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Heisenberg Hamiltonian for Poly-ynes. Extraction and Tests

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Heisenberg Hamiltonians, with distance-dependent spin couplings and σ-bond potential, have proved to be very efficient for the treatment of conjugated hydrocarbons. A similar approach is applied to C≡C triple bonds. The effective spin couplings are extracted from accurate CI calculations on acetylene. Tests show that the treatment of poly-ynes gives reliable results. The asymptotic trends of the lowest excited states geometry and energy are discussed.

I. Introduction

The possibility to treat efficiently the properties of the conjugated hydrocarbons in their ground state or their lowest excited states through a magnetic Hamiltonian,[1] namely, a geometry-dependent Heisenberg Hamiltonian, has been established more than 15 years ago.[2] Some extensions of that approach made possible its use for rather accurate descriptions of photochemical processes involving cyclizations and σ bond formations.[3] The success of that approach for the treatment of the most delocalized electronic systems of organic chemistry, namely, the π electron clouds, may seem paradoxical because in solid state physics[4] the magnetic approach is considered to be valid for the strongly correlated regime only, i.e., for systems where the electronic repulsion prevails on the electronic delocalization. In reference to the well-known Hubbard Hamiltonian[5]

$$H = \sum_{p,q} t_{p,q}(a_p^+ a_q + a_q^+ a_p) + U\sum_p n_{p\uparrow} n_{p\downarrow}$$

where $t_{p,q}$ is the hopping integral between the bonded atoms p and q and U is the repulsion between two electrons on the same site; the delocalization/repulsion ratio is measured by the t/U ratio. The most generally accepted $|t/U|$ ratio for hydrocarbons is close to 1, out of the $|t/U| < {}^1/_4$ strongly correlated (i.e., magnetic) region. The efficiency of the magnetic approach may be rationalized by considering that

(i) The neutral VB structures remain the leading components of the wave functions, and the spin order remains almost the same whatever $|t/U|$ ratio

(ii) The spin-coupling parameter is of course normalized, it deviates from its perturbative estimate $-2t^2/U$ and takes the value of half the exact energy difference between the singlet ground state and the lowest triplet state of the dimer.

Extensions to heteroatomic conjugated molecules have been proposed,[6] when the heteroatoms N or O bring one (or two) π electron. The present paper extends the same strategy to triple bonds or more precisely to their two π bonds. As will be recalled in the next section (II), the definition of the Heisenberg Hamiltonian for systems involving more than one electron per atom is not unique and faces important difficulties.[7] Nevertheless it is possible to define a Heisenberg Hamiltonian in terms of $S_z = \pm{}^1/_2$ particles from three low-lying states of the acetylene molecule. The knowledge of the corresponding potential-energy curves from accurate ab initio calculations defines uniquely a distance-dependent Heisenberg Hamiltonian.

Section III reports a few calculations from this model Hamiltonian concerning HC_nH linear chains. Some of them, concerning small molecules, are compared to ab initio calculations, showing the good transferability of the effective interactions extracted from the two center molecule to larger compounds. The comparison of the calculated and experimental geometries and spectrum of poly-ynes confirms the reliability of the here-proposed effective magnetic Hamiltonian.

II. Extraction of a Magnetic Hamiltonian for C≡C Triple Bonds

The magnetic Hamiltonians are effective Hamiltonians spanned by neutral valence bond (VB) determinants, i.e., determinants in which the atoms are neutral. The effect of the electronic delocalization between the atoms, i.e., of the interaction between the neutral and ionic VB configurations, results in a modification of the energies of the neutral VB determinants and of the interaction between them. When each atom brings one electron in one atomic orbital (AO), as occurs for the π electrons of a conjugated hydrocarbon, occupying a $2p_z$ AO, the model space is uniquely defined. This is no longer the case for systems where each atom brings two electrons in two orthogonal AO, as occurs for the carbon atom of a poly-yne which bears two π electrons in two π ($2p_x$ and $2p_y$) AO.

1. Choice of the Model Space. Considering the simplest (two-center) problem, with two atoms A and B, one has four orbitals X_A, Y_A, X_B, and Y_B bearing four electrons. The total number of neutral VB determinants $|i\rangle$ is 10, divided in five pairs.

