

A GENERALIZED TREATMENT OF LOCALIZED ELECTRONIC INTERACTIONS

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ABSTRACT

It is shown that the local space approximation can provide a basis for the self-consistent treatment of the electronic structure of large aperiodic systems. The use of this approach to study the atomic chemisorption of hydrogen on metallic surfaces, the hydrogen-bonding between organic molecules, and conformational defects in conjugated polymers is discussed.

1. INTRODUCTION:

There is a common feature in phenomena as diverse as the chemisorption of gases on a solid surface, the interaction between large biological molecules, or the doping of polymers: in all of them two (or more) subsystems interact in such manner that the corresponding disturbances in the electronic distribution have a "local" character, i.e. the perturbations in the electronic density are in "a certain degree" confined to the neighborhood of the region of contact between the subsystems. For example, it is well-known that i) the adsorption of an atom introduces both local and extended effects on the electronic structure of a surface¹, ii) short ranged hydrogen-bonds are involved in several important biological interactions², and iii) charge-transfer can occur between dopants and localized conformational defects (of soliton or polaron nature) in polyacetylene and similar conjugated polymers³.

However, the casting of this intuitive picture into a more quantitative basis is not a trivial task. The difficulties begin with the understanding of what one means by a local interaction. To be more specific, let's consider the chemisorption of an atom A on a metal surface B. We can define the initial single-particle Hartree-Fock (HF) density matrix associated with the isolated non-interacting systems as

$$R_0 = R_A + R_B .$$

After the chemisorption takes place, the perturbed density matrix can be formally written as

$$R = R_0 + \Delta R .$$

The discussion of the local character of the phenomenon can then be concentrated on the analysis of the behavior of ΔR , the change introduced in the electronic density of the system. In a naive approach one could consider ΔR to be completely restricted to a small region ("the surface complex") comprising the adsorbate plus a finite number of substrate atoms.

A fundamental property of the density matrix is its idempotency (which is associated to its representability in terms of a N-electron wavefunction)⁴; imposing the idempotency of R, we have

$$R_0 \Delta R + \Delta R R_0 = \Delta R , \quad (1)$$

in first-order on the changes. If we introduce the projector Q associated with the surface complex, we can write the desired condition that the changes be of complete local nature as

$$\Delta R = Q \Delta R Z . \quad (2)$$

eq. 1 can then be written as

$$R_0 Q \Delta R Q + Q \Delta R Q R_0 = Q \Delta R Q ,$$

and after multiplication to the left by X, the projector into the Hilbert space complimentary to that of Q, we obtain finally

$$X R_0 Q \Delta R Q = 0 ,$$

where we have used the projection properties of Q. The above expression expresses the fact that, barring the trivial case of no change in the electronic density, a completely local ΔR given by condition (2) would require the initial density matrix R to be solely comprised of states entirely localized either in the surface complex or in the complementary space. This is, of course, a too strong requirement, satisfied at most at very special situations.

On the other hand, the total change in the HF density matrix can be written in general as

$$\Delta R = U_0 X R_0 + R_0 X U_0 , \quad (3)$$

where the unknown matrix X can be determined from the variational condition for the change in the electronic energy. In fact, at convergence the stability condition

$$\delta E = \text{tr} [h \delta R] = 0 , \quad (4)$$

leads to a specific equation satisfied by h and thus, due to self-consistent nature of the hamiltonian, to a relation obeyed by X.

Given the fact that requirement (2) leads to unphysical results, the next level of compromise between the

empirical evidence of the local character of the chemisorption phenomenon and the idempotency condition of the density matrix can be attained by assuming X (and not ΔR) to be a local matrix, i.e.

$$X = QXQ \equiv X_Q \quad (5)$$

The use of condition (5) for the calculation of the ΔR given by (3) form the so-called **local space approximation (LSA)**⁵, which has found applications in a variety of physical situations.

