Environment effects on effective magnetic exchange integrals and local spectroscopy of extended strongly correlated systems.

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The present work analyzes the importance of the different components of the environment effects on the local spectroscopy of extended strongly correlated systems. It has been found that the usual formal charge definition of the charge transfer and Madelung potential are far too crude for an accurate determination of the local excitation energies in embedded fragment calculations. A criterion for the validation of the embedding against the infinite system density of states has been proposed.

INTRODUCTION

In the last twenty years the science of strongly correlated materials has attracted a lot of attention. Indeed, chemists have synthesized a large number of new families of materials which present unusual and fascinating properties directly related to the strongly correlated character of their electronic structure (to cite only a few systems, one can think of the copper oxides presenting $d$-wave, high-$T_c$ super-conductivity [1], manganites with giant magneto-resistance [2], Prussian Blue analogs with photo-magnetic properties [3], etc.). In all these materials the electrons responsible for their spectacular properties are few (per unit cell), usually unpaired and localized both spatially and energetically near the Fermi level. That is to say that the wave function of these systems is essentially multi-configurational and cannot be correctly treated by single-reference based methods such as Hartree-Fock plus perturbation theory or even Density Functional [4], the only $ab$ initio methods to be tractable on infinite crystals. Physicists have thus relied on semi-empirical models such as the Heisenberg [5], $t-J$ [6] or Hubbard [7] Hamiltonians in order to describe these strongly correlated materials. These effective models are of valence-bond (VB) type and belong to the zero differential overlap (ZDO) class. They are aimed at describing the effective microscopic interactions between the set of valence electrons responsible for the macroscopic low energy properties. For instance, the famous $t-J$ model has first been derived by Zhang and Rice et al [8] as a model for the high-$T_c$ copper oxides. Indeed, the $t-J$ model describes the dominant interactions between the magnetic electrons of the $CuO_2$ superconducting planes. These planes can be seen as a $Cu^{2+}$ square lattice, each copper ion supporting (before doping) one $d_{x^2-y^2}$ magnetic electron. These unpaired, Fermi level electrons (considered to be the important ones for the superconductivity properties) only interact between each others through super-exchange processes (via the bridging oxygen anions $O^{2-}$) and through effective hopping integrals (when the planes are doped as in the super-conducting phases), i.e. through a $t-J$ type of Hamiltonian.

One sees immediately that such representations necessary i) to clearly identify the pertinent electrons and orbitals responsible for the macroscopic low energy properties — they will be called from now on active electrons and active orbitals — ii) to determine the dominant interactions between these electrons iii) finally to evaluate their relative amplitudes. While the nature of the active electrons and orbitals, and even the form of the dominant interactions, are most of the time relatively easy to derived using simple chemical considerations, the quantitative determination of the interactions amplitudes is a much more troublesome problem, even though as crucial. Indeed, the low energy properties of the macroscopic systems are highly dependent on the relative amplitudes of the different effective integrals, since the latter can govern properties as important as the metallic versus insulating character of a compound. Unfortunately, experimental data are, most of the time, unable to totally determine them and it is necessary to rely on $ab$ initio quantum-chemical calculations for this purpose. Since these effective interactions (hopping, magnetic exchange, on-site bi-electronic repulsion, etc.) are essentially local (see references [8, 9] for detailed analyses of the locality of the different effective interactions) and involve a small number of bodies (most of the time only one or two), they can be accurately determined from the computation of the local excitation energies and related states. For instance, in the high-$T_c$ copper oxides, the magnetic coupling between two active $d_{x^2-y^2}$ electrons can be determined as the local singlet to triplet excitation energy between two nearest neighbors, oxygen bridged, copper atoms. The embedded cluster technique, where the local valence excitations are computed on an adequate fragment of the crystal, has proved to be one of the most efficient technique for this purpose. Indeed, the full power of the $ab$ initio molecular-spectroscopy methods can be used on such finite systems. One can cite the successes obtained on high-$T_c$ copper oxides [10], vanadates oxides [11, 12], fluoroperovskites [13], etc. For instance, the magnetic exchange in the high-$T_c$ superconductor
\( \text{Nd}_2\text{CuO}_4 \) has been computed within experimental accuracy \((J_{\text{calc}} = -126.4\text{ meV}\) being the computed value in reference \([10]\) and \(J_{\text{exp}} = -126 \pm 5\text{ meV}\) being the measured experimental value \([12]\)).