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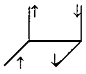
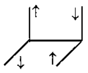
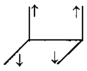
$$1 = \left|X_A Y_A \bar{X}_B \bar{Y}_B\right| \text{ and } 1' = \left|\bar{X}_A \bar{Y}_A X_B Y_B\right| \qquad (1)$$



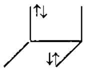
$$2 = \left|X_A \bar{Y}_A \bar{X}_B Y_B\right| \text{ and } 2' = \left|\bar{X}_A Y_A X_B \bar{Y}_B\right| \qquad (2)$$



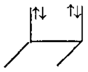
$$3 = \left|X_A \bar{Y}_A X_B \bar{Y}_B\right| \text{ and } 3' = \left|\bar{X}_A Y_A \bar{X}_B Y_B\right| \qquad (3)$$



$$4 = \left|X_A \bar{X}_A Y_B \bar{Y}_B\right| \text{ and } 4' = \left|Y_A \bar{Y}_A X_B \bar{X}_B\right| \qquad (4)$$



$$5 = \left|X_A \bar{X}_A X_B \bar{X}_B\right| \text{ and } 5' = \left|Y_A \bar{Y}_A Y_B \bar{Y}_B\right| \qquad (5$$



Notice that although the first six determinants have the same space part with one electron per AO and different spin distributions the last four have different space parts, with double occupancy of orbitals. This 10-dimensional space has the nice property of being invariant under the rotation μ of the system of axis {x,y} into {x′,y′}. $\{x',y'\} = \mu\{x,y\}$.

If one chooses this 10-dimensional space S of projector P_S

$$P_S = \sum_{i=1,10} |i\rangle\langle i| \qquad (6)$$

as model space, one faces two difficulties: (i) the effective Hamiltonian will not be a spin-only Hamiltonian, but because there is not a unique space part, it will be a magneto-angular Hamiltonian, which is in principle conceivable[8] but far less convenient than a magnetic Hamiltonian for the treatment of larger systems and (ii) it will be very difficult to define this effective Hamiltonian in the most rigorous sense.[9] An effective Hamiltonian is defined from a correspondence between a model space S and an isodimensional target space which is a stable subspace of the Hamiltonian, i.e., composed of the same number n (here 10) eigenfunctions of the Hamiltonian:

$$H|\Psi_m\rangle = E_m|\Psi_m\rangle \qquad m = 1, n \qquad (7)$$

The effective Hamiltonian satisfies the basic eigenvalue equation

$$H^{\text{eff}}|P_S\Psi_m\rangle = E_m|P_S\Psi_m\rangle \qquad m = 1, n \qquad (8)$$

i.e., gives exact n eigenenergies and the components of the n corresponding eigenvectors in the model space. Of course, the relevant eigenvectors are those which have the largest components in the model space.

Now looking at the list of model-space determinants, one sees immediately that the last two determinants $X_A^2X_B^2$ and $Y_A^2Y_B^2$ have such high energy that they are embedded in the continuum. There is no chance to find unambiguously bound eigenstates of H which have large projections on these determinants. In other words, one cannot expect to find a rational target space and, consequently, an appropriate operator Ω sending from the model space to the target space of projector $P_{S'}$

$$P_{S'} = \Omega P_S \qquad (9)$$

Hence, it is practically impossible to define the effective Hamiltonian[10a]

$$H^{\text{eff}} = P_S H \Omega P_S \qquad (10)$$

An alternative definition of the model space comes from the solid state physics tradition.[1] It consists of considering only the ground state of the atoms (for transition metal atoms) or here the triplet state of the local 2e$^-$ problem and its three components

$$T_A^+ = X_AY_A \qquad (S_z = 1) \qquad (11)$$

$$T_A^- = \bar{X}_A\bar{Y}_A \qquad (S_z = -1) \qquad (12)$$

$$T_A^0 = \frac{(X_A\bar{Y}_A + \bar{X}_AY_A)}{\sqrt{2}} \qquad (S_z = 0) \qquad (13)$$