Note that this approximation preserves the non-local nature of ΔR , which is associated to the fact that local perturbations on one part of the system have repercussions on the overall electronic density of the system. At the same time, the introduction of the projector Q allows the matrix manipulations required for the solution of (4) to be confined entirely to the surface complex (which has molecular dimensions). Thus, the two main characteristics of the method are that it allows i) the correct treatment of the flux of charge between the two interacting subsystems and ii) that even in the case where the original system has an extended character (as in the case of a metallic surface); the computational procedures can be entirely carried in the local region.

In the implementation of the LSA technique for the description of a given local phenomenon, a final step would be required to assure the convergence of the results with the chosen size N_Q of the local region. Since the physical requirements of charge conservation are correctly included in the present method, one can reasonably assume that the desired convergence would occur faster in the LSA procedure than in alternative treatments of local interactions (such as cluster approaches⁶⁻⁷) where the correct boundary conditions are not satisfied.

2. APPLICATIONS OF THE LSA METHOD:

The local space approximation can be implemented to any situation where one has reason to believe that a localized interaction has taken place. As a consequence, the method can find general application in the description of a multitude of different situations. In the following sections we describe recent applications of the LSA technique to a model of atomic chemisorption on metallic surfaces, to the coupling of organic molecules through hydrogen bonds, and to examine the electronic properties of spatially localized conformational defects in polymers.

2.1 Hydrogen Chemisorption on Transition Metals:

When an atom or molecule interacts with a surface, the translational symmetry of the bare substrate is disrupted by the presence of the adsorbate. Also, although the major part of the disturbances on the electronic density occur at the surface complex, induced spin and charge fluctuations on the substrate can extend over a large range. As a consequence, usual solid state techniques (which take advantage of the translational invariance of periodic systems) and quantum chemistry methods (which are appropriate for molecular systems) have met with only limited success in the description of the chemisorption phenomenon.

We have applied the local-space approximation to examine the chemisorption of atomic hydrogen on tran-

sition metals⁸ using a simple model where the substrate is represented by a semi-infinite linear chain. The metal atoms are described by a tight-binding hamiltonian, and self-consistency is introduced in the problem by a Anderson-Newns repulsive interaction $JR_{a-\sigma, a\sigma}$ (where $J=12.9$ eV)⁹ between electrons of opposite spins in the adsorbate. The appropriate parameters for the substrate are chosen as to reproduce the known band features for tungsten 100 surfaces. The adsorbate is considered to couple only to the "surface" metal atom. Previous treatments of similar models of atomic hydrogen chemisorption have limited the self-consistent recalculation of the atomic density to a few atoms in the surface complex¹⁰. In the LSA method, even when a small local space is considered, self-consistency is automatically assured for all atoms in the system. Our procedure was then to examine the convergence of the binding energies and of the charge and spin densities in the substrate, as N_Q is increased.

The corresponding results are presented in Tables I and II. It can be seen that a smoothly extrapolation of the calculated values for the case $N_Q \rightarrow \infty$ is possible. The long range of the spin and charge fluctuations is reflected in the fact that, for the $N_Q = 8$ case, after the first 30(60) atoms the value of the net charge was reduced to only 0.014e (0.007e), while the net magnetic moment had increased to 0.908e (0.955e). To examine the importance of the correct description of the charge flux throughout the system, we carried a similar convergence study for clusters described by the same hamiltonian. In rough terms, we have found that to achieve results of similar quality to those obtained for a given N_Q one has to use a cluster of dimension $2N_Q$; this difference on the size of the final quantum-chemistry problem is unmistakably associated to the artificial charge conservation imposed in a cluster calculation.

Another important feature of the LSA treatment for the chemisorption problem consists in the simple determination of the localized orbitals in the surface complex¹¹. This can be accomplished by the direct diagonalization of the projected density matrix into the local space R_Q ; the eigenvectors associated to eigenvalues equal to 1.0 are entirely confined to the local region. In the present case, two adsorbate-induced states of energies roughly equal to 6.6 eV and 5.0 eV below the Fermi level are found.

