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The Variable Core Approach in the SCF MO Calculation of Heteroatomic Systems

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A charge density dependency of the core energy in the SCF MO theory has been derived. According to the present theory, the core energy, U_μ, associated with the μ^{th} $2p\pi$–AO should linearly vary with the charge density, q_μ. SCF MO calculations based on this variable core approach have been carried out for some N-heterocycles, aromatic amino derivatives, and protonated pyridine. The results for the electronic spectra of neutral molecules are almost the same as those based on the conventional SCF MO method. However, the calculated charge distributions are somewhat different. An interesting result is that the present theory calculates a slightly negative net charge at the meta positions in aniline.

Es wird eine SCF-MO-Methode entwickelt, in der das dem $2p\pi$–AO μ entsprechende Rumpfintegral U_μ linear von der Ladungszahl q_μ abhängt. Es werden einige N-Heterocyclen, aromatische Aminoderivate und das Pyridinium-Ion durchgerechnet. Die Elektronenspektren der neutralen Moleküle ergeben sich wie mit der üblichen Methode; die Ladungsverteilung ist jedoch etwas verändert. Beispielsweise führt die neue Methode zu einer geringen negativen Überschußladung in der Metaposition des Anilins.

On a établi une relation de dépendance entre l'énergie de coeur et la densité de charge en méthode SCF MO. Salon la théorie ci-dessous l'énergie de coeur U_μ, associée à la μième orbitale atomique $2\varrho\pi$, devrait varier linéairement avec la densité de charge q_μ. Des calculs SCF MO basés sur cette hypothèse de coeur variable ont été effectués pour quelques N-hétérocycles, dérivés aminés aromatiques et pour la pyridine protonisée. Les résultats concernant les spectres électroniques des molécules neutres sont pratiquement identiques à ceux obtenus par la méthode SCF MO conventionelle. Cependant les distributions de charges obtenues sont quelque peu différentes. Un résultat intéressant de cette théorie est la faible charge nette négative en position méta dans l'aniline.

Introduction

Brown and Heffernan [1, 2] pointed out that in heteroatomic systems, valence state energies (VSE) must be varied with the charge distribution in the molecule. According to their variable electronegativity method, the orbital exponent Z_μ for the atomic orbital ϕ_μ is regarded as a functions of the electron density at the μ^{th} atom, and thus various basic integrals, all of which depend upon the values of orbital exponents, become functions of the electron distribution. Usually, π-electronic structures of aromatic derivatives having weak interacting substituents, such as OH, NH_2, etc., can be successfully calculated by the SCF MO method based on the constant VSE approximation [9], because the charge distributions do not greatly deviate from uniformity. However, for anions and cations, the effect of charge distribution might not be neglected. In this paper, we will propose a simple alternative method for estimating a dependency of the VSE on the charge distribution and apply it to SCF MO calculations of some conjugated systems.

Theory

According to Hinze, Whitehead, and Jaffé [5], the energy associated with an atomic orbital ϕ_μ of the μ^{th} atom, E_μ, is given by

$$E_\mu = \frac{I_\mu - A_\mu}{2} q_\mu^2 - \left(I_\mu + \frac{I_\mu - A_\mu}{2} \right) q_\mu , \tag{1}$$

where I_μ and A_μ are the valence state ionization potential and electron affinity, respectively; q_μ is the charge density. In the Pariser-Parr-Pople theory [12], the diagonal Hatree-Fock matrix element associated with ϕ_μ, which measures the one electron energy, is given by

$$F_{\mu\mu} = U_\mu + \frac{1}{2} \gamma_{\mu\mu} q_\mu + \sum_{\nu \neq \mu} \Delta q_\nu \gamma_{\mu\nu} , \tag{2}$$

where

$$U_\mu = \int \phi_\mu(1) \left[T(1) + V_\mu(1) \right] \phi_\mu(1) \, d\tau ,$$

$$\gamma_{\mu\nu} = \int \phi_\mu^2(1) \frac{e^2}{r_{12}} \phi_\nu^2(2) \, d\tau .$$