For the two-center problem, the $S_z = 0$ subspace is of dimension three, spanned by $T_A^+T_B^-$, $T_A^-T_B^+$, and $T_A^0T_B^0$ It is easy to express this basis in terms of the previously defined VB determinants (eqs 1−5):

$$T_A^+T_B^- = 1 \qquad (14)$$

$$T_A^-T_B^+ = 1' \qquad (15)$$

$$T_A^0T_B^0 = \frac{1}{2}(3 + 3' - 2 - 2') \qquad (16)$$

From these three configurations, it is possible to build a singlet state ${}^1\Sigma_g^+$, a triplet state ${}^3\Sigma_u^+$, and a quintet state ${}^5\Sigma_g^+$

$${}^1\Psi_g = \frac{1}{\sqrt{3}}(T_A^+T_B^- + T_A^-T_B^+ - T_A^0T_B^0) \qquad (17)$$

$${}^3\Psi_u = \frac{1}{\sqrt{2}}(T_A^+T_B^- + T_A^-T_B^+) \qquad (18)$$

$${}^5\Psi_g = \frac{1}{\sqrt{6}}(T_A^+T_B^- + T_A^-T_B^+ + 2T_A^0T_B^0) \qquad (19)$$

If the effective Hamiltonian is an Heisenberg Hamiltonian

$$H^{\text{eff}} = -J\vec{S}_A\vec{S}_B \qquad (20)$$

the energy spacings are $-J$ between the singlet and the triplet and $-2J$ between the triplet and the quintet.

One may understand that in acetylene ground state the leading determinants are 1 and 1′ which satisfy the atomic Hund's rules and make possible the interatomic electronic delocalization in both π bonds. In this molecule, the VB determinants 3 and 3′ which bear two electrons of parallel spins in each π bond do not interact with ionic VB states and actually have a very weak weight in the ground-state function, whereas the coefficients of the determinants 2 and 2′ are important

$$C_1 > C_2 \gg C_3$$

The singlet wave function ${}^1\Psi_g$ (eq 17) is certainly a poor approximation of the projection of the exact wave function in the neutral VB model space. Actually, the three-dimensions model space, i.e., the use of $S = 1$ atomic states, is only relevant when the intraatomic exchange integral

$$K_{xy} = \left\langle P_xP_x\left|\frac{1}{r_{12}}\right|P_yP_y\right\rangle = \left\langle P_xP_y\left|\frac{1}{r_{12}}\right|P_yP_x\right\rangle \qquad (21)$$

is much larger than the interatomic delocalization energy $2t^2/U$ (in absolute value). It is the case for the interaction between transition metal atoms d^n ($n \leq 8$) in organometallic complexes or in ionic solids, but it is not true for poly-ynes. The use of this reduced model space seems a priori irrelevant for poly-ynes.

A previous paper[7] has discussed the possibility to use the six-dimensional model space spanned by the determinant with one electron per AO. This model space suffers from a formal defect, it is not invariant under rotations between the x and y axes. As a consistent defect, it only provides one of the degenerate $\triangle$ states.

Another difficulty comes from the strong nonorthogonality of the projections of the six eigenstates of the relevant symmetry in the model space. The Bloch[10a] effective Hamiltonian, as rigorously defined from these eigenstates according to eq 22, is strongly nonhermitian and is nontransferable because it gives poor results for spectrum of large C_nH_2 compounds:

$$H^{\mathrm{eff}}_{\mathrm{Bloch}} = \sum_{m=1,n} |P_S\Psi_m\rangle E_m S^{-1}\langle P_S\Psi_m| \tag{22}$$

where S is the overlap matrix between the projections.

The hermiticity of the effective Hamiltonian may be forced by using the des Cloizeaux definition,[10b] i.e., by using symmetrically orthogonalized projections of the eigenstate in the model space:

$$|\Psi'_m\rangle = S^{-1/2}|P_S\Psi_m\rangle \tag{23}$$

$$H^{\mathrm{eff}}_{\mathrm{dC}} = \sum_{m=1,n} |\Psi'_m\rangle E_m\langle\Psi'_m| \tag{24}$$

but it involves very large four-body operators (which are quartic in terms of spin operators) and its transferability to larger poly-ynes is bad. Finally a reasonable solution, both hermitian and transferable, has been found[7] by orthogonalizing the projection of the second eigenvector of a given symmetry to the projection of the lowest one according to a Schmidt procedure, which keeps the largest information (energy and wave function) concerning the lowest state of its symmetry and sacrifices the information concerning the wave function of the second state of that symmetry.