2.2 Hydrogen Bond

It is well-known the important role played by hydrogen bonds in the interaction between large biological molecules². We have tested the LSA scheme¹³ by examining within the CNDO model the local character of hydrogen bonds, both weak (as in the coupling between neutral molecules) and strong (as in the case of ion-pair interactions).

As an illustrative example of the first case, we have studied the formation of formamide dimers (Fig. 1). For a fixed geometry of the linear dimer, local spaces of increasing sizes were considered. As can be seen from the corresponding results in Table III, inclusion of all orbitals in the $N-H \cdots O$ complex was required in order to reproduce the bond energy within 5%, although the atomic charges in the hydrogen and oxygen atoms and the corresponding bond orders were well reproduced for even smaller

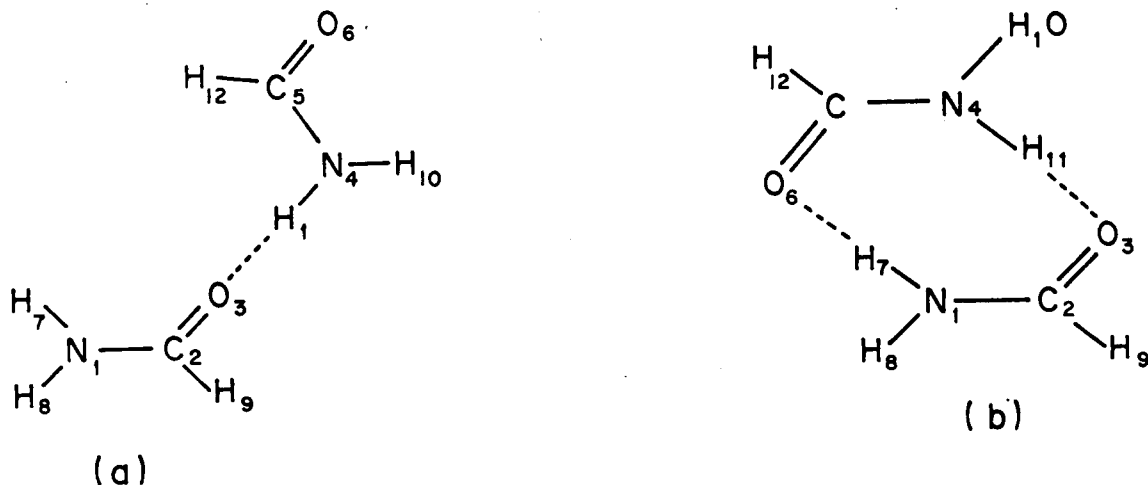


Fig. 1 – Linear antiparallel (a) and cyclic dimers of formamide.

local spaces. Similar results were found for the cyclic dimer. The potential surface for the interaction between the formamide monomers was also well reproduced by the $N-H \cdots O$ local space.

An interesting situation occurred when for the linear dimer the $N-H \cdots O$ angle deviates as much of 180° as to allow the H_7 and H_{12} atoms to interact: in this limit, the orbitals of the corresponding hydrogen atoms have to be added to the local space, since clearly the interaction now is not solely confined to the hydrogen bond. However, a subsequent study of the Watson-Crick adenine-thymine base pair indicates that, provided that only hydrogen bonds are involved in the interaction, even for large molecules local spaces comprising only the $N-H \cdots O$ orbitals for each hydrogen bond present appropriately reproduce the bonding energy, atomic charges and bond orders in the system.

Finally, the case of strong hydrogen bonds as those present in salt bridges and water oligomers was examined. Although in this case a large contribution to the bond energy comes from the charge transfer between the interacting subsystems, small local spaces involving only the orbitals on the bridge atoms were able to reproduce the binding energies and charge distribution of the total system. Once again, cluster calculations of dimensions equivalent to the adopted local spaces fail to satisfactorily account for the correct charge transfer.

