THE LIMITS OF THE EXTENDED HÜCKEL THEORY TO CALCULATE THE TOTAL DENSITY OF STATES OF MEDIUM-SIZED MOLECULES.

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ABSTRACT.

Two medium-sized molecular systems X60 (X=C,N) were analyzed using Extended Hückel, Density Functional and *ab initio* Hartree-Fock methods. The aim of the work was to test the reliability of the EHT methodology to calculate the total Density of States distribution curve. The Extended Hückel method is only reliable in the cases of the first valence and conduction bands of these systems. For the rest of the Density of States distribution curve EHT performs badly. The sources of error of EHT, come from the non-inclusion of the electron-electron interaction and from incorrect results regarding the relative ordering of the MO degeneracies. Both sources of error should disappear when the occupied and empty molecular orbitals become very similar in energy over a certain range, forming an almost continuous band, as happens in bigger molecular systems.

Keywords: Extended Hückel Method, N_{60}, C_{60}, Total Density of States, Density Functional Method.

INTRODUCTION.

In 1963, Hoffmann developed a semiempirical quantum mechanical method known as the Extended Hückel Theory (EHT) [1].

EHT is the simplest and most primitive of all all-valence-electron methodologies. EHT models all the valence orbitals based on the orbital overlaps and experimental electron affinities and ionization potentials. The diagonal elements of the Hamiltonian are taken as the negative of the normal first ionization energy of the atom corrected by spectroscopic terms to deal with the situation where the normal ionization is not removing the electron from the orbital in question. The off-diagonal matrix elements of

the Hamiltonian are calculated according to the modified Wolfsberg-Helmholz formula [2]. The use of experimental ionization energies for the atoms in the molecule implies that the correlation energy is taken care of. It is known that, in general, EHT performs rather poorly at predicting energy differences between isomers or even correct molecular geometries [3], but there are some exceptions [4]. Charge differences, particularly between atoms of very different electronegativity, can be grossly exaggerated. However it does give some useful results in some cases.

The strength of EHT is that it gives a good qualitative picture of the molecular orbitals (MOs). It is now known that for the occupied MOs the corresponding eigenvalues agree reasonably well with experimentally determined ionization energies from photoelectron spectroscopy (PES). In 1988 a study found that EHT is also useful to determine unoccupied levels [5]. It is concluded that EHT can be used to study both occupied and unoccupied orbitals of a molecule, since it is directly useful for the calculation of excitation energies [5].

The reasons for the good performance of EHT have elicited some interesting theoretical analyses. It was suggested that the EHT may be regarded as a method of simulating Hartree-Fock (HF) calculations by guessing the elements of the HF Hamiltonian matrix through the use of the Wolfsberg-Helmholz approximation [6]. More recently, it was shown that, within the Hartree-Fock-Rüdenberg picture (HFR), EHT is compatible with the nonempirical Hartree-Fock-Roothaan method [7-8]. HFR thus explains why EHT turned out to be qualitatively successful [see Ref. 9 for example].

With the above mentioned considerations, EHT is still undoubtedly a useful tool in areas where SCF calculations will not be feasible for some time to come. We must keep in mind that, as the EHT formalism does not take into account explicitly the electron-electron interaction, we should expect that the molecular orbital energies will be shifted downwards. Also a decrease in the energy difference between any pair of MOs is to be expected.

In a previous paper we have introduced the concept of "minimal length" (or minimal size) to set the boundary between a big molecule and a material properly speaking [10]. At least for the case of armchair and zigzag nanotubes this boundary implies that for a material we have to obtain the wave function of a system composed of more than one hundred atoms. Computing capabilities preclude for the time being the use of Hartree-Fock or Density Functional calculations.

Regarding molecular systems composed of hundreds or thousands of atoms in which a large or very large number of electrons are delocalized the following may be securely stated. Such systems have an extremely large number of molecular orbitals. The result, as the number of levels tends to infinity, is that MOs become very similar in energy over a certain range, forming an almost continuous band. In this case, and if we define zero energy as the midpoint between the Highest Occupied MO (HOMO) and the Lowest Unoccupied MO (LUMO) energies, the eigenvalues about zero will be almost the same in EHT, HF or DFT calculations.

In the case of medium size aromatic molecules, like the first members of the fullerene family, no work has been done to discuss band formation from the MO eigenvalues. Thereby, in this paper we analyze the performance and the limits of EHT to obtain molecular band structures for fullerene and fullerene-like molecules. Special emphasis is placed on the comparison of the EHT and DFT energy distributions of the eigenvalues. Also we examine whether or not at this molecular size level the MO eigenvalues have begun to form an almost continuous band. This last aspect is important because it provides data that could be applied to molecules whose study by *ab initio* or DFT methods is still very difficult or impossible due to their size (hundreds or thousands of atoms).