The present work will use this six-dimensional model space but according to a different strategy invoking the concept of intermediate effective Hamiltonian.[11]

2. Definition of an Intermediate Effective Hamiltonian. We would like to define a simple Heisenberg Hamiltonian spanned by the six determinants (1, 1′, 2, 2′, 3, and 3′) and involving only two-body operators, which has the form

$$\begin{aligned} H = R_{\mathrm{ab}} + K[&|\mathrm{x_a\bar{y}_a} - \mathrm{\bar{x}_a y_a}\rangle\langle \mathrm{x_a\bar{y}_a} - \mathrm{\bar{x}_a y_a}| + |\mathrm{x_b\bar{y}_b} - \mathrm{\bar{x}_b y_b}\rangle \\ &\langle \mathrm{x_b\bar{y}_b} - \mathrm{\bar{x}_b y_b}|] + g[|\mathrm{x_a\bar{x}_b} - \mathrm{\bar{x}_a x_b}\rangle\langle \mathrm{x_a\bar{x}_b} - \mathrm{\bar{x}_a x_b}| + \\ &|\mathrm{y_a\bar{y}_b} - \mathrm{\bar{y}_a y_b}\rangle\langle \mathrm{y_a\bar{y}_b} - \mathrm{\bar{y}_a y_b}|] \end{aligned} \tag{25}$$

where $|\mathrm{x_a\bar{y}_a}\rangle$ stands for $\mathrm{a^{+}_{x_a}a^{+}_{\bar{y}_a}}$ and $\langle\mathrm{x_a\bar{y}_a}|$ for $\mathrm{a_{\bar{y}_a}a_{x_a}}$.

This Hamiltonian involves an R_{ab} scalar term, the σ bond potential, a monocentric ferromagnetic (positive) exchange integral K, and an interatomic effective exchange g, which is antiferromagnetic (negative) and reflects the effect of the electronic delocalization in the π bonds.

This Hamiltonian may be written in the basis of the six determinants for the $S_z = 0$ space,

$$\begin{array}{c|cccccc} & 1 & 1' & 2 & 2' & 3 & 3' \\ \hline 1 & R+2g & 0 & -g & -g & 0 & 0 \\ 1' & & R+2g & -g & -g & 0 & 0 \\ 2 & & & R+2g+2K & 0 & -K & -K \\ 2' & & & & R+2g+2K & -K & -K \\ 3 & & & & & R+2K & 0 \\ 3' & & & & & & R+2K \end{array}$$

and its eigenvectors and eigenvalues are quite easy to obtain. The quintet and the three triplet states are defined by symmetry

$$^5\Sigma_g^+ = (1 + 1' + 2 + 2' + 3 + 3')/\sqrt{6},\ E(^5\Sigma_g^+) = R \tag{26}$$

$$^3\triangle_g = (3 - 3')/\sqrt{2},\ E(^3\triangle_g) = R + 2K \tag{27}$$

$$^3\triangle_u = (2 - 2')/\sqrt{2},\ E(^3\triangle_u,) = R + 2g + 2K \tag{28}$$

$$^3\Sigma_u^+ = (1 - 1')/\sqrt{2},\ E(^3\Sigma_u^+) = R + 2g \tag{29}$$

whereas the two singlet states $^1\Sigma_g^+$ are solutions of a 2 × 2 problem

$$E(^1\Sigma_g^+) = 2(K + g) \pm 2\sqrt{(K + g)^2 - 3kg} \tag{30}$$

It is impossible to reproduce the whole spectrum of the six eigenvalues from three parameters only (R,K,g). One solution would invoke a least-squares fit. However, it is not clear that the upper states, the excited $^1\Sigma_g^+$ state and $^3\triangle_g$ state, have to be reproduced as accurately as the lowest ones. In the spirit of the intermediate Hamiltonians, which are designed to reproduce only a part of the spectrum, we decided to concentrate on the lowest two states, i.e., the ground state $\tilde{X}^1\Sigma_g^+$ and $^3\Sigma_u^+$ state, to determine the parameters K and g and to identify the R parameter to the energy of the $^5\Sigma_g^+$ state. We may summarize the extraction as follows:

$$R = E(^5\Sigma_g^+),\quad 2g = E(^3\Sigma_u^+) - E(^5\Sigma_g^+),$$
$$K \text{ is extracted from eq 30}$$

