

Lawrence Berkeley National Laboratory

Recent Work

Title

Interdisciplinary applications of Pauling's metallic orbital and unsynchronized resonance to problems of modern physical chemistry: Conductivity, magnetism, molecular stability, superconductivity, catalysis, photoconductivity, and chemical reactions

Permalink

<https://escholarship.org/uc/item/3n17d1sd>

Journal

The Journal of Physical Chemistry A, 105(1)

ISSN

1089-5639

Author

Lester, William A.

Publication Date

2000-12-08

INTERDISCIPLINARY APPLICATIONS OF PAULING'S METALLIC ORBITAL AND UNSYNCHRONIZED RESONANCE TO PROBLEMS OF MODERN PHYSICAL CHEMISTRY: CONDUCTIVITY, MAGNETISM, MOLECULAR STABILITY, SUPERCONDUCTIVITY, CATALYSIS, PHOTOCONDUCTIVITY AND CHEMICAL REACTIONS

Antonio C. Pavão^a, Carlton A. Taft^b, Tereza C. F. Guimarães^c, Marcelo B. C. Leão^a, José R. Mohallem^d, and William A. Lester, Jr.^e

^aDepartamento de Química Fundamental, Universidade Federal de Pernambuco 50740 - 540, Recife, PE, Brazil

^bDept. de Materia Condensada e Física Estatística, Centro Brasileiro de Pesquisas Física, - Rua Dr. Xavier Sigaud, 150, CEP 22290-180, Rio de Janeiro Brasil

^cUniversidade do Estado de Bahia, Dept. de Ciências Exatas e da Terra, Estrada das - Barreiras 1, Narandiba, Salvador, Bahia

^dDepartamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas - Gerais, C.P. 702, 30161-970, Belo Horizonte, MG, Brazil

^eChemical Sciences Division, Lawrence Berkeley National Laboratory and Department of - Chemistry, University of California, Berkeley, California 94720-1460

ABSTRACT: The resonating valence bond theory, emphasizing unsynchronized resonance and metallic orbitals, introduced by Pauling 50 years ago, has become an easily visualized tool for describing some electron transfer processes. It has yielded simple, qualitative and useful descriptions of a wide variety of phenomena including the stability and geometry of molecules, conductivity, photoconductivity, superconductivity, magnetism, surface catalyzed reactions, chemical carcinogenesis as well as the stability of the metallic state.

I. Introduction

Linus Pauling's¹⁻⁴ resonating valence bond (VB) theory, hereafter denoted RVB, yields simple consistent explanations of several molecular phenomena, and *synchronized* resonance has become very popular, appearing in most chemistry textbooks. Although less familiar, *unsynchronized* resonance of covalent bonds through a metal has also proved to be a very useful concept for understanding electrical conductivity and other metallic properties.

General VB theory admits not only various spin-coupling schemes that label regions of a molecule or of a crystal where chemical bonds are formed, but also changes of orbital configuration arising from transfer of electrons between orbitals such that some atoms become formally negatively charged and others positively charged. The RVB theory considers that two electrons with opposite spins and occupying orbitals on adjacent atoms form a covalent bond, which may have some ionic character, and that these covalent bonds resonate among alternative positions in a metal.

Consider Pauling's original lithium example¹⁻². Much more important to the stabilization of a Li crystal than synchronized resonant structures (Fig. 1) are unsynchronized resonant structures such as shown in Fig. 2 in which one bond resonates independently from one position to another. Such unsynchronized resonance requires, however, that the atom receiving a bond (Li^+ or Li) have an orbital available for receiving the electron. It is the possession of this orbital, the *metallic orbital*, in addition to the orbitals required for occupancy by unshared electron pairs and

bonding electrons, by all or many of the atoms in the condensed phase that makes possible unsynchronized resonance of covalent bonds and gives rise to metallic properties. By a succession of shifts by single bonds, a negative charge is seen to move in the appropriate direction from atom to atom in a crystal⁶.

Fifty years ago Pauling identified the metallic orbital in describing the nature of transition metals¹. In 1987 he employed the concept of metallic orbital and the same statistical arguments to explain superconductivity in some copper oxide compounds⁴. The present authors recent VB and molecular orbital (MO) calculations showed that the metallic orbital and unsynchronized RVB structures yield useful descriptions of a wide variety of phenomena⁵⁻²². This paper presents a concise review of RVB theory with new applications based on both ab initio and semiempirical calculations. In Sec. II we describe conductivity in metals and organic polymers, photoconductivity in nickel dihalides, superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, magnetism of iron, dissociation of diatomic molecules on 3d-transition metal surfaces, O_4 formation, and chemical carcinogenesis—all in the RVB formalism⁵⁻²². Computational details are given in Sec. III. Conclusions follow in Sec. IV.

II.1 Generality of RVB Theory

Pauling's idea was based on empirical arguments when he demonstrated the value of unsynchronized resonant structures as a tool for understanding the properties of metals. However, we can also show that RVB theory works using ab initio calculations. In the lithium case, consider, for example, a Li_4 cluster with D_{2h} symmetry (Figs. 1 and 2). Labeling the orbitals of atom 1 as 1 (normal orbital, occupied in common Kekule covalent or ionic structures) and 1' (metallic orbital, occupied only in Pauling structures) and so on, the structures can be

represented as ordered sequences of numbers (labels of the occupied orbitals). A Kekule covalent structure, for example, with bonds 1-3 and 2-4 would then be represented as:

$$1324 = A[\phi_1(r_1) \phi_3(r_2) \phi_2(r_3) \phi_4(r_4)] \theta \quad [1]$$

A typical Pauling structure, say 133'4, would then be written

$$133'4 = A[\phi_1(r_1) \phi_3(r_2) \phi_{3'}(r_3) \phi_4(r_4)] \theta \quad [2]$$

in which the 1-3 bond involves the normal orbitals of atoms 1 and 3 but the 3'-4 bond involves the metallic orbital of atom 3 and the normal orbital of atom 4. Here θ denotes a $S = 0$ spin wavefunction, (cf, ref. 5). RVB calculations of the $\text{Li}_4 D_{2h}$ cluster show that the binding energy per atom increases from 1.21 eV to 2.18 eV as, in addition to the synchronized resonant structures, i.e., *Kekule structures* (Fig. 1), unsynchronized resonant structures, called *Pauling structures* (Fig. 2), are introduced.