Δq_ν gives the net charge on the ν^{th} atom. The one center electron repulsion integral, $\gamma_{\mu\mu}$, is given by

$$\gamma_{\mu\mu} = I_\mu - A_\mu .$$

In the orbital approximation (one electron approximation) each electron can move almost independently. Therefore, in order to make a comparison of E_μ with $F_{\mu\mu}$, we must subtract a correction term coming from ionic configurations, giving the probability that two electrons exist in the same space. For a core which provides one electron to the molecular system, this term is given by $(1/2)\gamma_{\mu\mu}q_\mu$ in Eq. (2). Therefore, the total atomic energies, E_{atom}, can be calculated by

$$E_{\text{atom}} = \sum_\mu E_\mu = \sum_\mu q_\mu \left(F_{\mu\mu}^\circ - \frac{1}{2} \gamma_{\mu\mu} q_\mu \right)$$

with

$$E_\mu = q_\mu \left(F_{\mu\mu}^\circ - \frac{1}{2} \gamma_{\mu\mu} q_\mu \right) \tag{3}$$

Substituting Eq. (1) into Eq. (3), we obtain the relation

$$U_\mu = -I_\mu + \frac{1}{2} \gamma_{\mu\mu} (q_\mu - 1) . \tag{4}$$

For a core which provides two electrons to the system, we must take another correction into account. U_μ represents the one electron core energy. However, ϕ_μ is occupied by two electrons and we can not physically distinguish them. That is, we must take

$$U_\mu^{\text{av}} = -\frac{I_2 + I_\mu}{2}$$

for this case. Here I_2 gives the second ionization potential associated with ϕ_μ. On the other hand, according to one electron approximation, U_μ may be given by $-I_2$. Therefore, $F_{\mu\mu}^\circ$ should be written as

$$F_{\mu\mu}^\circ = U_\mu + \frac{1}{2} \gamma_{\mu\mu} q_\mu = -I_2 + \frac{1}{2} \gamma_{\mu\mu} q_\mu$$

or

$$F^{\circ}_{\mu\mu} = -\frac{I_2 + I_\mu}{2} + \frac{1}{2}\gamma_{\mu\mu}(q_\mu - 1), \tag{5}$$

because $\gamma_{\mu\mu} = I_2 - I_\mu$ in this case. Consequently, the above-mentioned correction term is given by $(1/2)\gamma_{\mu\mu}(q_\mu - 1)$. Therefore, in the case that the μ^{th} core provides two electrons to the system, Eq. (3) should be rewritten as

$$E_\mu = \frac{\gamma_{\mu\mu}}{2} q_\mu^2 - \left(I_2 + \frac{\gamma_{\mu\mu}}{2}\right) q_\mu = q_\mu\left(F^{\circ}_{\mu\mu} - \frac{1}{2}\gamma_{\mu\mu}(q_\mu - 1)\right) = q_\mu\left(U_\mu + \frac{1}{2}\gamma_{\mu\mu}\right)$$

or

$$U_\mu = -I_2 + \frac{\gamma_{\mu\mu}}{2}(q_\mu - 2). \tag{6}$$

In the Brown-Heffernan [1, 2] theory, the core energy U_μ was expressed by a quadratic equation with respect to the orbital exponent Z_μ, whereas the present theory showed that it can be given by a linear dependency on the charge density on the μ^{th} atom. The diagonal Hatree-Fock matrix elements in the Pariser-Parr-Pople theory based on the present approach are, therefore, expressed as follows:

i) For the $+1$ core which provides one electron to the system,

$$F_{\mu\mu} = -\frac{I_\mu + A_\mu}{2} + \sum_{\nu=1} \Delta q_\nu \gamma_{\mu\nu}.$$

ii) For the $+1$ core which provides two electrons to the system,

$$F_{\mu\mu} = -I_\mu + \sum_{\nu=1} \Delta q_\nu \gamma_{\mu\nu}.$$

iii) For the $+2$ core which provides one electron

$$F_{\mu\mu} = -I_1 + \frac{1}{2}\gamma_{\mu\mu} + \sum_{\nu=1}^{n} \Delta q_\nu \gamma_{\mu\nu}.$$

iv) For the $+2$ core which provides two electrons,

$$F_{\mu\mu} = -I_1 + \sum_{\nu=1}^{n} \Delta q_\nu \gamma_{\mu\nu},$$

where I_1 is the first ionization potential of a lone pair of the μ^{th} atom.