3. Ab initio Potential-Energy Curves of C_2H_2 and Definition of an R-Dependent Heisenberg Hamiltonian. The potential-energy curves $E(r_{\mathrm{CC}})$ have been calculated for the $\tilde{X}^1\Sigma_g^+$, $^3\Sigma_u^+$, $^3\triangle_u$, and $^5\Sigma_g^+$ of the acetylene molecule using a DZP basis set plus diffuse s and p orbitals. The calculation of the energies was performed according to a multireference second-order perturbation theory.[12] The multireference space involved all determinants where coefficients are larger than 0.02. The diagonalization of these selected variational subspaces provides zero-order functions which are perturbed to the second order in energy according to be CIPSI algorithm, adopting a Möller−Plesset[13] barycentric definition of the unpertubed Hamiltonian. The calculation was performed for six values of the r_{CC} distance between 2.1 and 3.1 bohr, keeping the linear geometry and a fixed CH bond length.[14]

The potential-energy curves appear in Figure 1. The ground state equilibium geometry is 1.2297 Å to compare to the 1.2033 Å experimental value.[14] The vertical spectrum is in good agreement with the experiment[15,16] because

$$\Delta E = (\bar{X}^1\Sigma_g^+ - {}^3\Sigma_u^+) = 5.30\ \mathrm{eV} \quad \text{(experiment[15,16] 5.23 eV)}$$

$$\Delta E(\tilde{X}^1\Sigma_g^+ - {}^3\triangle_u) = 6.33\ \mathrm{eV} \qquad \text{(experiment[15,16] 6.2 eV)}$$

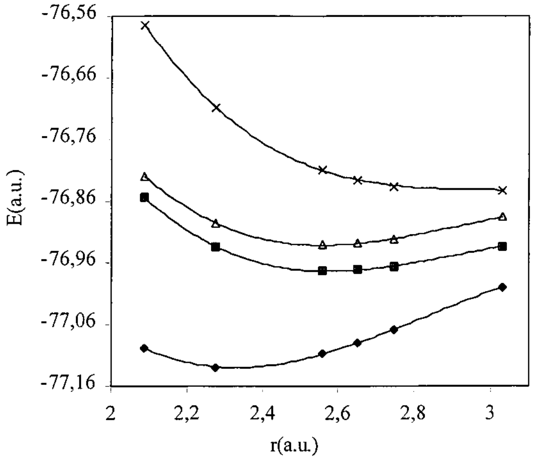


Figure 1. Potential-energy curves of the acetylene molecule: from the bottom $\tilde{X}^1\Sigma_g^+$ ground state and $^3\Sigma_u^+$, $^3\Delta_u$, and $^5\Sigma_g^+$ lowest excited states.

TABLE 1: *r*-Dependence of the g(*r*), *K*(*r*), and *R*(*r*) Functions

r (a.u.)	2.2747	2.5582	2.6527	2.7472	3.0308
g (a.u.)	−0.113 031	−0.081 551	−0.072 982	−0.065 213	−0.045 964
K (a.u.)	0.039 78	0.040 276	0.040 895	0.042 328	0.051 950
R (a.u.)	−0.708 729	−0.809 117	−0.825 324	−0.835 584	−0.842 036

The vertical transition energy to the $^5\Sigma_g^+$ state, which is repulsive, is 11.45 eV. Table 1 reproduces the values obtained for the three parameters R, g, and K at five interatomic CC distances. Of course, R is an essentially repulsive curve in that domain of distance, although it presents a minimum for $r \cong 3$ bohr, typical of σ_{CC} single bond. The antiferromagnetic exchange g, which reflects the electronic delocalization in the π bonds, is negative, and its magnitude rapidly decreases when the CC bond increases, as expected. The direct exchange positive integral K is essentially monocentric and varies more slowly with the interatomic CC distance. It increases by 30% between 1.20 and 1.60 Å but only by 8% between 1.20 and 1.40 Å, which covers the relevant domain of distances for C(sp)−C(sp). However, it is difficult to take into account this distance dependence because in poly-ynes the internal carbon atoms are involved in two CC bonds and in the further calculations the value of K has been kept constant and equal to 1.083 eV.