In addition to predictions of the behavior of general metallic clusters, these RVB calculations yield a finding that links conformation, electronic structure, and stability. The finding may be stated: *As Pauling structures enable each atom to make a covalent bond with all its neighbors, the system will seek a conformation that makes the bonds as equal in length as possible, leading to more metal-metal pathways and to increase of the coordination number of the atoms.* This finding applies particularly well to even n systems, for which all the electrons can be paired in covalent links, and immediately predicts high stability for $n = 6$ in a plane and $n = 8$ in three dimensions. It has been shown that among the planar alkali clusters, $n = 6$ should be a magic number⁵. Our first ab initio VB calculations on lithium clusters with explicit use of unsynchronized resonance structures confirmed the importance of the metallic orbital and the

covalent character of the metal-metal bond⁵. Pauling structures for Li_4 substantially stabilize the ground state electron structure, and the pivotal switch of their bonds does provide a VB representation for electron conduction.

Harcourt and co-workers have done some important work using the VB formalism²³⁻²⁹. These authors provide an alternative representation²³ which involves one-electron transfer into antibonding MOs. This formulation, which can now be somewhat modified, might also be considered. For the $\text{Li}^{(+)}\text{Li}-\text{Li}^{(-)}-\text{Li}^*$ Pauling structure, the (truly) divalent $\text{Li}^{(-)}$ uses orthogonal s and p atomic orbitals (AOs) to form the two bonds, Either Heitler-London type wavefunctions (as in Ref. 5) or (essentially) orthogonal localized MOs can then be used to formulate the wavefunctions for electron-pair bonds.

We have also recast the RVB theory in a nonorthogonal ab initio VB formalism and applied it to the study of small anionic lithium clusters. The Pauling structures have large weight compared to the Kekule structures, which emphasizes the importance of RVB theory in the VB description of these systems. The preference of small anionic clusters for linear geometries and the influence of the extra electron have a clear connection to Pauling structures²².

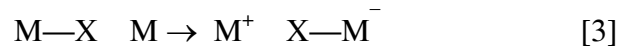
RVB theory can also describe conductivity in some organic polymers. Polyacetylene, $(\text{CH})_x$, is a particularly important example in which the degenerate ground state should lead to important soliton excitations in which the π band is half-filled, implying the possibility of metallic conductivity. In conjugated polymers, carbon sp^2p_z hybridization leads formally to one unpaired electron per carbon atom. Consequently, the electronic structure is determined by chain symmetry (i.e., the number and kind of atoms in the repeat unit) with the result that such polymers can be expected to exhibit semiconducting and possibly metallic properties³⁰. A chain

of atoms (or more generally, monomers made up of groups of atoms) can be dimerized in two distinct patterns that have the same energy. Labeling the atoms (or monomers 1,2,3, . . .), one could have the bonding structures 1=2-3=4-5=6 or 1-2=3-4=5-6 denoted as A and B phases. Clearly, if all monomers are equivalent and the chain is infinite in extent, the energies of these bonding structures are the same. In the language of quantum field theory, the vacuum state is two-fold degenerate. The domain wall is a nonlinear shape-preserving excitation which propagates freely called a soliton. A moving soliton converts A-phase material into B-phase material (and vice versa). The undoped trans-(CH)_x resembles a semiconductor with a band gap but through doping the electronic properties can be controlled³⁰. At dilute doping levels, the intrinsic resistivity of the material dominates but heavy doping can lead to a regime of high conductivity in which the amount of unsynchronized resonance becomes so great as to make the conducting state more stable than the insulating state. The electrical conductivity in trans-(CH)_x can be rationalized in terms of unsynchronized resonating structures (Fig. 3.) In Figure 3, the apparently pentavalent carbon carbon atoms in the second and third VB structures arise only if two non-orthogonal localized MOs are used to accommodate the four π electrons. The types of unsynchronized resonance used for the two cases differ, see for example refs. 24-26.

In the presence of an applied electromagnetic field, electrons tend to move from atom to atom. By a succession of bond shifts, negative charge moves toward the anode. In a similar way positive charges (electron holes) move toward the cathode. The probability of resonance is small for a chain of atoms with alternating single and double bonds - there are only two structures. As the sequences are interrupted, for example, by oxidation (or reduction) of a carbon center, the probability of unsynchronized resonance is increased. The mobile charge carriers introduced in the π -electron system are responsible for the electrical conductivity of conducting polymers. It

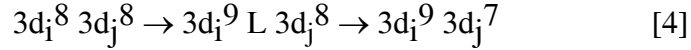
must be noted, however, that charge transport is limited by microscopic defects and sample imperfections.

We now consider RVB in describing insulating materials. Mott-Hubbard theory predicts that the band gap in insulating transition metal compounds involves transitions of the type $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$, where i and j label transition metal sites³¹. We note, however, that for these materials, a unified theoretical description of the observed band structure has not been achieved. The 3d orbital interaction is at the center of the controversy. Other authors have interpreted the optical absorption gap in terms of a $p \rightarrow d$ transition, an interpretation which involves only one transition metal atom. In fact, photoconductivity experiments in nickel dihalide compounds (NiCl₂, NiBr₂, and NiI₂) indicate an optical gap corresponding to $p \rightarrow d$ charge-transfer transitions⁶. By applying RVB theory to describe the photoconductivity in nickel dihalide compounds, it is possible to unify these interpretations. Based on the band structure and on the nature of the chemical bond of insulating nickel difluoride constructed using the s, p, d Multiple Scattering X α (MS-X α) spin-polarized orbitals of an octahedral (NiF₆)⁻⁴ cluster, unsynchronized resonance of the covalent bonds can be depicted as follows⁶:



where X represents F, Cl, Br, and I. As required for unsynchronized resonance of covalent bonds, the atom receiving a bond must have an orbital available for electron reception. MS-X α calculations indicated that this orbital can be identified as the unoccupied metallic 3d: e_g spin minority molecular orbital (the 4 e_g molecular orbital in the NiF₆⁻⁴ cluster has large Ni:3d character [8]). The $p \rightarrow d$ charge transition creates the M^- state Ni(3d⁹) as well as the hole in the p band. Therefore, the structure required for unsynchronized bond resonance ($M^+ X - M^-$) is

attained when the photohole is transferred from the anion p band to the 3d state of the nearest-neighbor nickel ion, creating the M^+ state $Ni(3d^7)$. The process can be described as:



where L is a ligand hole. The creation of the M^+ and M^- charge polarized states is a charge-transfer process in which one electron moves from the ligand to the metal and a hole moves from the ligand to another nickel in the opposite direction. The photohole excited state $3d^9 2p^5 3d^8$ decays to the $3d^9 2p^6 3d^7$ state. The global process is equivalent to the shift of a covalent bond from one nickel to another in the crystal, making RVB equivalent to Mott-Hubbard theory in the sense that two metal atoms are involved in the electron transfer. There is a resonance from $2Ni^{+2}$ to Ni^+ and Ni^{+3} . A direct consequence of this interpretation is that the magnitude of the band gap is determined by

$p \rightarrow d$ charge-transfer energy, i.e., there is a dependence of the band gap on the electronegativity of the ligand and it is possible to reduce the conductivity gap by an appropriate choice of ligand. The difference between the insulator NiO and the conductor NiS, for example, is that in the insulator the electrons are localized in the 2p band and require energy for the first step of the unsynchronized resonant-valence-bond mechanism, while for metallic NiS the first step is facilitated by itinerant electrons of the hybridized Ni(3d) and S(3p) band, with no charge transport gap⁶.

It has been noted that $(NiF_6)^{4-}$ with a ${}^3A_{2g}$ ground-state is a hypoligated transition metal complex²⁷. A VB description for this complex involves resonance between 15VB structures, each of which involves four (polar) Ni-F electron-pair bonds (each as (σNiF^2) $(\sigma^* NiF^0)$), using a simple MO formulation of the wavefunction for the electron-pair) and two Ni-F Pauling three-

electron bonds (each as (σNiF^2) (σNiF^1)). The two (parallel-spin) odd-electrons occupy the two antibonding MOs. With this type of VB description, perhaps the photoconductivity could also be formulated via the transfer of an electron from an antibonding $\sigma^*\text{NiF}$ MO located around an adjacent metal center²⁷.

II.2. Superconductivity

In BCS superconductivity theory, the interaction of electrons and phonons causes a clustering of electrons that move in phase with a phonon when the energy of this interaction is greater than the phonon energy⁴. In RVB theory the electronic structure of the metal is described in successive steps involving integrals of decreasing magnitude. At first, two electrons with opposite spins and occupying orbitals on adjacent atoms form a covalent bond, which may have some ionic character. Second, these covalent bonds resonate among alternative positions in the metal. RVB theory is in many ways equivalent to the conventional band theory of metals, but it has the advantage that it far more easily permits discussion of the dependence of metal properties on the identity of the constituent metal atoms. Pauling⁴ suggested that for the superconductor La ($T_c = 6\text{K}$) the rate of $M^- M^0 \rightarrow M^0 M^-$ (electrons moving to the right on the crest of the phonon), is greater than that of the $M^+ M^0 \rightarrow M^0 M^+$ (holes moving to the right on the trough of the phonon) because the exchange integral is smaller for the motion of the hole as a result of the smaller size of M^+ relative to M^- . This characteristic causes holes to fall behind electrons in following the phonons.

The mechanism of superconductivity of copper oxide compounds can be described by the theory of unsynchronized resonance of covalent bonds. Although electron pairs can move along a string of atoms in synchronism, if some O atoms are missing, so that vacancies interrupt the

sequence, then there would be the possibility of unsynchronized resonance⁴. If the segments are short enough, the amount of unsynchronized resonance can become so great as to make the conducting state more stable than the insulating state, as is the case for metals. Suitable doping may be required and the interactions with La (Ba, Sr) are also essential for high-temperature superconductivity. The critical temperature (T_c) increases as scattering of electrons by phonons decreases, i.e., as the strength of the electron-phonon interaction decreases.

In summary, several structural features, including electron transfer between atoms of different electronegativity, oxygen deficiency, and unsynchronized resonance of valence bonds, as well as tight binding of atoms, cooperate to confer metallic properties and high-temperature superconductivity on copper oxide superconductors. The superconducting transition temperature decreases considerably when group VIII, IB and IIB metal ions are substituted for Cu ions. We have, in collaboration with other authors⁷⁻⁹, investigated the substitution of CuO by NiS in these superconductors and reported x-ray diffraction, resistivity, and ac magnetic susceptibility findings for a set of samples with nominal composition $YBa_2\{(Cu_3)_{1-x}(NiS)_x\}_3O_{4-\delta}$. We found a small increase in T_c and a decrease of the room temperature resistivity in a certain substitution of CuO by NiS. These results seem to agree with RVB theory which predicts increasing T_c as unsynchronized resonance increases, which is the case when semiconducting CuO rings are substituted for conducting NiS rings. Our fluorescence x-ray emission spectra show that sulphur atoms enter the lattice and form oxyanion groups⁹.

II.3. Magnetism in Iron

A theory of superconductivity should explain the Meissner effect, which shows that a superconductor is a perfect diamagnetic system; magnetic flux is excluded from all but a thin

penetrable region near the surface. A complete quantitative treatment of the magnetic behavior of transition metals does not exist. Magnetism in Fe, Co, and Ni is problematic because 3d electrons are neither completely localized onto single centers nor entirely delocalized. Both the localized Heisenberg picture and the itinerant-electron theory developed by Stoner, implemented in connection with band theory, have been invoked to explain different aspects of the observed magnetic properties of Fe, Co, and Ni¹⁰. Further, molecular field theory, either from the view of localized electrons or itinerant electrons, has been unable to satisfactorily explain the observed magneton number. Over the past decade a large number of experimental and theoretical studies have been performed on small metallic clusters, including bimetallic systems, which are of great interest in surface physics and chemistry, nucleation, heterogeneous catalysis, alloy formation and magnetism.