As we will see in details later on, the local character of the effective interactions refers to the local character of the electronic processes involved in the local excitations, once the mono-electronic part of the wave function is defined, that is, once the shape of the fragment orbitals and their energies are defined. It is however obvious that the latter, and in consequence the effective interactions amplitudes, are strongly influenced by the fragment crystalline surrounding. Indeed, the orbitals and orbital energies of an isolated fragment are very different from the orbitals and orbital energies of the same fragment in a crystalline environment. It is therefore crucial to embed the studied fragment into an environment reproducing the main effects of the rest of the crystal.

The purpose of this paper is to analyze, review and clarify the requirements for a good embedding and in this light to discuss the most common practices. We will also propose a general technique for checking the quality of an embedding and study the sensitivity of some effective parameters, such as the magnetic super-exchange and the effective hopping integrals, to the quality of the embedding and the crystalline environment. The next section will therefore be devoted to the analysis of the environment-fragment interactions and the proposal of a simple criterion measuring the embedding quality. Section three will review the usual practices, exemplify the influence of the crystalline environment on real systems and point out the larger importance of the different embedding components on the effective parameters than is commonly assumed. Finally, the last section will be devoted to conclusions and perspectives.

INTERACTIONS BETWEEN THE FRAGMENT AND THE REST OF THE CRYSTAL

The interactions between a selected fragment and the rest of the crystal can be classified into two different types: the effects on the fragment of the crystal average electrostatic field and the effects of its fluctuations.

Let us first start with the second kind: the electrostatic and spin fields fluctuations, that is the instantaneous response of the rest of the crystal to a particular electronic configuration of the fragment. In other words we are talking about the dynamical correlation effects of the rest of the crystal on the fragment valence states under consideration. The spatial separation between the active centers and their crystalline environment allows us to conduct a multi-polar analysis of the different contributions to the excitation energies, following the same pattern used in the description of the inter-molecular interactions. Along this line, it is very simple to see that the leading dynamical-correlation contributions are the polarization responses of the environment first to a local charge, then to a dipole moment or transition dipole moment on the fragment \( \mathbb{S} \). In other words, these effects correspond to excitations from the average environment (chosen as its zeroth order description) in response to a particular fragment configuration. In a perturbative scheme they can be described as the coupling between single excitations in the environment to a local charge, a local dipole or a local transition dipole on the fragment. From multi-polar expansion combined to second order perturbation theory, it is easy to see that the leading contributions come from the interactions between a charge on the fragment and a dipole on the environment. Such effects decrease as \((1/R^2)^2\), that is quite rapidly. For a complete description and analysis of the different contributions one can refer to \( \mathbb{S} \). Provided that the largest \(1/R^2\) terms — i.e. the terms coming from single-excitations on the first neighbors of the magnetic centers — are correctly treated, the rapid decrease of these effects as a function of \(R\) allows us to consider the rest of them as reasonably negligible. Indeed, while the first neighbor shell of atoms surrounding the magnetic sites are usually at a distance of 2Å to 3Å (from 3.8a.u. to 5.7a.u.) the second neighbor distances are usually of the order of 3Å to 5Å, (5.7a.u. to 9.5a.u.). The second neighbor contributions can therefore be expected to be of an order of magnitude \(10^{-3}\) to \(10^{-4}\) smaller than the on-site polarization contributions. One can therefore consider that including in the studied fragment, the first coordination shell of all the atoms involved in the local excitations under consideration, is enough to take into account the essential contributions to the modification of the effective interactions by the environment dynamical correlation effects.

