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Relationes

An Improved Iterative Extended Hückel Method for Conjugated Molecules

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The deficiencies of iterative extended Hückel theory as applied to conjugated molecules are discussed. An improved treatment is suggested which sacrifices complete rotational invariance but which is capable of a better representation of the π-electron energy levels and molecular ionization potentials.

Introduction

The utilization of extended Hückel theory (EHT) [1] for the calculation of approximate molecular wavefunctions has become increasingly popular in recent years despite the severe limitations of this method. A great improvement in the basic EHT formalism is the iterative extended Hückel theory (IEHT) as developed by Rein *et al.* [2, 3] and Pullman and coworkers [4]. The IEHT calculations which have thus far been reported indicate that this method gives essentially the correct charge distribution in molecules, thus overcoming perhaps the worst feature of EHT. Inspection of calculated results found by IEHT for conjugated systems, however, indicates that a major change must be made if the π-electron energy levels are to be given in even approximate agreement with *ab-initio* SCF results. The difficulty is that the π-electron energy levels for both occupied and virtual orbitals lie within a very narrow band so that the energy of the lowest lying π-orbital is generally too high, the energy of the highest occupied π-orbital is usually too low and the first virtual orbital energy level is negative and lies very close to the occupied band. Furthermore, if the usual assumption is made that the first molecular ionization potential is given approximately by the negative of the energy of the highest occupied MO, then IEHT cannot even account for basic trends. For example, the computed ionization potentials of acetylene, ethylene, and benzene are all predicted to be about the same in an IEHT calculation using reasonable parameter values, whereas the experimental results for these molecules are about 11.5, 10.5, and 9.5 eV, respectively. The same calculation also predicts a splitting of the occupied e_{2g} and a_{2u} levels in benzene of only about 1.7 eV, whereas the *ab-initio* results of Schulman and Moskowitz [5] give a value of 4.4 eV. It is even more disturbing that the IEHT computation predicts the virtual e_{2u} π-level to lie about 4.5 eV above the e_{2g} whereas Schulman and Moskowitz report a result of 13.6 eV for this same splitting.

It appears obvious from the above discussion that the π-electrons in a molecule must be treated by a parameterization different from that utilized for the σ-electrons if this can be conveniently carried out. This fact has been pointed out previously by Newton, Boer, and Lipscomb [6] in their formulation of NEMO. These investigators emphasized that rather striking anisotropies in SCF diagonal matrix elements for p-orbitals occur in conjugated molecules, the $2p_\pi - 2p_\pi$ diagonal elements being a good deal smaller in absolute magnitude than those for the $2p_\sigma$ orbitals. Newton *et al.* have suggested that this anisotropy should be taken into account with the concomitant sacrifice of complete rotational invariance, provided that the conjugated portion of the molecule lies in a single plane. It is the purpose of this note to show that such a procedure can also be carried out in IEHT calculations leading to much more satisfactory results for π-electron energy levels.

Method of Calculation

The formulation developed by Rein and coworkers [2] is utilized for computing the dependency of the diagonal matrix elements on the total net charges at the various nuclei of the molecule. These charges are determined by a Mulliken population analysis [7]. Specifically, we write

$$\alpha_{n+1} = 0.9\,\alpha_n + 0.1\,(\alpha_0 + q_n \Delta\alpha) \tag{1}$$

where q_n is the total net charge after n iterations on the atom at which the orbital in question is centered. Eq. (1) does not apply if this orbital is a π-type function in a conjugated portion of the molecule and the atom on which it is centered donates a single π-electron to this conjugated system. For such orbitals, we take

$$\alpha^\pi_{n+1} = \gamma \alpha^\sigma_{n+1}\,, \tag{2}$$

where γ is a constant for a given atomic species. The off-diagonal matrix elements are evaluated by the expression

$$H_{ij} = 1/4\,(k_i + k_j)\,(\alpha_i + \alpha_j)\,S_{ij}\,, \tag{3}$$

where k_i is 1.75 for a σ-orbital and 3.7 for a π-orbital in a conjugated system, and S_{ij} is the overlap integral between the two orbitals. A summary of the parameter values used in the calculations reported here is given in Table 1.