For the magnetic 3d transition metals, Fe, Co, and Ni, systematic studies by various authors show serious discrepancies with experiment. A long-standing goal is better comprehension of the origin of magnetism in these metals. For iron, in particular, chemical properties cannot be divorced from magnetic properties, since ferromagnetism leads to shifts on the order of an electron volt or more in energy levels due to spin polarization. Pauling also made important contributions to the phenomenon of magnetism in transition metals and proposed an interesting correlation between the magnetic properties of transition metals and the bonding of 4s and 3d electrons, metallic orbitals, and resonance of covalent bonds. The present authors¹⁰ reported ab initio Hartree-Fock calculations on the *quintet spin* state of Fe₂ in a study of the electronic, magnetic, and chemical bonding properties as well as the hyperfine interactions. Good agreement was found with band-theoretical and experimental parameters. The calculations support Pauling's model of occupation and bonding of valence orbitals, resonance of covalent

bonds, and conduction-band metallic orbitals. The calculated magneton number was found to be in good agreement with experiment.

II.4. O₄ Molecule

Various experimental and theoretical studies of O₄ lead to different descriptions of its stability and geometry (see Ref. 18 and references contained therein.) The present authors carried out ab initio MCSCF (multi-configuration self consistent field) calculations to clarify discrepancies regarding the structure and stability of this molecule. The study indicated a stable O₄ molecule. The system is found to be more stable for D_{2h} symmetry than for D_{4h} symmetry, in agreement with experimental studies of the O₂ dimer¹⁸.

Further support for D_{2h} symmetry for O₄ is provided by Pauling's RVB theory. An easy visualization of O₄ formation is as a two step charge transfer process involving two O₂ molecules (see Fig. 4).

The first step of the mechanism is O₂ → □ O₂ electron transfer with corresponding bond transfer from one O atom of one O₂ molecule (which acquires a positive charge) to an O atom (which acquires a negative charge) of the other O₂ molecule. RVB theory requires that the atom receiving a bond must have an orbital available for electron reception. In the case of O₂⁻, this orbital is identified with the 2π* antibonding molecular orbital. In this process, the first electron transfer creates the O₂⁺ — O₂⁻ bond. The O — O bond of the O₂⁻ unit is weakened due to the occupation of the 2π* antibonding orbital while the O — O bond of the O₂⁺ unit is stronger due to the loss of an electron from an antibonding MO. The second step of the mechanism is O₂⁻ → O₂⁺ electron back-donation. This second interaction is similar to the first one in the sense that for both interactions the orbital receiving the electron is a 2π* antibonding

MO. In this RVB mechanism the electron completes a cycle and forms new bonds. The resulting O_4 molecule must have D_{2h} symmetry since the bonds between the two O_2 units, $O_2 - O_2$, are different from the $O - O$ bonds in each O_2 unit. This prediction of D_{2h} symmetry by RVB theory is in agreement with experiment and with MCSCF calculations¹⁸.

More recent work²⁸⁻²⁹ yields additional details of O_4 formation. The O_2 structures have $S = 0$ spin excited states and $S = 1$ spin ground states and the O_4 VB structure does not retain double-bond character for the O_2 moieties. The (Linnett-type) VB structures 6 and 7 of ref. 28 with two Pauling three-electron bonds $(\pi_x)^2(\pi_x^*)^1$ and $(\pi_y)^2(\pi_y^*)^1$ for the six π electrons, and parallel spins for the two antibonding electrons, are the appropriate VB structures for the O_2 ground state. The primary dimerization²⁸ process involves the spin pairings of the antibonding unpaired electrons to generate an increased-valence structure for D_{2h} O_4 with fractional intermolecular bonds. This spin pairing process alone, however, does not stabilize the dimer relative to the two separated O_2 monomers. Although the VB calculation which are reported in ref. 29 are not necessarily definitive, they do indicate that dispersive interactions, with some help from charge-transfer, are primarily responsible for the small stabilization of the dimer. Attention has been focused on the importance of dispersive interactions by others; see, for example, refs. 2 and 3 of ref. 29.

II.5. Dissociation of Diatomic Molecules on Transition Metal Surfaces

Heterogeneous catalysis serves today as the basis for most petroleum and chemical technologies and has substantial importance for the life sciences as well as for environmental protection. It

has been intensively investigated with the tools of physics, quantum chemistry, and surface science. A particularly interesting and important area of catalysis is the interaction of diatomic molecules (CO, N₂, NO, H₂, and O₂) with transition metal surfaces which can lead to breaking and making chemical bonds and trigger important surface catalyzed reactions. In particular, the CO interaction with transition metals has been described in terms of charge transfer from the metal to CO (back donation) and from CO to metal (forward donation) charge transfer, i.e., the Blyholder model³². This model does not consider, however, the existence of tilted states or the unusually low CO stretching frequencies observed for CO on some transition metal surfaces. The present authors have published a number of papers¹⁰⁻¹⁵ in which ab initio molecular orbital calculations and the unsynchronized resonating-valence-bond mechanism formed the basis for a modification of the Blyholder model that explains tilted states, dissociation of diatomic molecules and low stretching frequencies observed on some transition metal surfaces. The RVB mechanism of CO dissociation is schematically represented in Fig. 5 where A = C, B = O.

The first electron-transfer step leads to bond formation between the surface, M(s), which acquires a positive charge (M⁺). It is the possession of the lowest unoccupied 2π* molecular orbital, as required by Pauling's theory, that makes possible the interaction of CO as a Lewis acid with the metal surface. The primary interaction in the CO adsorption process on a transition metal surface is the so-called metal → (2π*) CO back-donation. The metal attacks the carbon atom where the unoccupied 2π* molecular orbital is mainly localized. The charge transfer process leads to a build up of negative charge mainly on carbon, although a significant portion also delocalizes onto oxygen^{11-17, 21}. In the next step, the C-O bond is transferred to the metal surface. Then CO dissociation occurs when the electron returns to the surface, restoring electrical neutrality as it must in a catalytic process. The electron traverses a closed loop while

dissociating the CO molecule. Note that the condition for the dissociation is determined by the amount of charge-transfer in the first step, which is generally larger in the tilted configuration (and the consequent C-O weakening.) If there is no metal $\sigma \rightarrow$ CO charge transfer, then molecular adsorption will be observed.