Let us now examine the effects on the fragment, of the average electrostatic field of the rest of the crystal. At this point it is important noticing that a majority of the strongly correlated materials are ionic or at least partly ionic. This is for instance the case of the high-\(T_c\) superconducting cuprates for which the super-conducting planes are hole-doped \(\text{Cu}^{2+}\text{O}_2^-\) lattices. Similar observations can be made for vanadate, manganites, cobaltites and even the organic conductors which are charge transfer salts. It is therefore clear that electrostatic effects such as the Madelung potential have to be properly treated and that, unlike the field fluctuations, the average electrostatic and spin fields of the environment strongly affect the fragment under consideration. This problem has been carefully studied by Barandiarán and Seijo in the case where the fragment borders do not cut any covalent bond. They analyzed the crystalline environment contributions as Coulomb interactions, quantum exchange interactions and orthogonality of the fragment orbitals to the orbitals of the rest of the crystal (quantum orthogonality interactions) \([13]\). Out of
these one can separate the short range contributions: short range Coulomb repulsions, quantum exchange interactions and quantum orthogonality, from long range ones, that is essentially Coulomb interactions such as the Madelung potential. The latter can be easily reproduced using the dominant terms of a multi-polar expansion, that is for an ionic (or even partly ionic) crystal the point charge Madelung potential as described using the Ewald formulation or, as it is more commonly done, by a large enough set of point charges modified at the set borders by the Evjen’s procedure. The short range contributions necessitate a more sophisticated treatment since the fragment orbitals should be orthogonal to the orbitals (non-included in the calculation) supporting the electrons of the rest of the crystal, that is essentially with the electrons located on the fragment first-shell neighboring atoms. The resulting exclusion of regions in the $R^3$ space for the fragment electrons wave-function has proved to be well treated by total ion pseudo-potentials (TIP) approaches. Indeed, the TIPs are explicitly derived in order to render on the fragment orbitals the quantum orthogonality, quantum exchange and short range Coulomb potential effects. As for the Madelung potentials, the short range contributions acts essentially at the mono-electronic description level (Hartree-Fock). Indeed, both the electrostatic potential and the TIPs modify only the mono-electronic integrals. Thus these effects affect the Fock operator and strongly influence the shape of the fragment orbitals and their energies.

While the determination of the TIPs modeling the short range contributions is quite unambiguous, the determination of the Madelung field is more tricky. Even though experimental determinations of the electrostatic potential at points locations may be available, this is usually not the case and the question of what are the average charges supported by the different atoms remains open. Most authors use simple chemical considerations such as the standard atomic oxidation states and charge equilibrium to derive the formal charges supported by the different atoms in the crystal. For instance, $Na^{0+}, Cu^{2+}$ and $O^{2−}$ in the neodymium-doped superconductor $Nd_{3}CuO_{4}$, or $Na^{1+}, V^{4.5+}, O^{2−}$ in the famous inorganic spin-Peierls $\alpha’NaV_{2}O_{5}$ compound. Such simple considerations assume totally ionic systems. However in most systems the ionicity is not as strictly total and for systems presenting ionic-covalent bonds the field created by the formal charges does not accurately reproduce the real Madelung potential. The problem of determining the degree of polarization of such systems or the real charges supported by the atoms is therefore crucial. That was for instance the case in the $\alpha’NaV_{2}O_{5}$ compound which was commonly assumed in the literature to be $Na^{1+}V^{4.5+}O^{2−}$, while crystal ab initio mean-field calculations (Hartree-Fock calculations with valence triple zeta + polarization type of basis sets) run using the CRYSTAL code yield M"ulliken atomic charges of $Na^{0.95+}V^{2.3+}O^{2.95−}O^{1.3−}O^{1.15−}$. It is well known that the M"ulliken charges are strongly dependent of the chosen basis set and in particular of its spatial extension. However, the above mean-field calculations clearly exhibit a strongly-covalent triple bond between the vanadium atom and its corresponding apical oxygen, a strong donation from the apical oxygen to the vanadium atom — in order to form the third bond — and a weaker donation of the other oxygen anions to this $V \equiv O$ system. This result, which couldn’t have been derived from simple chemical considerations, have been latter confirmed by embedded fragments Complete Active Space Self Consistent Field (CASSCF) calculations. As a conclusion, the choice of the atomic charges generating a physically correct Madelung field is a crucial issue that cannot be solved by simple charge transfer considerations.