Table 1. *Parameter values*

Atom	ζ[a]	α^0_s[b]	α^0_p[b]	$\Delta\alpha$[b]	γ
H	1.2	−13.0	—	−14.0	—
C	1.625	−21.5	−11.5	−11.0	0.62
N	1.950	−26.0	−13.5	−12.0	0.75
O	2.275	−33.0	−17.0	−15.0	0.85

[a] Orbital exponent.

[b] Values in eV.

It should be noted that because of the restrictions given above for modification of the π-orbital parameters, atoms such as the nitrogen in pyrrole and the oxygen atom in conjugated ethers, phenols, or esters do not have modified π-parameters since they classically donate two electrons to the π-system. This also applies to a methyl group bonded to a conjugated moiety.

Results and Discussion

The parameters utilized here represent a compromise in that we have not been able to eliminate negative values of virtual-orbital energy eigenvalues while at the same time maintaining good results for the occupied levels. We have therefore chosen to use parameters which tend to give the best representation of ionization potential data. A summary of some of the computed orbital energies and corresponding ionization potentials are given in Table 2. It is observed that, in general, very good agreement is found between computed and observed ionization potentials. We have been able, in fact, to obtain better results in this respect using IEHT than Newton, Boer, and Lipscomb [8] found using NEMO I. It is noted in the latter calculations that if conjugation in the molecule extends over more than two atoms, the splitting of the π-levels is predicted to be too large and the ionization potential for a π-electron is much too small. For example, the computed energy eigenvalues for the highest filled π-MO in butadiene, naphthalene, azulene, and benzaldehyde are -7.34, -5.90, -4.61, and -7.33 eV, respectively, from the NEMO calculations. The nonbonding or n-levels are generally predicted quite well, however, indicating that the difficulty in NEMO I calculations is in the treatment of the π-system. Some modification is therefore necessary to produce better agreement with experiment and *ab-initio* calculations.

Both NEMO I and the formulation of IEHT given in this paper correctly predict trends in ionization potentials and give a fairly quantitative account of the effect of methyl group substitution on n- or π-electron ionization potentials. In general, NEMO I tends to exaggerate the effect of methyl group substitution on π-levels whereas we underestimate them slightly in this study. A summary of predicted and experimental methyl group substituent effects are given in Table 3. In general, the results of this study are more satisfactory than those of Newton, Boer, and Lipscomb.

The only molecule considered in this study for which agreement between the experimental and observed ionization potential is particularly poor is the seven-membered cyclic ketone, tropone. It is significant that this molecule is also anomalous in the NEMO I studies, and it is suggested that the experimental value may be for the ionization of an n- rather than a π-electron. The result of 9.7 eV is completely unreasonable for a molecule with conjugation extending over 8 atoms.

Dipole moments have also been computed for several molecules both from the wavefunctions obtained using modified π-parameters and also from functions computed without this latter modification. These are given in Table 4 along with the experimental results and values computed by Newton, Boer, and Lipscomb from NEMO I wavefunctions. The modified wavefunctions tend to give a better overall prediction of dipole moments and values computed by this method are

Table 2. *Computed orbital energies and experimental ionization potentials*[a]