Experiments have established that CO adsorption on the first-row transition metal surfaces, Sc to Fe, leads to dissociation, whereas for Co to Cu, CO remains adsorbed on the surface. Ab initio charge transfer calculations for the monocarbonyl complexes are in agreement with these experimental results. It was found that each metal from Sc to Fe is positively charged in the monocarbonyl M-CO system consistent with the unsynchronized resonating-valence bond mechanism of CO dissociation. For Co, Ni, and Cu, however, no net charge transfer was found. Furthermore, higher metal $\sigma \rightarrow$ CO charge transfer is obtained for the inclined molecule ($\sim 45^\circ$ relative to the surface.) The tilted state was identified as the precursor state for CO dissociation. The observed preference for charge transfer in the bent structure is consistent with the present model, since a bent and charged adsorbed molecule is predicted as the intermediate state in the second step of the unsynchronized RVB mechanism. Our model was also extended to N_2 (A, B = N) interaction with transition metal surfaces as well as the diatomic molecules O_2 , H_2 , and NO . In general, in the tilted configuration, large charge transfer weakens A-B bonds and lowers stretching frequencies^{11-17, 21}. We note, however, that more accurate VB calculations would be helpful in order to shed more light on how the CO bond and other diatomic-molecule bonds are fully broken. For discussions regarding the types of unsynchronized resonances which could be relevant for the phenomena described in Fig. 5, see refs. 24-26.

II.6. Chemical Carcinogenesis

Over fifty years ago Hammett suggested the correlation of biological response with electronic parameters³³. Since the pioneering work of Miller³⁴, it has been recognized that chemical carcinogens are, or are converted by metabolism into, electrophilic reactants that exert their biological effects by covalent interaction with cellular macromolecules (DNA, RNA and proteins)³⁵⁻³⁸. In our previous work¹⁹, large electron affinities (EAs) were calculated for several families of carcinogens, confirming experiments and other computational studies that show that these species react as electrophiles³⁵⁻³⁸. The present analysis of the DNA-carcinogen interaction implies that the ultimate chemical metabolite becomes covalently bound to liver DNA as a consequence of HOMO (DNA) \rightarrow LUMO (carcinogen) electron donation. This electron transfer, which leads to DNA-carcinogen bond formation, can be described in the framework of RVB theory (see Fig. 6). The benefit of introducing Pauling's theory is that it permits the rationalization of the electron transfer process in terms of the molecular structure of the isolated molecules. Using the frontier orbital approximation, the DNA-carcinogen interaction is treated as an electron transfer from the HOMO of DNA to the LUMO of the carcinogen. This unsynchronized resonance requires that the system receiving a bond have an orbital available for electron reception. It is the existence of such an orbital, the LUMO of the carcinogen with the appropriate energy that makes possible DNA \rightarrow carcinogen electron donation and subsequently DNA-carcinogen bond formation. Chemical carcinogens can be divided into two main groups: those that act directly on DNA, and those that act indirectly. In the majority of compounds that can induce cancer, the ultimate carcinogen is a metabolite of the original compound. Nitrosamines, for example, are not carcinogens per se; they must be metabolized to be converted into ultimate carcinogens³⁸⁻⁴⁰. Nitrosoureas, unlike nitrosamines, are direct-acting carcinogens.

For dimethylnitrosamine (DMN), a considerable body of evidence indicates that damage to cellular DNA and proteins is caused by diazomethyl and dazomethane metabolites³⁹.

Notwithstanding the considerable research on carcinogens, many features of their formation and metabolism are still not fully understood. There is evidence that different carcinogen-derived alkylating agents react at specific guanine sites⁴⁰. Oxygen alkylation is believed to be a critical mutagenic event, whereas nitrogen alkylation may be innocuous. The DNA to carcinogen electron transfer mechanism²⁰ combined with MO calculations show that carcinogens are converted by metabolism into strong electrophilic reactants. In the framework of RVB theory, this electron transfer leads to the formation of a DNA-carcinogen covalent chemical bond. We have calculated the electron affinity (EA) of known carcinogens including some common species such as water, ethanol, and glucose, which are found in animal plasma. The ultimate carcinogens have the highest EAs compared to the original compound or to the other metabolites. On the other hand, ionization potential (IP) calculations of the 35 tautomers of the DNA bases indicate that guanine has the lowest IP, being the preferential base for carcinogen electrophilic attack. An analysis of HOMO contour maps shows that DNA alkylation occurs at specific nitrogen and oxygen sites, in agreement with experiment³⁵⁻⁴¹.

To obtain an approximate view of the nucleophilic sites of DNA, we considered the HOMO energy of the DNA/RNA base units. The tautomeric forms of these bases were also calculated. Among the DNA bases, guanine has the highest HOMO energy and can be considered the preferential site for carcinogen attack. The major HOMO components of the guanine base are localized at specific nitrogen and oxygen sites indicating that these atoms are the most appropriate centers for interaction with the carcinogen. Experimental evidence leads to the same conclusion³⁴⁻³⁶. Pauling and Cameron⁴² pointed out that vitamin C has anticancer action.

According to the present model one can consider that the protector agent competes with the substrate (DNA, proteins) in donating an electron to the carcinogen. We found that the ascorbate HOMO energy (-3.19 eV) lies well above the guanine HOMO energy (-7.91 eV), indicating that the ascorbate ion is energetically favored for the interaction with the carcinogen relative to the DNA base. It is known that ascorbic acid metabolizes (almost 100%) to ascorbate anion in the human body. In general, anions have high HOMO energies and hence they can react as protectors. It has been reported that the increase of degenerative diseases has been correlated to the reduction of anions in air⁴³.

