retrieve the hermiticity and the simplicity is either (i) the abandonment of the exact

reproduction of the computed excitation energies and wave functions to the profit of an approximate representation through a least square fit method (see previous section), or (ii) the abandonment of the reproduction of part of the target states in order to focus on the accurate description of a set of selected states. In the above example of asymmetric hopping the choices would translate into either the approximate representation of the two doublets by average states as resulting from a Löwdin orthogonalisation procedure

$$\frac{P|\Psi_1\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} \longrightarrow \cos\frac{\alpha+\beta}{2}|a\rangle + \sin\frac{\alpha+\beta}{2}|b\rangle$$
$$\frac{P|\Psi_2\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} \longrightarrow -\sin\frac{\alpha+\beta}{2}|a\rangle + \cos\frac{\alpha+\beta}{2}|b\rangle$$

or the accurate reproduction of one of the doublets (for instance $|\Psi_1\rangle$), the second one being accordingly defined for this purpose (Smidt orthogonalisation)

$$\frac{P|\Psi_1\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} \longrightarrow \cos\alpha|a\rangle + \sin\alpha|b\rangle$$
$$\frac{P|\Psi_2\rangle}{\sqrt{\langle\Psi_1|P|\Psi_1\rangle}} \longrightarrow -\sin\alpha|a\rangle + \cos\alpha|b\rangle$$

More generally this second choice is related to the guidelines of the intermediate hamiltonian theory[35] : reproduction by a subset of the active space of a selected number of target states, both in terms of energies and wave functions. One should therefore partition the active space underlying the model hamiltonian into two subspaces.

- A main active space of dimension ($m_{ma} < m_a$). This subspace will be supported by the eigenstates of the model hamiltonian aimed at reproducing the target states. m_{ma} should therefore be equal to the number of target states to reproduce ($m_{ma} = m_t$).

- An intermediate active space of dimension $m_{ia} = m_a - m_{ma}$, supported by the remaining eigenstates of the model hamiltonian. These states are devoted to provide to the model the necessary flexibility to both verify the (formal) requirements and to best reproduce the target states. They have a formal purpose but no physical purpose even though they may be related — however not a trustworthy representation — to meaningful physical states.

Such a procedure, based on a selective choice, send us back to the aim, in fine, of the model. Indeed the partition of the active space must be determined by the physics targeted at, that is the states of the entire lattice one would like to describe. From the embedded fragment point of view, it means an accurate reproduction of the local physical content of these infinite system states, that is of the fragment states which are highly populated (as can be computed by the density matrices projected on the fragment) in the infinite system states.

Let us illustrate our purpose by a simple example : the low energy physics of a half-filled magnetic system. The infinite system is therefore a lattice which low energy physics is based on equivalent magnetic centers supporting each one active orbital and one active electron. The states responsible for the magnetic properties are therefore neutral in a Valence-Bond sense, that is configurations where each magnetic center support a unique active electron are dominant in the low energy states of the entire system. Considering now an embedded fragment containing two magnetic centers (say A and B), the active orbitals (a and b) and electrons define a $2\bar{e}$, 2 orbitals CAS underlying a Hubbard model hamiltonian.

$$H_{mod} = \begin{array}{c} \begin{array}{cccc} |a\bar{b}\rangle & |b\bar{a}\rangle & |a\bar{a}\rangle & |b\bar{b}\rangle \end{array} \\ \begin{pmatrix} 0 & 0 & t & t \\ 0 & 0 & t & t \\ t & t & U & 0 \\ t & t & 0 & U \end{pmatrix} \end{array}$$