2.3 Solitons in Polyacetylene

The study of the electronic structure of polymers has experienced a surge of interest in recent years as a consequence of the discovery that some conjugated systems

have their transport properties dramatically altered by doping³; for example, the electrical conductivity of polyacetylene (PA) samples can be varied over several orders of magnitude by exposure to appropriate dopants. Su, Schrieffer and Hegger (SSH)¹³ have proposed that conformational defects of soliton nature (Fig. 2) play a crucial role on the electronic properties of these systems. In their analysis, the interruption in the normal ordering of single and double bonds in the defect region would lead to a singly occupied localized state halfway between the valence and conduction bands of the material. Electrons could then be easily exchanged between this localized level and the neighboring dopant molecule, resulting in charged defects. Since the thermal barrier to motion is estimated to be small, the defects are assumed to move freely along the conjugated chains. This is the reason for the name **soliton** attached to the defect which is essentially a mobile radical in chemical terms.

Resonance studies¹⁴ have confirmed the general features predicted by simple electronic structure calculations^{13,15} for the wavefunction associated with the neutral solitons. For a defect centered at a reference site zero, for example, the calculated wavefunction is a damped oscillatory spin wave which vanishes at the odd carbon sites. Subsequent ENDOR studies¹⁶ have shown, however, that a small negative spin density should be present at the odd sites. It is generally believed that correlation effects absent in the simple electronic models used could give origin to the observed negative spin densities at alternate sites. This has been confirmed by finite chain calculations using more elaborate hamiltonians¹⁷⁻¹⁸. However, the

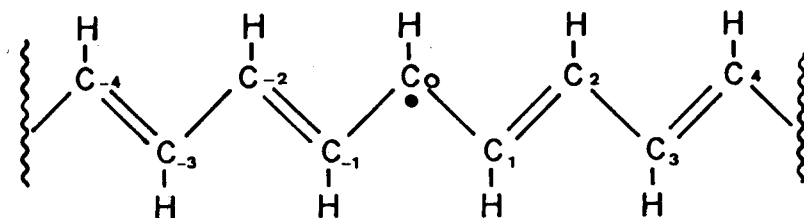


Fig. 2 – Single-site model of a soliton defect in polyacetylene.

difficulties of handling aperiodic systems (as a soliton-bearing chain) in a self-consistent manner have precluded the use of similar treatments for the infinite system.

At this point, the unique features of the local space method present an advantage, since a soliton can be considered as a localized electronic perturbation in an otherwise regular polymer. We have then applied the LSA to describe the self-consistent treatment of single-site solitons in infinite PA chains¹⁹. We have considered as our zeroth order system the soliton-bearing chain described by a SSH hamiltonian, the perturbation being the switching of the correlation terms of Hubbard-like (i.e. on-site repulsion) nature. Far from the defect region all carbon atoms must remain equivalent and therefore the perturbation should be short-ranged. For a local-space comprising seven carbon atoms, for example, we have found that the spin wave associated with the soliton is "squeezed" into the vicinity of the central atom, as more density is drained into this region. From the values of Table IV one can see that inclusion of correlation effects leads to negative spin densities at the odd carbon sites as experimentally observed.

3. CONCLUSION

The examples discussed above show the potentiality of the local space approach for the treatment of localized

electronic perturbations in extended systems. While the hydrogen bond studies were performed basically for the testing of the method, we continue presently pursuing the study of the chemisorption problem and of the electronic structure changes introduced by conformational defects in conjugated polymers. In the first case, we plan to apply the LSA to describe the interaction between adsorbed atoms in a surface, while the effect of defects on the optical properties of polymers is object of interest in the latter. For both, we believe that the local space approach offer unique advantages, as the possibility of describing in a self-consistent manner these broken symmetry systems.