In the absence of more sophisticated calculations we suggest that the carcinogen-DNA interaction be described as an electron transfer from the HOMO of the substrate to the LUMO of the carcinogen. It is found that this electron transfer occurs preferentially from the guanine base. Molecular orbital calculations indicate that chemical carcinogens have electrophilic character, in agreement with experimental results. Carcinogenesis involves many complex factors, however, the overall picture emerging from the present simple analysis corresponds to the interpretation of the observed action of chemical carcinogens.

III. METHODS

Various forms of ab initio VB theory are in current use. We used the approach in which structures of arbitrary type are admitted and a unique set of nonorthogonal orbitals, expressed as linear combinations of a global set of basis functions, are fully optimized⁵. The basis function used for the Li_n cluster calculations consist, for each atom, of a 7-term gaussian contraction for the lithium 1s core plus a valence basis having 3 single s type gaussians with exponents 0.020, 0.047, 1.051, and 2 p type gaussians (p_x , p_y) with exponent 0.1135. The MS-X α method was

employed to describe the electronic structure¹⁰ of nickel halides clusters of the type $[\text{NiX}_6]^{4-}$. The interatomic distances were taken from experiment. The α value is 0.72 for all the muffin-tin regions of the cluster. The self consistent field (SCF) ab initio HF as well as the semiempirical AM1 (Austin Method 1)⁴⁴ MO calculations were performed for selected systems studied here. Different gaussian basis sets were employed. Diffuse functions and Hartree-Fock gradient techniques were used to obtain a better description of the wavefunction in the valence region and consequently of the anion properties that depend on a reasonable description of this region. For the systems M_nAB ($\text{M} = \text{Sc to Cu}$, $\text{AB} = \text{CO, N}_2, \text{NO, O}_2$, and $n = 1-5$) an effective core potential (ECP) with the Hay and Wadt basis set were used⁴⁵. Electron correlation is included at the MP2 level (second order Moller-Plesset correlation energy correction). Geometry optimizations were obtained at different levels of calculation. The EAs of the carcinogens were calculated using Koopmans theorem ($\text{EA} = -E_{\text{LUMO}}$) and using total energy differences (ΔSCF adiabatic): $\text{EA} = E_{(\text{neutral})} - E_{(\text{anion})}$. The bond distances for the ground state configurations of O_4 and O_2 were fully optimized using the MCSCF method. The computer codes used were MOPAC 93⁴⁶, GAUSSIAN 94⁴⁷ and GAMESS⁴⁸.

IV. CONCLUSIONS

After almost 200 years since its introduction, “*the concept of chemical bond is still one of the most valuable concepts in chemistry,*” but the quantum mechanical concept of resonance of covalent bonds, introduced by Pauling, has turned out to be an illuminating concept in the modern theory of the chemical bond. Although, one-electron transfers rather than electron-bond

pair bond transfers may provide a more important guide to electronic processes in chemistry and the Pauling RVB formulation, $A-B C-D \leftrightarrow A^{(+)}B-C^{(-)}-D$, may not often be the appropriate way to represent electronic reorganization theory, the easily visualized RVB model has proven to be a very useful guide to simple qualitative descriptions of electron transfer processes in chemistry. In addition to the numerous applications discussed in this work, further investigations could reveal an even wider variety of phenomena that can be explained by the RVB theory.

ACKNOWLEDGEMENTS

We thank the referee for very helpful comments. T.C.G., A.C.P. and J.R.M. acknowledge financial assistance from CNPq (Brasil). C.A.T. received financial assistance from PRONEX/FINEP/CNPq (Brasil). W.A.L. was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy.

REFERENCES

1. Pauling, L., The metallic state, *Nature (London)* **1948**, 61, 1019-1020.

2. Pauling, L., The metallic orbital and the nature of metals, *J. Solid State Chem.* **1984**, 54, 297-307.
3. Pauling, L., The nature of the chemical bond, *J. Chem. Educ.* **1992**, 69, 519-521.
4. Pauling, L., Influence of valence, electronegativity, atomic radii and crest-trough interaction with phonons on the high-temperature copper oxide superconductors, *Phys. Rev. Lett.* **1987**, 59, 225-227.
5. Mohallem, J.R., Vianna, R.O., Quintão, A.D., Pavão, A.C. and McWeeny, R., Pauling's resonating valence bond theory of metals: some studies on lithium clusters, *Zeitschrift fur physik D-atoms molecules and clusters*, **1997**, 42, 135-143, and references therein.
6. Pavão, A.C. and Da Silva, J.B.P., Electronic structure and charge-transfer transitions in $(\text{NiF}_6)^{4-}$, *J. Phys. Chem. Sol.* **1989**, 669-673 (1989) and references contained therein.
7. Structural and superconducting properties of MS (M=Fe, Ni or Zn) substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, Aguiar, J.A, Ramos A.S., Cabral L.R.E., Barbosa, M.V., Awana, V.P.S., Ferreira J.M., Pavão, A.C., Chavira E., Kurmaev E.Z., *Journal of Physics – Condensed Matter* **1996**, 8, 10545-10550.
8. Aguiar, J.A., Ferreira, J.M., De Melo, M.T., Schettini, C., Schneider, F., Barbaso, M.V.S., Madeiro de Melo, L.R., Pavão, A.C. and Van Ruitenbeek, J.M., Effect of substitution of CuO by NiS on the superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, *J. of Magnetism and Magnetic Materials*, **1992**, 104, 547-548.
9. Yarmoshenko, Yu M., Trofimava, V.A., Dolgih, V.E., Korotin, M.A., Kurmaev, E.Z., Aguiar, J.A., Ferreira, J.M. and Pavão, A.C., X-ray emission spectra and valence state of sulphur atoms of $\text{YBa}_2[(\text{CuO})_{1-x}(\text{NiS})_x]_3\text{O}_4$, *J. Phys. Condens. Matter* **1995**, 7, 213-218.
10. Pavão, A.C., Hammond, B.L. and Lester, W.A., Jr., A molecular model for magnetic iron, *Phys. Rev. B* **1989**, 40, 2879-2884.
11. Pavão, A.C., Braga, M., Taft, C.A., Hammond, B.L., and Lester, W.A., Jr., Theoretical study of the CO interaction with the Fe (100) surface, *Phys. Rev. B* **1991**, 44, 1910-1913.
12. Pavão, A.C., Braga, M., Taft, C.A., Hammond, B.L, and Lester, W.A., Jr., Theoretical study of the CO interaction with 3d-metal surfaces, *Phys. Rev. B* **1991**, 43, 6962-6967.
13. Pavão, A.C., Soto, M.M., Lester, W.A., Jr., Lie, S.K., Hammond, B.L., and Taft, C.A., Theoretical study of the CO interaction with the Cr(110) surface, *Phys. Surf. Science* **1995**, 323, 340-344.
14. Guimarães, T.C., Pavão, A.C., Taft, C.A, and Lester, W.A., Jr., Interaction mechanism of N_2 with the Cr(110) surface, *Phys. Rev. B* **1997**, 56, 7001-7010.