Results and Discussions

SCF MO calculations based on the variable core and variable β [9] approximations for pyridine, quinoline, isoquinoline, aniline, α-naphthylamine, β-naphthylamine, and protonated pyridine have been carried out. For comparison, SCF MO calculations based on the fixed core approximation have been also carried out. The basic parameters used in this paper were given in Ref. [10], except for the $=N^+-$ core. For a nitrogen $2p\pi$–AO, the valence state ionization potential and electron affinity given by Hinze and Jaffé [4] are reduced by 14%, that is, $I_N = 12.14$ eV, $A_N = 1.53$ eV and $a_N = 1.357$ Å. The reason was explained in a previous paper [10]. Electron repulsion integrals are evaluated by a new procedure (electron interaction in molecules, [10]). The transition energies have been calculated by including configuration interactions between all singly excited configurations within D eV of lowest excited (singlet or triplet) states.

In this paper, a covalent model is assumed for the protonated pyridine. However, as shown in Table 3, the result is not satisfactory. Calculations, which are not included in this paper, show that an intermediate between a covalent and an electrostatic model gives a quite good result for the calculation of the electronic spectrum of protonated pyridine. Anyway, as protonated N-heterocycles form a very interesting group for theoretical challenge, we will discuss them in detail in a separate paper.

The calculated results are summarized in Tables 1—3 and compared with the experimental data. The numbering of the atoms for the calculated molecules are

Table 1. *Comparison of calculated charge densities and bond orders of some aromatic compounds; fixed core (A) and variable core (B) approximations*

	Pyridine		Protonated pyridine		Aniline	
	A	B	A	B	A	B
q_1	1.204	1.118	1.492	1.639	0.977	0.995
q_2	0.906	0.959	0.904	0.854	1.077	1.041
q_3	1.008	0.988	0.943	0.914	0.989	1.007
q_4	0.969	0.987	0.815	0.825	1.040	1.022
q_7	—	—	—	—	1.850	1.887
p_{12}	0.656	0.665	0.574	0.505	0.614	0.628
p_{23}	0.662	0.661	0.695	0.707	0.676	0.674
p_{34}	0.668	0.669	0.641	0.622	0.661	0.662
p_{17}	—	—	—	—	0.389	0.335

	Quinoline		Isoquinoline		α-Naphthylamine		β-Naphthylamine	
	A	B	A	B	A	B	A	B
q_1	1.220	1.133	0.875	0.940	0.976	0.996	1.098	1.049
q_2	0.875	0.940	1.213	1.127	1.098	1.048	0.979	0.997
q_3	1.011	0.999	0.925	0.962	0.984	1.006	1.054	1.027
q_4	0.959	0.976	1.012	0.998	1.047	1.021	0.987	1.005
q_5	1.010	0.995	0.996	0.997	0.998	0.999	1.003	1.005
q_6	0.996	1.002	0.993	0.991	1.004	1.006	1.013	1.007
q_7	1.001	0.993	0.994	1.000	1.009	1.005	1.006	1.007
q_8	0.986	0.998	1.002	0.993	1.013	1.012	1.005	1.003
q_9	0.938	0.968	1.007	0.998	1.039	1.021	0.986	1.002
q_{10}	1.002	0.998	0.984	0.989	0.989	1.002	1.019	1.009
q_{11}	—	—	—	—	1.843	1.885	1.851	1.889
p_{12}	0.741	0.754	0.740	0.752	0.696	0.713	0.701	0.717
p_{19}	0.522	0.531	0.524	0.522	0.482	0.494	0.534	0.532
p_{23}	0.561	0.559	0.560	0.569	0.578	0.575	0.517	0.529
p_{34}	0.760	0.761	0.753	0.752	0.751	0.753	0.771	0.768
$p_{4,10}$	0.528	0.529	0.529	0.530	0.523	0.524	0.516	0.519
p_{56}	0.762	0.763	0.762	0.762	0.758	0.759	0.758	0.759
p_{67}	0.560	0.559	0.561	0.561	0.566	0.565	0.563	0.563
p_{78}	0.763	0.764	0.762	0.762	0.755	0.757	0.760	0.761
p_{89}	0.518	0.516	0.523	0.523	0.536	0.532	0.522	0.522
$p_{9,10}$	0.564	0.563	0.567	0.568	0.569	0.568	0.563	0.564
$p_{5,10}$	0.521	0.521	0.521	0.521	0.525	0.525	0.529	0.527
$p_{1,11}$ or $p_{2,11}$	—	—	—	—	0.396	0.338	0.387	0.332