Methods, models and calculations.

Three molecular systems were selected to achieve our objective: C_{60}, N_{60} and B_{60}. Buckminsterfullerene, C_{60}, is an aromatic system. N_{60} has no delocalized electrons but sixty lone pairs.

The calculations were performed as follows. For the effects of comparison, the geometry of the molecules was fully optimized with Molecular Mechanics (MM), with the AM1 semiempirical method and with an *ab initio* RHF calculation at the 6-31G** basis set level. Using the nomenclature "single point//geometry" we calculated the MO energies for the cases EHT//MM, EHT//AM1, and B3LYP/6-311G**//6-31G**.

The Hyperchem package was employed for MM, AM1 and EHT calculations [11]. The RHF 6-31G** and B3LYP/6-311G** (hereafter DFT) calculations were performed with the Gaussian package [12]. We also used DFT C_{60} (BP/DZP//BP/DZP) results from an earlier publication [13]. Unpublished N_{60} results, obtained within the DFT methodology of Ref. 13, are also reported here.

The valence (VB) and conduction (CB) bands were obtained separately through a convolution of the occupied and empty MO energies with a Gaussian function [14]. A value of 0.1 eV was used for the broadening parameter and the scanning distance [13]. For the sake of comparison, in the case of the VB the HOMO energy was placed at E=0.0 eV for both EHT and DFT results. For the CB the LUMO energy was placed at E=0.0 eV.

RESULTS AND DISCUSSION.

The first point to note is that we could not obtain a stable icosahedral structure for B_{60} with the 6-31G** basis set. Neither the use of other basis sets (B3LYP/6-31G**, 3-21G**, 3-21G and 6-311G**), nor semiempirical methods (CNDO/2, AM1, PM3, INDO), produced an icosahedral stable structure. Interestingly, Molecular Mechanics indeed produces a stable structure for B_{60} with Ih symmetry. The B-B distance is about 1.7 Å which compares well with similar distances in B_8Cl_8 [15], boron sheets [16], B2O2 [17] B2F4 [18] and B2Cl4 [19]. Thus, here we present the above B_{60} EHT//MM results only for the sake of information.

The second point to stress is that Molecular Mechanics was not able to produce a stable icosahedral structure for N_{60}. Therefore we used AM1 for geometry optimization of both, C_{60} and N_{60}.

DFT, AM1 and *ab initio* results for the final geometries are very similar for the bond angles and dihedral angles. In the case of bond lengths, AM1 results show a very small difference with respect to the *ab initio* and DFT ones. For example, in Fig. 1 and for C_{60} DFT and *ab initio* results we have d(a-b) = 1.37 Å and d(b-c)= 1.45 Å. Equivalent AM1 results are 0.01 Å longer. A-b-c and d-b-c bond angles have the same values for all optimization methods. In dihedral angles differences of about 0.04 degrees are observed. A full list of final bond lengths, bond angles and dihedral angles for C_{60}, N_{60} and B_{60} is available on request. Therefore we should not expect a noticeable influence of the final geometries on the single point results. Our AM1 results for N_{60} agree with those of an earlier study [20].

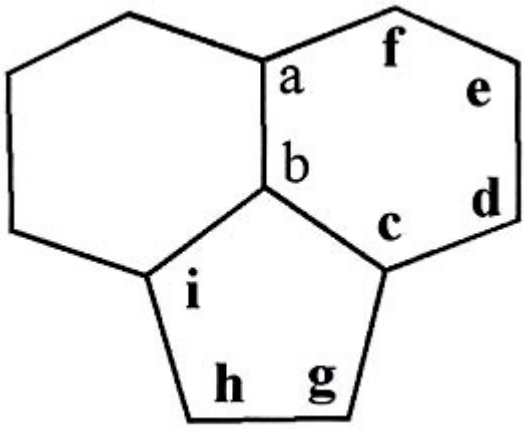

Figure 1. A section of X_{60} (X=C,N)

This first important result is that the order of the degeneracies of the MOs is not the same for B3LYP/6-311G**//6-31G** and BP/DZP//BP/DZP calculations. Tables 1 and 2 show, respectively, the degeneracies of the first 10 occupied and empty MOs. We can see that the HOMO and HOMO-1 multiplicities of C_{60} appear reversed in *ab initio* results compared with DFT ones. In the case of N_{60}, the same happens.