15. Pavão, A.C., Taft, C.A, Guimarães, T.C. and Lester, W.A., Jr., Breaking bonds of diatomic molecules on transition metal surfaces, Trends in Chemical Physics, **1994**, 3, 109-128 and references contained therein.
16. Pavão, A.C., Guimarães, T.C., Lester, W.A., Jr. and Taft, C.A., Modeling the adsorption and dissociation of CO on transition metal surfaces, J. Mol. Struct. **1999**, 458, 99-121.
17. Guimarães, T.C., Pavão, A.C., Taft, C.A, and Lester, W.A., Jr., Dissociation of N₂ on chromium alloys: general mechanism for dissociation of diatomic molecules, Phys. Rev. B **1999**, 60,11789-11794.
18. Pavão, A.C., Seabra, G.M., and Taft, C.A, Theoretical study of the O₄ molecule, J. Mol. Struct. **1995**, 335, 59-61 and references therein.
19. Leão, M.B.C. and Pavão, A.C., Molecular orbital analysis of chemical carcinogens, Int. J. Quant. Chem. **1997**, 62, 323-328 and references contained therein.
20. Pavão, A.C., Soares Neto, L.A., Ferreira Neto, J. and Leão, M.B.C., Structure and activity of Aflatoxin-B and Aflatoxin-G, J. Mol. Struct. **1995**, 337, 57-60.
21. Taft, C.A, Guimarães, T.C.F., Pavão, A.C. and Lester, W.A., Jr., Adsorption and dissociation of diatomic molecules on transition-metal surfaces, Int. Rev. Phys. Chem. **1999**, 18, 163-233 and references contained therein.
22. Quintao, A.D., Vianna, R.O., and Mohallem, J.R., Resonating valence bond calculations on small anionic lithium clusters, European Physical Journal D, **1999**, 6, 89-97.
23. Harcourt, R. D., Diatomic antibonding σ^* s orbitals as ‘metallic orbitals’ for electron conduction in alkali metals, J. Phys. B: Atom. Molec. Phys., **1974**, 7, L41-45.
24. Harcourt, R. D., On the “pentavalent nitrogen atom and nitrogen pentacoordination, J. Mol. Struct., **1993**, 300, 245-256.
25. Harcourt, R. D., Increased-valence structures and hypervalent molecules, Int. J. Quantum Chem., **1996**, 60, 533-566.
26. Harcourt, R. D., Four-electron three-center bonding: One-electron and concerted two-electron delocalizations into Bonding and Antibonding Molecular orbitals, J. Phys. Chem. A, **1999**, 103, 4293-4297.
27. Harcourt, R. D., and Scollary, G. R., A valence-bond description for hypoligated transition-metal complexes, Inorg. Nucl. Chem. Lett., **1975**, 11, 821-823.
28. Harcourt, R. D., Valence bond studies of the D_{2h} isomer of O₄: An interim report, Int. J. Quantum Chem., **1997**, 63, 547-555.
29. Harcourt, R. D., Pypers, N., Charge transfer and dispersion interaction stabilization of the D_{2h} isomer of O₄, Int. J. Quantum Chem., **1998**, 68, 129-134.

30. Heeger, A.J., Kivelson, A.J.S., Schrieffer, J.R. and Su, W.P., Solutions in conducting polymers, *Rev. Mod. Phys.* **1988**, 60, 781-850 and references contained therein.
31. Fujimori, A., Namatame, H., Matoba, M., and Anzai, S., Photoemission study of the metal-nonmetal transition in NiS, *Phys. Rev. B* **1990**, 42, 620-623 and references contained therein.
32. Blyholder, G., Molecular orbital view of chemisorbed carbon monoxide, *J. Phys. Chem.* **1964**, 68, 2772-2778.
33. Hammett, L.P., *Physical Organic Chemistry*, (McGraw-Hill, New York, 1940).
34. Miller, E.C., Some current perspectives on chemical carcinogenesis in humans and experimental-animals. Presidential address, *Cancer Res.* **1979**, 38, 1479-1496.
35. Ladik J. and Förner, W. *The Beginnings of Cancer in the Cell*, (Springer-Verlag, Berlin, 1994).
36. Pitot, M.H.C., Stevenson, D.E., McClain, R.M., Poop, J.A, Slaga, T.J., and Ward, J.M. *Mouse Liver Carcinogenesis: Mechanism & Species Comparisons* (John Wiley, New York, 1990).
37. Flemming, I., *Frontier Orbitals and Organic Chemical Reactions*, (John Wiley, New York, 1976).
38. Ford, G.P. and Scribner, J.D., Theoretical study of gas-phase methylation and ethylation by diazonium ions and rationalization of some aspects of DNA reactivity, *J. Am. Chem. Soc.* **1983**, 105, 349-354.
39. Reynolds, C.A. and Thompson, C., Ab initio calculations relevant to the mechanism of chemical carcinogenesis by N-nitrosamines. 6. The dissociation of methyldiazohydroxide, *J. Mol. Struct.* **1987**, 34, 345-351.
40. Reynolds, C.A. and Thompson, C., Ab initio calculations relevant to the mechanism of chemical carcinogenesis by nitrosamines. 5. The role of diazomethane, *J. Chem. Soc. Perkin Trans. II.* **1986**, 12, 1927-1931.
41. Blackburn, G.M. and Gait, M.J., *Nucleic Acids in Chemistry and Biology* (Oxford University Press, Oxford 1996).
42. Cameron, E. and Pauling, L. *Cancer and Vitamin C* (Weidenfeld and Nicholson, London, 1980).
43. Soyka, F. and Edmonds, A. *The Ion Effect* (Bantam Books, New York, 1977).
44. Dewar, M.J.S., Zoebisch, E.G., Haly, E.F. and Stewart, J.J.P., AM1 (Austin Method 1) *J. Am. Chem. Soc.* **1985**, 107, 3898-3902.