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TABLE I

Variation of the binding energy (ΔE_b) as well as the electronic charge on hydrogen (n_H) and on the first seven atoms of the metal chain (n_1, \dots, n_7) as a function of the number of metal atoms included in the local space (N_Q). The energies are in eV; the charges in units of e. The adsorbate-surface coupling is $V_{as} = -4.156$ eV; the Fermi level is at -4.6 eV; and the total d-band width is 10 eV.^a

N_Q	ΔE_b	n_H	n_1	n_2	n_3	n_4	n_5	n_6	n_7
1	2.560	1.129	0.959	0.936	1.000	0.990	1.000	0.996	1.000
2	2.776	1.156	0.937	0.985	0.975	0.979	0.999	0.991	1.000
3	2.869	1.164	0.922	1.000	0.981	0.963	0.997	0.922	0.999
4	2.924	1.170	0.917	1.013	0.980	0.987	0.977	0.988	0.997
5	2.957	1.174	0.912	1.019	0.978	0.993	0.988	0.974	0.996
6	2.980	1.177	0.909	1.025	0.976	0.999	0.988	0.989	0.983
7	2.995	1.179	0.906	1.029	0.974	1.002	0.987	0.992	0.991
8	3.013	1.181	0.903	1.033	0.973	1.006	0.986	0.996	0.991

^adetailed results can be found in Ref. 8.

TABLE II

Variation of the magnetic moment (μ_H) and on the first seven atoms of the metal chain (μ_1, \dots, μ_7) as a function of the number of metal atoms in the local space (N_Q). The magnetic moments are in units of e .^a

N_Q	μ_H	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6	μ_7
1	0.604	-0.186	0.419	0.000	0.067	0.000	0.028	0.000
2	0.493	-0.188	0.283	0.114	0.120	0.006	0.050	0.001
3	0.436	-0.192	0.241	-0.016	0.245	0.013	0.080	0.003
4	0.402	-0.184	0.211	-0.031	0.164	0.080	0.106	0.009
5	0.377	-0.179	0.193	-0.040	0.146	0.007	0.180	0.015
6	0.355	-0.173	0.177	-0.043	0.129	-0.004	0.121	0.069
7	0.340	-0.168	0.166	-0.045	0.120	-0.013	0.110	0.014
8	0.322	-0.162	0.154	-0.045	0.110	-0.016	0.097	0.005

^adetailed results can be found in Ref. 8.

TABLE III

Variation of hydrogen-bond energy and charge and bond-order parameters of the $O \cdots H$ complex as a function of the local space in formamide antiparallel linear dimer ($R_{N \cdots O} = 2.535 \text{ \AA}$). Detailed discussion can be found in Ref. 12.

Local Space ^a	H-bond energy ^b	Atomic charges ^c		Bond orders ^d	
		H	O	1s/2s	1s/2p _{σ}
$H \cdots O(\sigma)$	7.50	0.175	-0.383 ^e	0.118	0.158
$H \cdots O$	7.66	0.177	-0.368	0.119	0.159
$N(\sigma) \cdots H \cdots O(\sigma)$	8.39	0.182	-0.387 ^e	0.118	0.161
$N-H \cdots O$	8.68	0.185	-0.370	0.120	0.162
$N-H \cdots O \cdots C$	8.86	0.185	-0.372	0.120	0.164
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full space	9.05	0.188	-0.375	0.121	0.165

^aThe notation $O(\sigma)$, $N(\sigma)$ means that only σ orbitals on the atom in question are included. Otherwise both σ and π are present.

^bIn units of kcal/mole.

^cIn units of electronic charge.

^dThe notation 1s/2s indicates that the bond order between the hydrogen 1s orbital and the oxygen 2s. For calibration purposes note that the bond order in H_2 is 1.000.

^eThe number of π electrons on oxygen was taken from the results of the calculation listed on the next line of this table.

TABLE IV

Spin densities for carbon atoms in local space.

Atom	0 (central site)	1	2	3
LSA calculation ^a	0.3014	-0.0174	0.1680	-0.0113
Ref. 15 ^b	0.2708	0.0000	0.1554	0.0000

^aself-consistency is included through a Hubbard-like diagonal term $UR_{i\sigma, i-\sigma}$; U was taken as 1.0 eV.

^bnon self-consistent calculation using a tight-binding (simple Huckel) hamiltonian.

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