Table 1. Degeneracies of the first ten occupied molecular orbitals.

C_{60}			N_{60}		
MO	EHT	BP/DZP	B3LYP/6-311G*	MO	EHT	BP/DZP	B3LYP/6-311G*

HOMO	5	5	5	HOMO	3	4	5
H-1	5	4	5	H-1	4	5	4
H-2	5	5	4	H-2	4	3	3
H-3	4	4	4	H-3	5	4	4
H-4	5	5	5	H-4	3	5	5
H-5	4	3	3	H-5	5	3	3
H-6	4	5	5	H-6	3	3	3
H-7	4	4	4	H-7	3	3	3
H-8	5	5	5	H-8	5	5	5
H-9	3	3	3	H-9	4	4	5

Table 2. Degeneracies of the first ten empty molecular orbitals.

	C_{60}				N_{60}		
MO	EHT	BP/DZP	B3LYP/6-311G*	MO	EHT	BP/DZP	B3LYP/6-311G*
LUMO	3	3	3	LUMO	3	3	3
L+1	3	3	3	L+1	3	5	5
L+2	5	3	3	L+2	5	3	3
L+3	3	5	5	L+3	5	3	4
L+4	5	5	5	L+4	3	4	5
L+5	4	4	4	L+5	4	4	3
L+6	4	4	4	L+6	5	5	4
L+7	3	3	3	L+7	3	5	5
L+8	3	3	3	L+8	4	3	3
L+9	3	5	5	L+9	3	5	3

Given that BP/DZP//BP/DZP results agree with other theoretical studies we suggest that the source of error in the B3LYP/6-311G**//6-31G** results lies in employing different levels of calculation for single point and geometry optimization calculations. Therefore in the following we shall compare only EHT and BP/DZP//BP/DZP results. Notice that in the case of N_{60} we are assuming that BP/DZP//BP/DZP results are the best ones because no experimental data are available.

From earlier results we know that the DOS spectrum of C_{60} shows several independent bands that do not overlap [13]. Figures 2 and 3 show, respectively, the EHT and DFT DOS curves for the valence and conduction regions of C_{60}. Figures 4 and 5 show the corresponding EHT and DFT DOS curves for the conduction region of C_{60}. In the valence region of C_{60} the first band is identical in the DFT and EHT schemes, but in the inner bands there is a total disagreement between both methods.

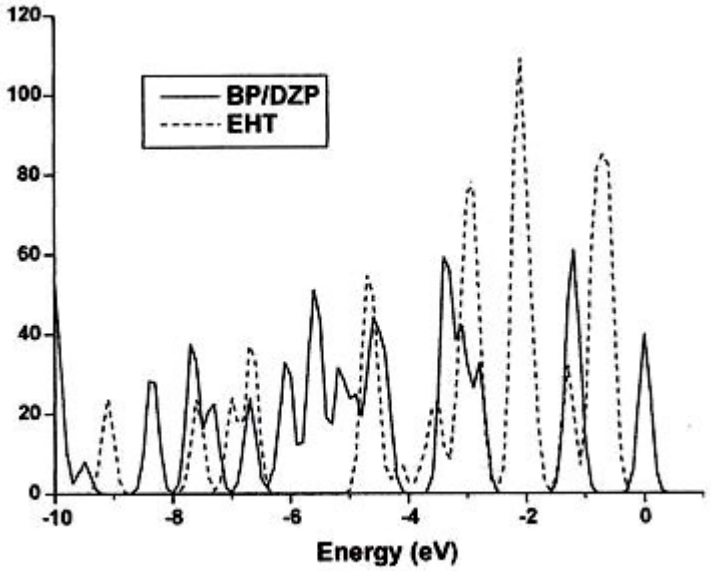

Figure 2. EHT and DFT Total Density of States of the valence region of C_{60}.

In the case of the valence region of C_{60} (Fig. 2), the first ten DFT occupied eigenvalues span 5.0 eV, while the corresponding EHT eigenvalues span 2.18 eV. This is a direct consequence of the neglect by EHT of the electron-electron interaction. This difference in the eigenvalue packing produces very different valence spectra. In the region of conduction bands (Fig. 3), the first band is the same in DFT and EHT methods. Interestingly, the second and third bands generated by both methods are very similar in shape and location in the energy axis.