45. Hay, J. and Wadt, W.R., Ab initio effective core potentials for molecular calculations – potentials for the transition metal atoms Sc to Hg., J. Chem. Phys. **1985**, 82 270-283.
46. MOPAC, Stewart, J.J.P., Quant. Chem. Prog. Exch. Bull, **3**, 43 (1983).
47. Gaussian 94, Frisch, M.J., Trucks, G.W., Head-Gordon, M., Gill, P.M.W., Wong, M.W., Foresman, J.B., Johnson, B.G., Schlegel, H.B., Robb, M.A., Repllogle, E.S., Gomperts, R., Andres, J.L., Raghavachari, K., Binkley, J.S., Gonzalez, C., Martin, R.L., Fox, D.J., Defrees, D.J., Baker, J., Stewart, J.P., and Pople, J.A., Gaussian Inc., Pittsburg PA 1994.
48. GAMESS, Quantum Chemistry Exchange Program, QCPE Bulletin, **10**, 52 (1990).

FIGURE CAPTIONS

- Fig. 1 Synchronized resonance Kekule structures of Li₄**
- Fig. 2 Unsynchronized resonance Pauling structures of Li₄**
- Fig. 3 Unsynchronized resonating structures in trans-(CH)_x**
- Fig. 4 Resonating valence band theory for the D_{2h} structure of O₄**
- Fig. 5 Resonating valence band model for diatomic molecular dissociation on transition metal surfaces**
- Fig. 6 Unsynchronized resonance description of the DNA $\square \rightarrow$ carcinogen electron donation and bond formation**

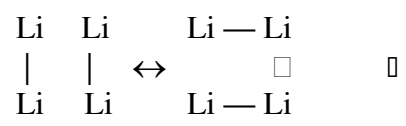


Fig. 1

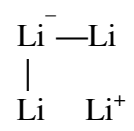


Fig. 2

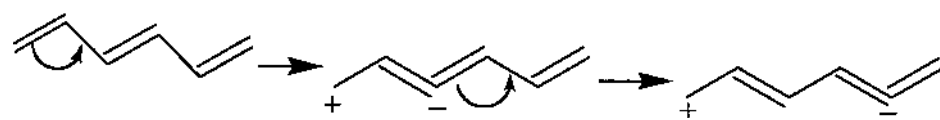


Fig. 3

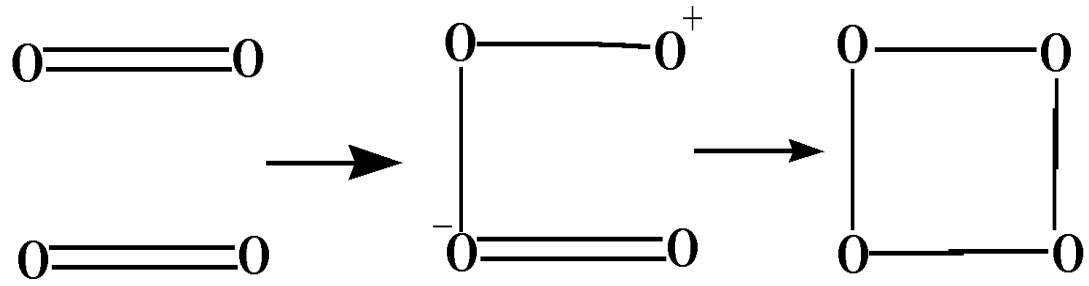


Fig. 4

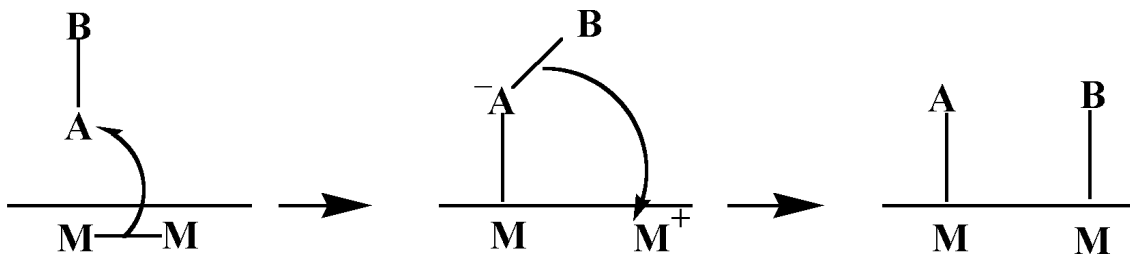


Fig. 5

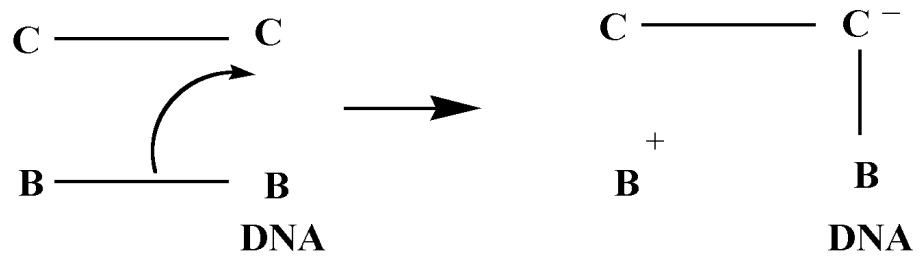


Fig. 6