Molecule	$-\varepsilon_\pi$ [b]	$-\varepsilon_n$ [c]	ε_π^* [d]	Ionization potential[e]
Acetylene	11.24	...	+2.52	11.41
Ethylene	10.54	...	+0.04	10.48–10.80
Benzene	9.97	...	−0.08	9.24–9.52
trans-Butadiene	9.09	...	−1.86	9.07–9.18
trans-Hexatriene	8.36	...	−2.66	8.23[f]
Styrene	8.85	...	−1.79	8.86[g]
Naphthalene	8.36	...	−2.29	8.12–8.26
Azulene	7.62	...	−3.41	7.72
Methyl acetylene	10.58	...	+1.94	10.36
Propylene	10.05	...	+0.15	9.73–9.94
Toluene	9.61	...	−0.18	8.82–9.20
p-Xylene	9.31	...	−0.27	8.44–8.86
Formaldehyde	13.48	11.44	−2.30	10.88 (n), 14.39 (π)
Acetaldehyde	12.46	10.93	−1.94	10.21–10.28 (n)
Acetone	11.85	10.55	−1.76	9.69–9.92 (n), 12.16 (π)
trans-Acrolein	10.48	10.70	−3.41	10.10–10.34 (π)
trans-2-Butenal	10.05	10.52	−3.19	9.73–9.81 (π)
trans-3-Butenone	10.38	10.43	−3.28	9.91 (π)?
Benzaldehyde	9.90	10.63	−3.19	9.52–9.82 (π)
Tropone	8.29	9.11	−2.97	9.68?
Hydrogen cyanide	13.01	12.82	+1.13	13.9[g]
Pyridine	10.27	10.80	−1.43	9.28–9.76 (π), 10.54 (n)
Pyrazine	10.59	10.53	−2.35	10.01 (n?)
Pyrrole	8.64	...	−0.07	8.97

[a] All values in electron volts.

[b] Energy of the highest occupied π-MO.

[c] Energy of the highest occupied nonbonding MO.

[d] Energy level of the lowest virtual orbital.

[e] All experimental values taken from the tabulation by Newton, Boer, and Lipscomb, Ref. [8] unless otherwise noted.

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Table 3. *Effects of methyl group substitution on ionization potentials*

Molecule	Parent molecule	ΔE, IEHT[a]	ΔE, NEMO[a]	ΔE, Exp
Methyl acetylene	Acetylene	0.66	1.10	1.05
Propylene	Ethylene	0.49	1.17	0.75–0.86
Toluene	Benzene	0.36	0.71	0.32–0.42
p-Xylene	Toluene	0.30	0.64	0.34–0.37
Acetaldehyde[b]	Formaldehyde	0.51	0.40	0.56–0.66
Acetone[b]	Acetaldehyde	0.38	0.51	0.37–0.53
trans-2-Butenal	Acrolein	0.43	0.81	0.37–0.45
trans-3-Butenone	Acrolein	0.10	0.00	uncertain

[a] Lowering of the first ionization potential due to methyl group substitution.

[b] Lowering of the n-level.

Table 4. *Computed and experimental dipole moments*[a]

Molecule	μ, π-Modification	μ, No modification	μ, NEMO	μ, Experimental
Methyl acetylene	0.97	0.91	1.66	0.75
Propylene	0.40	0.40	0.84	0.36
Toluene	0.38	0.44	0.76	0.43
Azulene	3.51	2.31	4.79	1.0–1.08
Formaldehyde	1.93	1.44	1.26	2.17–2.34
Acetaldehyde	2.58	2.12	1.93	2.68
Acetone	3.01	2.49	2.54	2.87–2.97
trans-Acrolein	3.29	2.74	1.57	3.04–3.11
trans-2-Butenal	4.10	3.59	2.71	3.7
Hydrogen cyanide	1.12	0.73	—	2.99
Pyridine	0.86	0.66	1.14	2.15–2.25
Pyrrole	0.59	1.20	4.98	1.55–1.84

[a] All values are in debye units. Experimental results are taken from McClellan, A. L.: Tables of Experimental Dipole Moments, San Francisco: W. H. Freeman and Company 1963.

usually in fairly good agreement with experiment except for azulene and the three nitrogen-containing molecules. It would appear that it is not feasible to parametrize the nitrogen atom in such a way so as to obtain good values for both ionization potentials and dipole moments since this difficulty also arises in NEMO calculations.

Summary

The studies undertaken here indicate that an improved treatment of conjugated systems is possible in IEHT if the sacrifice of complete rotational invariance is made. The results are satisfactory for the occupied MO's but negative virtual orbital levels are still observed although a much larger gap between the occupied and virtual orbitals is found. A more extensive experimentation may yield parameter values which are somewhat more satisfactory in this respect.

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