A polynomial interpolation (in a.u.) has been performed for g and R

$$R(r) = -0.270\,962r^3 + 2.488\,090r^2 - 7.602\,320r - 69.112\,000$$

$$g(r) = 0.011\,396r^3 - 0.135\,171r^2 + 0.563\,600r - 0.829\,733$$

The corresponding curves appear in Figures 2 and 3.

As a control of the quality of the so-extracted Heisenberg Hamiltonian, we have checked the equilibrium distances and vertical transition energies for the prototype C_2H_2 molecule. The neglect of the dependence of the K integral on the r_{CC} distances introduces some error on the $\tilde{X}^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves, the ab initio equilibrium distance is now 1.200 Å for the $^1\Sigma_g^+$ state, (experiment 1.203 Å, ab initio 1.227 Å), 1.354 Å for the $^3\Sigma_u^+$ (ab initio 1.368 Å), and 1.354 for the $^3\Delta_u$ (ab initio 1.352 Å). The vertical transition energies to the $^3\Sigma_u^+$ and $^5\Sigma_g^+$ states are identical to the ab initio ones, because K is the exact one for this distance.

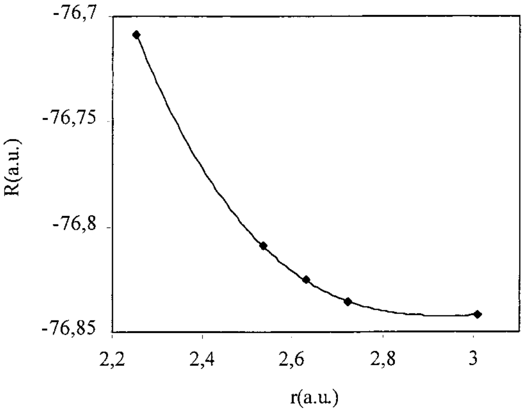


Figure 2. r-dependence of the σ-bond potential R.

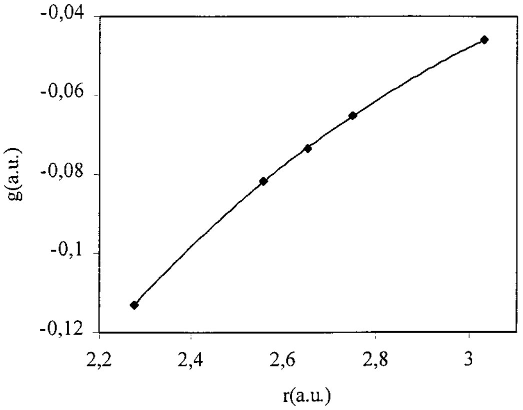


Figure 3. Bond length dependence of the interatomic effective exchange g.

The impossibility for the Heisenberg spectrum to reproduce the spectrum of the six states appears from an important error in the $\bar{X}^1\Sigma_g^+ \rightarrow {}^3\Delta_g$ vertical transition (7.47 eV instead of 6.2 eV in the experiment, 6.33 eV in the ab initio calculation) and in the $\tilde{X}^1\Sigma_g^+ \rightarrow {}^3\Delta_g$ transition (14.94 eV instead of 12.98 eV in the ab initio calculation). The transition energy of the $\tilde{X}^1\Sigma_g^+ \rightarrow {}^3\Delta_g$ is 13.62 eV at the ab initio level and 12.98 eV in the magnetic calculations.

III. Test Applications

1. Even Poly-ynes. The efficiency of the magnetic Hamiltonian may be studied on poly-ynes with an even number of atoms C_4H_2, C_6H_2, and C_8H_2. These molecules are linear and exhibit a strong bond alternation, their ground state is of $\tilde{X}^1\Sigma_g^+$ symmetry. The results of the geometry optimization appear in Table 2. The calculated bond lengths of C_4H_2 (1.211 and 1.380 Å) are in good agreement with the experimental values[17] (1.2176 and 1.3831 Å). The lengths of the external bonds are almost the same for larger poly-ynes, and the internal bonds in C_8H_2 present a slight tendency to a decrease of bond alternations (triple bond 1.227 Å and single bond 1.368 Å) as occurs to a larger extent for polyenes.