The problem can be solved by going back to the question of how the electrostatic potential acts on the fragment wave-function. As already mentioned, the potential generated by the rest of the crystal acts through the mono-electronic integrals, and thus, on the orbital shapes and orbital energies through the Fock operator definition. All these effects belong to zeroth-order description of the fragment and are present at the Hartree-Fock level. It is therefore possible to calibrate these effects by a direct comparison of the Hartree-Fock description of the embedded fragment and the Hartree-Fock description of the infinite crystal. Indeed, the density of states (DOS) of the infinite crystal ($\rho^{\text{sys}}(E)$) can be projected on the atomic orbitals involved in the fragment under consideration and compared with the embedded fragment orbitals atomic contents and energies. It is easy to define a projected density of states (PDOS) function for the finite fragment in a similar way as in an infinite system. The major difference between the two is that the finite system PDOS is a discrete function. If $\rho^{\text{sys}}_{\mu}(E)$ is the PDOS of the entire crystal on the atomic orbital $\mu$, $\rho^{\text{sys}}_{\mu}(E) = \frac{1}{V_{\text{BZ}}} \sum_{n, \nu} \int_{BZ} c_{\nu n}^{*}(\vec{k}) S_{\nu \mu} c_{\mu n}(\vec{k}) \delta(E - E_{\nu n}(\vec{k})) d\vec{k}$ (1) the embedded fragment density of states, $\rho^{\text{frag}}_{\mu}(E)$, can be defined in a similar way as $\rho^{\text{frag}}_{\mu}(E) = \sum_{j} \sum_{\nu} f_{\nu j} S_{\nu \mu} f_{\mu j} \delta(E - E_{j})$ (2) where BZ refers to the Brillouin zone, $V_{\text{BZ}}$ to its volume, $\vec{k}$ is the wave vector, $c_{\mu n}(\vec{k})$ is the coefficient of the $n$th - band crystalline orbital at point $\vec{k}$ on the atomic orbital $\mu$ (the star representing the complex conjugate) and $E_{\nu n}(\vec{k})$ the associated orbital energy. Finally, $f_{\mu j}$ is the usual coefficient of the $j$th molecular orbital of the fragment on the atomic orbital $\mu$ and $E_{j}$ the associated orbital energy. If the embedding correctly reproduces the average effects
of the rest of the crystal on the fragment, the discrete function $\rho_{\mu}^{\text{frg}}(E)$ should be located at the same energetic positions as the crystal PDOS $\rho_{\mu}^{\text{crys}}(E)$, and the main contributions of both functions should coincide.

**SOME PRACTICAL EXAMPLES**

As already mentioned, the most usual practice used to define a fragment embedding consists in

- building the Madelung potential using formal charges,
- using TIPs on the first shell of cations in order to set up the main exclusion effects.

In the following subsections, we will analyze on different examples the validity and limitations of such a procedure, as well as the influence of the different parameters on the embedding quality.

**The importance of a covalent bond : the NaV$_2$O$_5$ compound**

The $\alpha'$NaV$_2$O$_5$ crystal is formed by layers of VO$_5$ square-pyramids stacked along the c axis. The oxygen atoms of the pyramid basis form a quasi-square planar lattice along the a and b directions. The pyramids are alternatively pointing on top and below these planes. Periodical vacancies of the VO top of the pyramids are replaced by Na$^+$ ions forming chains parallel to the b axis (see fig. 1). This system can be modeled as planes of weakly coupled ladders, the low energy physics being supported by the $d_{xy}$ magnetic orbitals of the vanadium atoms and by the $p_y$ orbitals of the bridging oxygen atom on the ladders rungs [12].

![FIG. 1: Schematic structure of $\alpha'$NaV$_2$O$_5$, (a) along the (a,c) plane and (b) along the (a,c) plane. The oxygen atoms are denoted by open circles, the vanadium atoms by filled circles and the sodium atoms by dots.](image)