with the eigenstates

$$|Sg\rangle = \cos\alpha\frac{|a\bar{b}\rangle + |b\bar{a}\rangle}{\sqrt{2}} + \sin\alpha\frac{|a\bar{a}\rangle + |b\bar{b}\rangle}{\sqrt{2}}$$
$$\text{of energy } \frac{U - \sqrt{U^2+16t^2}}{2}$$
$$|Tp\rangle = \frac{|a\bar{b}\rangle - |b\bar{a}\rangle}{\sqrt{2}} \text{ of energy } 0$$
$$|Sg^*\rangle = -\sin\alpha\frac{|a\bar{b}\rangle + |b\bar{a}\rangle}{\sqrt{2}} + \cos\alpha\frac{|a\bar{a}\rangle + |b\bar{b}\rangle}{\sqrt{2}}$$
$$\text{of energy } \frac{U + \sqrt{U^2+16t^2}}{2}$$
$$|Su\rangle = \frac{|a\bar{a}\rangle - |b\bar{b}\rangle}{\sqrt{2}} \text{ of energy } U$$

In a Bloch effective hamiltonian theory the above problem is over-determined since one has 3 energy differences and 2 singlet eigenstates which wave functions are not totally determined by the sym-

metry. The result is 5 conditions for only 2 unknown parameters. The infinite system physics being supported by neutral VB configurations it is crucial that the local neutral states are best reproduced. One should therefore prefer an intermediate hamiltonian guideline and focus on the reproduction of the $|Sg\rangle$ and $|Tp\rangle$ energy difference and wave functions, yielding a well defined problem with two conditions (reproduction of the singlet-triplet energy difference and ionic configurations coefficient in the singlet state) and two unknowns. The main consequence of this choice is that the on-site effective bi-electronic repulsion integral U is determined so that to best reproduce the correct component in the singlet ground state of the ionic VB configuration $|a\bar{a}\rangle + |b\bar{b}\rangle$. As a corollary the energies of the essentially ionic states $|Su\rangle$ and $|Sg^*\rangle$ are overestimated. Indeed, it can be seen from a simple perturbative expansion that the dynamical correlation effects on the ionic configurations strongly depend on whether they belong to an essentially neutral or essentially ionic state. In case of a neutral state the rescaling of the ionic configurations energy by the dynamical correlation processes is (at the second order of perturbation)

$$U \longrightarrow U_0 - \sum_i \frac{|\langle a\bar{a}|1/r_{12}|\Phi_i\rangle|^2}{E_i}$$

while in case of an ionic state it comes

$$U \longrightarrow U_0 - \sum_i \frac{|\langle a\bar{a}|1/r_{12}|\Phi_i\rangle|^2}{E_i - U}$$

One should thus be conscious that while the model determined under the previous criteria will be appropriate for the determination of the low energy physics it is unsuitable to study the transitions toward essentially ionic VB states.

In this example the reduction of the number of target states to reproduce provides a solution to two different problems. The first one is getting a mathematically well conditioned inversion problem. The second one is the resolution of the dilemma between an accurate reproduction of the ground state wave function and of the transition energy towards ionic excited states. While the second type of problems can be solved by the usage of intermediate hamiltonian guidelines, the solution to first type of problems may require such drastic reduction of the target space (one state per irreducible representation) that the model may become meaningless. In such a case a thoughtful combination with square fit techniques will provide the exit.

7. Conclusion

The fascinating properties observed in the new materials synthesized in the last couple of decades are commanded by their electronic structure and more specifically by strong electron-electron correlations. The understanding of the observed collective effects necessitates a clear picture of the interplay between the dominant microscopic local interactions. Quantum chemists with their extensive culture of correlation effects in finite systems, of valence correlation but also dynamical correlation and its retroactive effects on the valence shell, in the ground state but also in excited, multireference states, have the intellectual tools to answer this question. We have seen in this paper how up-to-date quantum chemical spectroscopic methods associated to a controlled description of the crystalline embedding, a clear understanding of the model hamiltonians aims, an appropriate extension and usage of effective hamiltonian methods that allow a controlled reduction of the ab initio information into a few dominant interactions, are the clues to a controlled and accurate modelisation of these materials.