The geometries of the $^3\Sigma_u^+$ state have also been calculated, and it presents a strong tendency to equalization of the central bond lengths around a value of 1.30 Å, which can be seen as the mean CC distance in poly-ynes, halfway between the triple and the single bonds lengths. The results of Table 2 concerning the $^3\Sigma_u^+$ geometry can easily be rationalized if one considers this state as the resonance between a ^{3}(n → n*) excitation in the π_x system with the same excitation in the π_y system.

TABLE 2: Optimized Bond Distances (in Å) in Even Poly-ynes in the Two Lowest States, Starting from the External Bond[a]

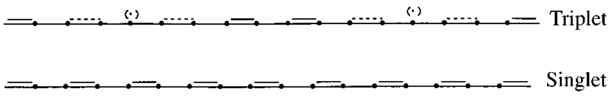
		r_1	r_2	r_3	r_4
C_2H_2	$^1\Sigma_g^+$	1.200 (1.203)			
	$^3\Sigma_u^+$	1.354			
C_4H_2	$^1\Sigma_g^+$	1.211 (1.2176)	1.380 (1.3831)		
	$^3\Sigma_u^+$	1.298	1.300		
C_6H_2	$^1\Sigma_g^+$	1.213	1.375	1.224	
	$^3\Sigma_u^+$	1.265	1.310	1.313	
C_8H_2	$^1\Sigma_g^+$	1.214	1.373	1.227	1.368
	$^3\Sigma_u^+$	1.248	1.325	1.301	1.295

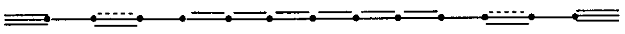
[a] Experimental values in parentheses.

TABLE 3: Lowest Singlet−Triplet Transition Energy in Even Poly-ynes (in eV)

	C_2H_2	C_4H_2	C_6H_2	C_8H_2
vertical absorption	5.24	3.79 (3.84)	3.00	2.53
emission	3.67	2.53	1.90	1.50

Knowing the bond lengths deviations from their mean value (1.40 Å) for polyenes in their ground singlet and lowest triplet states and adding these deviations to the mean CC distance in poly-ynes (1.30 Å), one practically obtains the results of Table 2. Let us consider for instance the butadiyne C_4H_2 and the polyene parent butadiene C_4H_6. The deviation of CC bond length from the mean CC distances in polyenes (1.40 Å) are respectively −0.05 and +0.05 Å for the external and internal bond in the singlet state and −0.05 and +0.05 Å for the same bonds in the triplet state.[2] The sum of these deviations is zero, and actually, the triplet state bond length of butadiyne are very close to the mean CC distances in poly-ynes (1.30 Å). As a consequence of that rationalization, one may predict that because the triplet state in conjugated polyenes tends to be a solitonic pair separated by a reversed bond alternation[2] in the central half part of the chain, the $^3\Sigma_u^+$ geometry of poly-ynes should present a strong bond alternation on the two sides and a long central region without bond alternation. This agrees with the calculated geometry for the $^3\Sigma_u^+$ state of octatetrayne (C_8H_2).





The transition energy for the lowest $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transitions are reported in Table 3. One may see first that for C_4H_2 the Heisenberg Hamiltonian provides a vertical transition energy of 3.79 eV, in perfect agreement with the ab initio value obtained according to the CIPSI algorithm (3.84 eV). This result confirms the relevance of our magnetic Hamiltonian. In view of the above remarks on the nature of the excited state, one may expect a decrease of the transition energy with the number N of atoms, which, as occurs for polyenes, should roughly follow an N^{-1} dependence. Extrapolation suggest a 1.1−1.2 eV asymptotic vertical transition. This value is larger than for polyenes, as expected because the mean bond lengths are smaller (larger hopping integrals).

The emission transition energies are significantly smaller, and the asymptotic value should be around 0.6 eV. For the polyene chain, the asymptote is zero because for the relaxed triplet geometry the two unpaired electrons are localized far away and do not interact, generating a singlet−triplet degeneracy. This is no longer the case for poly-ynes because the compromise in the geometric structure maintains a delocalization and interaction of the unpaired electrons in the π system they occupy, prohibiting the singlet−triplet degeneracy.