Following a simple chemical analysis, the system was given for a long time as a fully ionic system, with a formal charges repartition of Na$^{+}$($V_2$)$^{9+}$O$_5^{2-}$ and a mixed valency on the vanadium atom. Later on, quantum chemical calculations [11] showed that the vanadium-apical oxygen ($V - O_{\text{ap}}$) bond is in fact a multiple strongly covalent bond with a small degree of polarization (about $1/2\varepsilon$). The system should then be seen as ($V \equiv O_{\text{ap}}$)$^{2+}$ or $3^+$ molecules on an oxygen $O^{2-}$ square lattice. A modification of the charge repartition in the average (VO$_{\text{ap}}$)$^{2.5+}$ group, from $V^{4.5+}O_{\text{ap}}^{2-}$ to $V^{3^+}O_{\text{ap}}^{0.5-}$ is considerable and one can expect that it strongly affects the potential felt by the magnetic orbitals. Indeed the electrostatic potential (computed by the Ewald summation procedure) felt by the atoms supporting the active orbital goes from $\text{Pot}(V) = 1.735\text{a.u.}$ and $\text{Pot}(O_{\text{br}}) = -1.103\text{a.u.}$ (where $O_{\text{br}}$ refers to the oxygen atom bridging the two vanadium atoms on the rungs) when formal charges are used to $\text{Pot}(V) = 1.242\text{a.u.}$ and $\text{Pot}(O_{\text{br}}) = -0.930\text{a.u.}$ when the polarity of the Vanadium-apical oxygen bond has been corrected. One notices immediately that the difference of the electrostatic potential felt by the V and $O_{\text{br}}$ is increased by more than 30% when formal charges are used and thus that the energy difference between the $Vd_{xy}$ orbital and the $O_{\text{br}}p_y$ orbital should be strongly affected.

Figure 2 reports the projected densities of states on the rung active orbitals as computed at the Hartree-Fock level from a periodic calculation, and from three fragment calculations with different embeddings : without embedding (isolated fragment), with an embedding using the formal charges Madelung potential and with an embedding using the charges corrected to take into account the covalency of the $V \equiv O_{\text{ap}}$ bond. The rung fragment has been chosen as including the $VOV$ rung and the set of first neighbors atoms (see fig. 2). One sees immediately that the isolated fragment DOS are very different from the periodic DOS, emphasizing, if necessary, the crucial importance of the embedding. Indeed, in the isolated fragment, even the Fermi level orbitals — Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) — are not the correct ones, i.e. the bonding, anti-bonding combinations of the vanadium $d_{xy}$ orbitals. The fragment, embedded with the formal charges Madelung potential, yields a reasonable representation of the occupied orbitals, the HOMO is correctly of vanadium $d_{xy}$ nature and the bridging oxygen $p_y$ orbital is at the correct energy difference. However, the unoccupied part of the spectrum is much more troublesome, in particular the contribution to the virtual orbitals of the vanadium $d_{xy}$ orbitals is totally unreal-
The influence of geometrical details: the incommensurate $Sr_{14}Cu_{24}O_{41}$

In the light of the previous example one may wonder how much the details of the Madelung part in the embedding can influence the computed local excitations. This point is of particular importance for the incommensurate systems composed of several electronically quasi-independent subsystems with incommensurate periodicity. Indeed, it is of crucial importance to know up to which point the incommensurability influences the periodicity of the local effective interactions within one of the subsystems. In other words, what is the amplitude of the magnetic exchange, hopping, etc. modulation in one subsystem due to the electrostatic influence of the other subsystem.

An interesting candidates to study this problem is the superconducting ladder-chain copper-oxide family $Sr_{14-x}Cu_xCu_{24}O_{41}$. Indeed, these compounds are constituted of alternate layers of weakly-coupled doped spin-ladders and weakly-coupled doped spin-chains (see figure 4). We will use for this study the totally saturated $x=0$ compound in an ideal geometry where the modulation of the chains (resp. ladders) geometry around their average structure has been ignored. In this ideal system the two isolated subsystems are perfectly periodical and the modulation of the local excitations energies along the chain (resp. the ladder) can only be attributed to the non-periodicity of the electrostatic influence of the other subsystem.

The incommensurability of such a system does not allow us to run benchmark periodic calculations in order to check the validity of our embedding. However in the copper oxides, the oxidation numbers of the different atoms (Cu, O as well as alkaline-earth elements) do not seem to raise much controversy. Indeed, both the chemical analysis and the ab initio calculations on similar systems such
as the chain system $Sr_2CuO_3$ \[21\], the ladder systems $SrCuO_3$ [22], or even the perovskites super-conducting parent compounds such as the $HgBa_2Cu_3O_{8+n+2+4}$ family \[11\], yield Cu$^{2+}$ and O$^{2-}$ oxidation states, which we will assume for the present system.