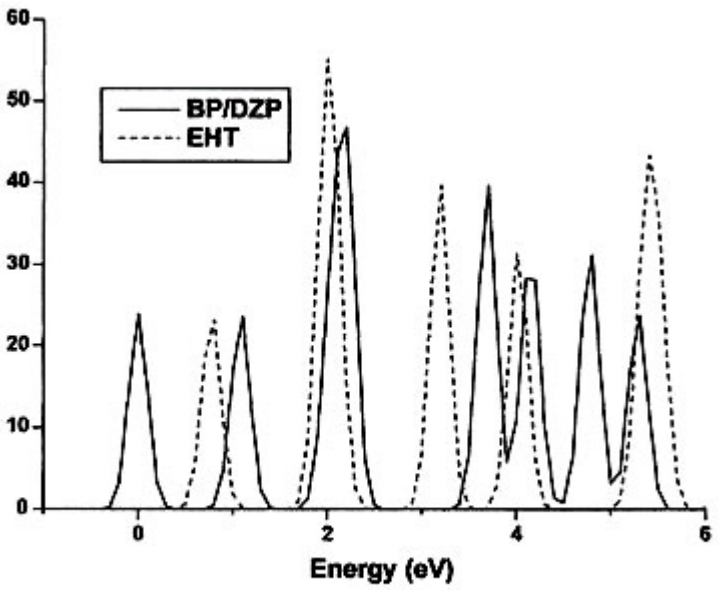

Figure 3. EHT and DFT Total Density of States of the conduction region of C_{60}.

In the case of the first valence band of N_{60}, both methods give bands with the same width, the shape changing slightly because of the differences in the relative ordering of the MO multiplicities (see Tables 1 and 2) which influence the total DOS. In the conduction band of N_{60}, only the first band is similar for both methods of calculation. In the rest there is a total disagreement.

Therefore, the first general conclusion of this work is that EHT is only reliable for the first valence and conduction bands of medium sized molecules. In this kind of molecules the eigenvalues are still well separated in energy. As there is still no "compaction" of the occupied MO energies, the main source of error of EHT calculations comes directly from the non-inclusion of the electron-electron interactions. This source of error should disappear only in the case when the occupied MOs become very close in energy (i.e., in bigger molecules).

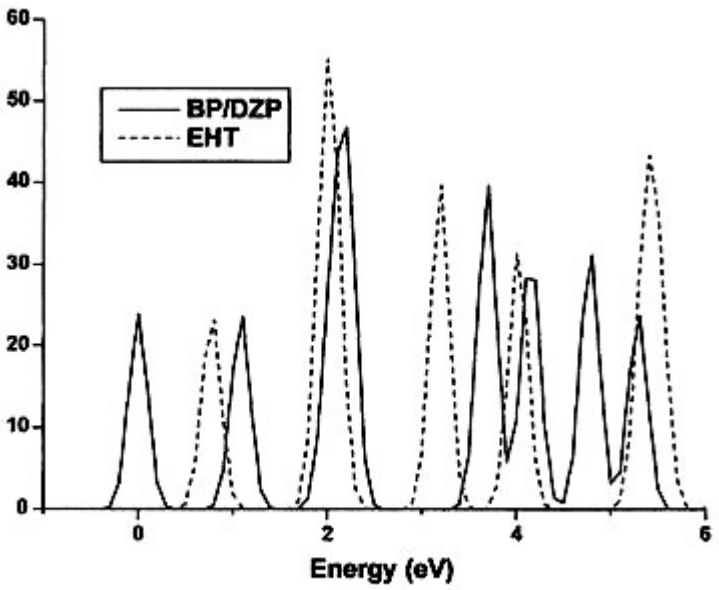

Figure 3. EHT and DFT Total Density of States of the conduction region of C_{60}.

Note that in C_{60} the first 10 occupied MOs span an energy range of 5 eV in DFT calculations while in EHT ones the energy range is only 2.18 eV. In N_{60} the respective energy ranges are very similar. In the case of the conduction regions of C_{60} and N_{60} a different effect appears. In C_{60} the first eight empty MOs span an energy range of 5.3 eV in DFT calculations while in EHT the range is 5.5 eV. EHT empty MOs have separated slightly in energy and not contracted as in the case of occupied MOs. This is confirmed in the N_{60} results: an energy range of 4.1 eV for DFT and 5.2 for EHT. Here the source of divergence in N_{60} results is mainly due to the relative ordering of the MO degeneracies (Tables 1 and 2). In theory this second source of error should also disappear when the empty MOs become very close in energy.