TABLE 4: Optimized Bond Distances (in Å) in Odd Poly-ynes in the Two Lowest States, Starting from the External Bond[a]

		r_1	r_2	r_3
C_3H_2	$^3\Sigma_g^-$	1.278		
	$^1\Delta_g$	1.277		
C_5H_2	$^3\Sigma_g^-$	1.246	1.321	
	$^1\Delta_g$	1.243	1.324	
C_7H_2	$^3\Sigma_g^-$	1.233	1.340	1.287
	$^1\Delta_g$	1.233	1.341	1.286

[a] Experimental values in parentheses.

TABLE 5: Vertical Absorption and Emission Lowest Transition Energies (in eV) of Odd Linear Poly-ynes

	C_3H_2	C_5H_2	C_7H_2
vertical absorption	2.23	2.30	2.37
emission	2.23	2.30	2.37

2. Odd Poly-ynes. On the odd poly-ynes $C_{2n+1}H_2$, the two π systems bear an unpaired electron. The two π systems both have a doublet ground state, which prefer a localization of the unpaired electron on the central atoms. For an odd polyene, the bond alternation is strong in the external bonds and vanishes in the center of the system.[2] Because the trends of the two orthogonal π systems are compatible, one may expect an equilibrium geometry with a marked bond alternation on the external parts, vanishing in the central region.

The low-lying states will be of $^3\Sigma_g^-$ and $^1\Delta_g$ character. Notice that our Heisenberg Hamiltonian can only produce one of the $^1\Delta$ components (the xy one, the $x^2 - y^2$ components cannot be reached from our reduced model space). Because the two unpaired electrons are ferromagnetically coupled through the intraatomic integrals K and because they remain in the center of the system, one may expect that

(i) The energy ordering will be $^3\Sigma_g^- < {}^1\Delta_g$.

(ii) The energy difference should not vanish when the size of the chain increases.

(iii) The equilibrium geometries of both states should be a lot smaller.

The results appear in Tables 4 and 5 for C_3H_2, C_5H_2, and C_7H_2, and they perfectly confirm the above statements regarding the geometry (bond length equalization), the near identity of the equilibrium geometry of both states. The triplet to singlet lowest transition energy is almost size independent, and of course, the vertical and adiabatic absorption energies coincide (and coincide with the emission energy).

IV. Conclusion

Heisenberg Hamiltonians are now widely used for the study of the covalent states of conjugated molecules and their photochemistry, despite the large effective $|t/U|$ ratio of the π systems. The present work presents an extension to the CC triple bonds. The major difficulty is not the expected larger $|t/U|$ ratio for the very short triple bonds. The main problem is logical; it concerns the choice of the model space. If one rejects the largest model space, spanned by all of the neutral VB determinants, which would not lead to an Heisenberg Hamiltonian, one may in principle express the magnetic Hamiltonian in terms of $S_z = {}^1/_2$, spanned by electrons in atomic π orbitals, or $S = 1$ spins, spanned by atomic triplet states. The latter solution is of course the relevant one for transition metal atoms (e.g., Ni in d^8 configuration), but it seems questionable for the conjugated hydrocarbons where the intraatomic ferromagnetic exchange integral K is not larger than the interatomic antiferromagnetic coupling $J(-2t^2/U)$. The present work has followed the other strategy, leaving the use of the Bloch's Hamiltonians and extracting the relevant J, K, and R parameters as functions of the interatomic CC distance from the energies of three states ${}^1\Sigma_g^+$, ${}^3\Sigma_u^+$, and ${}^5\Sigma_g^+$ of the dimer.

The extraction uses the potential-energy curves of the acetylene molecule, calculated via accurate variation-perturbation CI methods, which are in good agreement with the available experimental information. The results concerning larger C_nH_2 poly-ynes, from $n = 3-8$, are satisfactory, confirmed by a few additional ab initio CI calculations and exhibiting very consistent trends regarding both the equilibrium structures and the lowest transition energies.

Of course, the here-produced Heisenberg Hamiltonians is not limited to the study of poly-ynes, it may be used for triple-bonds containing conjugated hydrocarbons.

Although it might be useful to calculate a $HC-CH_2$ system to define properly the interactions between sp and sp^2 carbons, it would be possible as well to fit the R and J values for this interaction as the mean functions for the now available sp^2-sp^2 and sp−sp interactions. Allenic systems might be treated accordingly. A further work will explore these possibilities.

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