Figure 5 shows the modulation of the local singlet-triplet energy difference (computed at the Complete Active Space Self Consistent Field (CASSCF) level) on the chain subsystem fragments as a function of their reference unit cell along the chain subsystem. The CAS space includes either only the copper magnetic $d_{z^2-y^2}$ orbitals (the $x$ and $y$ axes corresponding to a and c crystallographic axes in figure 4), or as well the orbitals of the bridging oxygen atoms — supporting the through-bridge, super-exchange mechanism. As for the vanadium oxide the embedded fragments have been chosen such as to include two nearest neighbors magnetic sites (here the copper atoms), the bridging atoms (here one oxygen atom on the ladders and two oxygen atoms on the chains) and the first neighbor atoms to the previously cited ones. The ladder and chain fragments are Cu$_2$O$_7$ and Cu$_2$O$_6$ respectively. Unlike the change in the polarization of the chains and of $10^{-5}$ a.u. along the ladders. However, it should be noticed that the relative variation of the spectroscopic parameters, such as the effective magnetic exchange, is two orders of magnitude larger than the relative variation of the Madelung potential, pointing out the extreme sensitivity of these local excitation energies to the electrostatic potential.

**The influence of anions TIPs : the $Pt_2I(dta)_4$**

Finally we will analyze the importance of the short-range effects, as modeled by the TIPs, on local excitations. These effects, excluding the fragment electrons from the space supposed to be occupied by the electrons of the rest of the crystal, are much more important for cations than for anions. Indeed, while the positive charges of the former have a tendency to attract the fragment electrons, the negative charges of the latter already repulse them. Therefore, we will not discuss the cations case for which it is commonly admitted that these short range exclusion effects are crucial, and we will rather analyze the effects due to anions, more subject to controversy.

For this purpose we have chosen the $Pt_2I(dta)_4$ compound [24] since the influence of the large $I^-$ ion, first neighbor of the $Pt^{3+}$ magnetic centers, can be expected to be rather important. The $Pt_2I(dta)_4$ system is a quasi-unidimensional system built from the alternation of platinum dimers and iodine anions. The coordination spheres of the $Pt$ atoms are completed by four $\mu$-bridging dithioacetate (dta) ligands (see figure 6). The iodine anion is located at the mid center position between two $Pt_2$ dimers. Its distance to the closest platinum atom is only 2.98Å, while the sum of its ionic radius (2.16Å) and

| Chains | Ladder rungs |
|--------|--------------|
| Position (a.u.) | Potential (a.u.) | Position (a.u.) | Potential (a.u.) |
| 0.7215601 | 1.9155856 | 1.8537347 | 1.8195387 |
| 5.9126401 | 1.9155567 | 9.2097116 | 1.8195275 |
| 11.1037201 | 1.9155625 | 16.6856884 | 1.8195245 |
| 16.2948001 | 1.9155681 | 24.1016653 | 1.8195183 |
| 21.4858801 | 1.9155959 | 31.5171231 | 1.8195173 |
| 26.6769601 | 1.9155856 | 32.571231 | 1.8195298 |
| 31.8680401 | 1.9155676 | 46.3490769 | 1.8195183 |
| 37.0591201 | 1.9156425 | 48.4252001 | 1.9155681 |
| 42.2502001 | 1.9155681 | 47.4412801 | 1.9159595 |