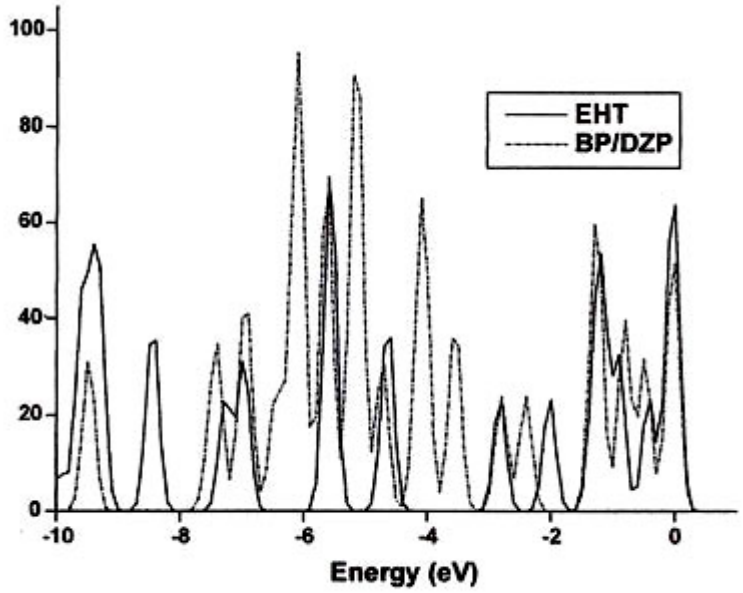

Figure 4. EHT and DFT Total Density of States for the valence region of N_{60}.

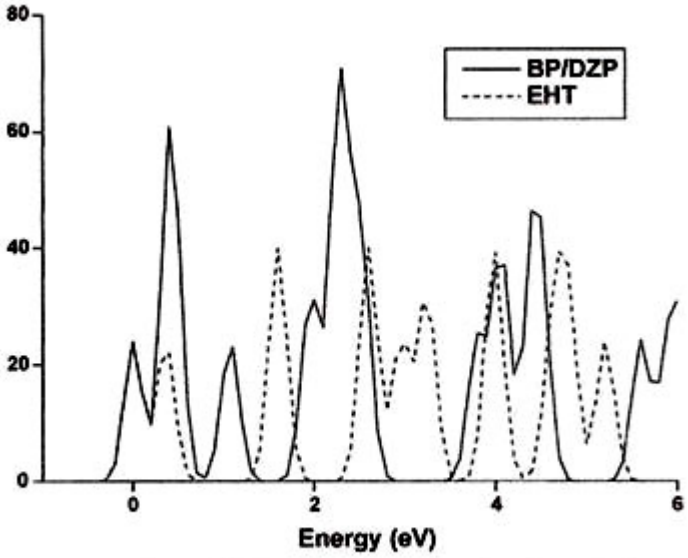

Figure 5. EHT and DFT Total Density of States for the conduction region of N_{60}.

Is there any mathematical relationship between the X60 (X=C,N) set of EHT eigenvalues and the DFT ones? If we can find one, we may "correct" the EHT eigenvalues to get a better DOS spectrum. But we may stress that this kind of relationship will not correct the disagreements in the relative ordering of the MO degeneracies. To explore this idea, and keeping in mind that we are interested in the DOS around the Fermi Level, we performed the following linear fits:

a) Between the first sixty occupied DFT and EHT eigenvalues, for C_{60} and N_{60}, and

b) Between the first thirty empty DFT and EHT eigenvalues for C_{60} and N_{60}.

For the case of C_{60} occupied eigenvalues the result is:
EHT = 0.19 (±0.08) + 0.50 (±0.02) * DFT
with n= 60, R^2=0.92, SD=0.29 and p<0.0001. (1)

For the case of C_{60} empty eigenvalues we obtained:
EHT = -0.29 (±0.12) + 1.07 (±0.03) * DFT
with n=30, R^2=0.98, SD=0.31 and p<0.0001 (2)

For the case of N_{60} occupied eigenvalues the result is:
EHT = -0.54 (±0.07) + 0.54 (±0.01) * DFT
with n=60, R^2=0.96, SD=0.34 and p<0.0001. (3)

For the case of N_{60} empty eigenvalues we obtained:
EHT = 0.44 (±0.17) + 1.41 (±0.10) * DFT
with n=30, R^2=0.86, SD=0.52 and p<0.0001. (4)

We may see immediately that the standard deviation is too high in all equations. We conclude therefore that it is not possible to build a "corrected" set of EHT eigenvalues.

The main conclusion of this work is that the use of the EHT eigenvalues to get the total DOS curve for medium sized molecules is not reliable despite the interesting results regarding the first valence and conduction bands. All the error sources reported here should disappear when the occupied and empty molecular orbitals become very similar in energy over a certain range, forming an almost continuous band, as happens in bigger molecular systems.

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