It is a fascinating challenge for the quantum chemist used to small finite systems, to enter this condensed matter field where the answers can only be find by the integration over all physical scales from first principle microscopic local electronic interactions, to the nanoscopic scale (fragments) up to the macroscopic properties.

Appendix

The Heisenberg model

The Heisenberg model was first devised by Heisenberg[11] and formalized by Van Vleck and Dirac[12] in order to rationalize isotropic ferromagnetic interactions between localized electrons or spin 1/2 particles supported by orbitals localized on well separated centers. Its validity has later been extended by Anderson[18] to antiferromagnetic interactions by the famous superexchange mechanism : stabilisation of the singlet state compared to the triplet state by the effective effect of the ionic configurations. The general expression of the Heisenberg Hamiltonian is for a system with one spin, one orbital per center (half-filling)

$$H_{Heis} = \sum_{<i,j>} J_{ij} \left(\mathbf{S}_i.\mathbf{S}_j - \frac{1}{4} n_i n_j \right) \qquad (1)$$

When the spins represent electrons (spin 1/2) the Heisenberg Hamiltonian can be rewritten as

$$H_{Heis} = \sum_{<i,j>} J_{ij} \left(\frac{a^\dagger_{i\uparrow} a^\dagger_{j\downarrow} - a^\dagger_{j\uparrow} a^\dagger_{i\downarrow}}{\sqrt{2}} \right) \left(\frac{a_{i\uparrow} a_{j\downarrow} - a_{j\uparrow} a_{i\downarrow}}{\sqrt{2}} \right) \qquad (2)$$

where $a^\dagger_{i\sigma}$ (resp. $a_{i\sigma}$) is the creation (resp. annihilation) operator of an electron of spin σ on site i, n_i is the number operator on site i and $\mathbf{S}_i$ the spin operator on site i. The sum over $< i, j >$ runs on nearest neighbors sites i and j.

The $t - J$ model

The $t - J$ model was first devised by Zhang and Rice[13] in order to described the movement of holes in an anti-ferromagnetic background such as found in the copper oxide planes of the cuprate high T_c super-conductors. It applies to magnetic systems away from half-filling (number of magnetic orbitals different from the number of electrons or spins). According to the sign of the doping (extra electrons or extra holes compared to the half-filled system) the hamiltonian applies to the electrons or holes. Its general form is

$$\begin{aligned} H_{t-J} = & \sum_{<i,j>} J_{ij} \left(\mathbf{S}_i.\mathbf{S}_j - \frac{1}{4} n_i n_j \right) + \\ & \sum_{<i,j>} t_{ij} \sum_\sigma \left(a^\dagger_{i\sigma} a_{j\sigma} + a^\dagger_{j\sigma} a_{i\sigma} \right) \end{aligned} \qquad (3)$$

The extended Hubbard model

The extended Hubbard model is basically a simplified version of the Pariser-Parr-Pople hamiltonian. It contains essentially four types of interaction parameters, two mono-electronic ones corresponding to the Hückel approximation and two bielectronic ones

- the orbitals energies,
- the hopping integrals (usually limited to adjacent centers),
- the bielectronic coulomb repulsion between two electrons located on the same orbital,
- and the bielectronic coulomb repulsion between two electrons located on different orbitals (most of the time limited to nearest neighbors centers).

The three first terms define the Hubbard model and the addition of the inter-site repulsions leads to the extended Hubbard model. It comes the following generic formulation

$$\begin{aligned} H_{Hub} = & \sum_{<ij>} t_{ij} \sum_\sigma \left(a^\dagger_{i\sigma} a_{j\sigma} + a^\dagger_{j\sigma} a_{i\sigma} \right) + \\ & \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \\ & \sum_{<ij>} V_{ij} \left(n_i - Z_i \right) \left(n_j - Z_j \right) \end{aligned} \qquad (4)$$

where Z_j is the effective nucleus charge of the center i.

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