**TABLE II: Electrostatic potential in atomic units for the copper atoms along a chain and one side of a ladder.** The incommensurate structure have been approached by the usual 10 : 7 commensurate one in the chain/ladder direction. The 10 chain cells, 7 ladder cells mismatch is of 0.145Å out of 27.45Å.
the ionic radius of the Pt$^{2+}$ cation (0.98 Å) is 3.14 Å. The computed fragment is composed of two Pt atoms bridged by the four dta ligands. In this system the electronic structure is supposed to be essentially supported by the $d_{x^2-y^2}$ orbitals of the Pt atoms (the quantification axis being set to be the chain axis). The local singlet to triplet excitation energy of the $[\text{Pt}_2(\text{dta})]^{2+}$ system has been computed with and without $I^-$ TIPs [24] on the first iodine neighbors on both sides of the fragment. The system has been found to have a metal-ligand triplet ground state. It is noticeable that the singlet, first excited state is also a metal-ligand strongly open-shell state. The triplet to singlet excitation energy, computed at the CASSCF level (the CAS being defined by 4 electrons in 3 orbitals) has been found to be of 46 meV when the $I^-$ anions are only represented by a $1/R$ repulsive potential, that is by punctual charges. When $I^-$ TIPs are used, it becomes 50 meV. As can be expected, the TIPs destabilize more the singlet state than the triplet state. Indeed, while the two states have the same average number of electrons, the larger charge fluctuations in the singlet state increases the probability of the configurations having an extra electron on one of the Pt sites, yielding larger repulsive contributions due to the $I^-$ TIPs. It can therefore be expected that on systems where the singlet state is less open-shell than this one, the first neighbor anions exclusion effects are larger than in the present case, reducing the singlet to triplet excitation energy when the coupling is anti-ferromagnetic and increasing it for ferromagnetic couplings. However, the absolute value of the TIPs effect (4 meV) is quite small and can be expected never to be very large (since in the present case the iodine-platinum distance is already smaller than the sum of the respective ionic radii). One can therefore conclude, that the cations TIPs will be of importance essentially when the excitation energies sought at are small (of the order of the tens of milli-electron-Volts or smaller).

**CONCLUSION**

We have studied the effects of the environment on the local spectroscopy of strongly correlated extended systems, as treated in embedded fragment methods. A particular interest have been devoted to strongly correlated systems and the local effective interactions (magnetic exchange, hopping, repulsion, etc) between the active electrons responsible for the low energy physical properties. We have analyzed the different contributions of the rest of the system on the considered fragment, originating both from the average electrostatic and spin fields and from theirs fluctuations. A multi-polar analysis showed that the dominant terms of fields fluctuations contributions scales as a charge-dipole contribution ($1/R^4$). These terms decrease rapidly as a function of the fragment response excitation distance $R$ and can therefore be neglected except from the short range contributions. On the contrary, the effects of the average fields are quite strong and their long range contributions, originating in the Madelung field decrease very slowly. These effects (both the short ranged quantum orthogonality and quantum exchange and the long range Madelung potential) can however be treated at the mono-electronic level and thus act essentially on the orbitals shapes and energies. We have therefore defined a discrete function, equivalent for the finite systems to the Density of States in periodic materials, and based a criterion for testing the embedding quality on the concordance of the infinite system DOS and its discrete equivalent on the embedded fragment. A detailed analysis of different systems have shown that unlike what is commonly assumed in the community, the definition of the Madelung potential by the formal charges issued from simple chemical considerations is not accurate. Indeed, these charges usually overestimate the charge transfers, often miss the possibility of partial covalent bonds, and in any cases are unable to evaluate the degree of polarization of the latter. From the study of the NaV$_2$O$_5$ compound, we have shown that the crucial importance of these problems. Indeed, the orbital shape and energy (and in consequence to the discrete density of states) are very sensitive to these charge transfer problems, as well as the local excitation energies. Let us point out that the singlet to triplet local excitation energy on the NaV$_2$O$_5$ rungs differ from a factor 1.7 when the Madelung potential is defined from formal charges and when the partial covalency of the vanadium apical-oxygen bond is correctly defined. On the contrary, other effects such as the short range exclusion effects due to the fragment first neighbor anions are very small and dominated again by the $1/R$ electrostatic repulsion term.

**FIG. 6:** $Pt_2I(dta)_4$ crystal structure. The large empty circles are the Pt atoms, the large dark gray circles are the I atoms, the middle size light gray atoms are the S atoms, the small black circles are the C atoms and the tiny black circles are the H atoms.
In conclusion we would like to emphasize again the importance of a correct evaluation of the charge transfer processes and a validation of the embedding by checking the embedded fragment orbital shapes and energies against the infinite system density of states.

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