shown in Fig. 1. The effects of the variation of the core energies on the molecular properties are summarized as follows.

i) *Charge distributions.* In amino derivatives, a variable core approximation gives negative net charges everywhere, except on NH_2 groups and on carbon atoms connected with the substituents. On the other hand, a fixed core approximation gives positive net charges on carbon atoms in *m*-positions (meta positions).

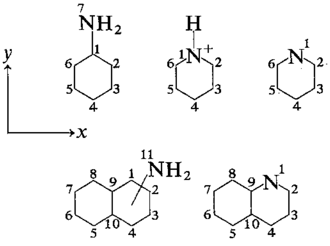

Fig. 1. Numbering of atoms

In N-heterocycles, every carbon atom has a positive net charge in the variable core approximation, whereas a fixed core approximation calculates negative net charges on the β-carbons.

ii) *Bond orders.* Although the core energy variation has a pretty small effect on the bond orders, it always brings an increase of the C–N bond orders in N-heterocycles. It is interesting to note that in pyridine, an inversion in the order of magnitudes is found between the 1—2 and 2—3 bond.

Table 2. *Comparison of calculated ionization potentials of some aromatic compounds; fixed core (A) and variable core (B) approximations*

Molecule	A	B
Pyridine	9.45 eV	9.57 eV
Quinoline	8.58	8.54
Isoquinoline	8.38	8.43
Aniline	8.09	8.30
α-Naphthylamine	7.56	7.68
β-Naphthylamine	7.72	7.82
Protonated pyridine	14.35	14.90

iii) *Ionization potentials.* Table 2 shows that the core energy variation has the effect of increasing the ionization potentials for all molecules, except quinoline. However, the magnitudes of the changes are rather small.

iv) *Electronic spectra.* The core energy variation brings very small changes in the electronic transition energies. However, the intensities are very sensitive to the change in valence state energy. Particularly, the intensities of the longest wavelength absorptions (^1L_b species) usually decrease to almost the half. Furthermore, in aza-naphthalenes and naphthylamines, the intensities of the transitions in the region of 5—6 eV are greatly changed by the core energy variations. These

Table 3. *Comparison of electronic transition energies (eV) and the intensities of some aromatic compounds; fixed core (A) and variable core (B) approximations*

Singlet Transition energy and (Oscillator strength)			Polarization*		Triplet Transition energy		
A	B	Obs.	A	B	A	B	Obs.
Pyridine ($D = 4.0$ eV)							
4.81 (0.056)	4.85 (0.021)	4.90 (0.04)^a	x	x	3.20	3.17	—
6.15 (0.047)	6.15 (0.050)	6.17 (0.10)	y	y	3.92	4.11	
6.94 (1.078)	6.96 (1.083)	6.94 (1.30)	y	y	4.27	4.26	
7.02 (1.107)	6.97 (1.164)	—	x	x	5.12	4.96	
Protonated pyridine ($D = 4.0$ eV)							
4.70 (0.155)	4.44 (0.272)	4.83^b	x	x	3.22	3.11	—
5.84 (0.014)	5.66 (0.057)	5.50	y	y			
6.91 (1.045)	6.88 (1.018)	—	y	y			
6.92 (0.820)	7.15 (0.607)	—	x	x			
Aniline ($D = 4.0$ eV)							
4.38 (0.048)	4.49 (0.028)	4.40 (0.028)^c	x	x	3.14	3.29	3.49^d
5.50 (0.265)	5.62 (0.195)	5.39 (0.144)	y	y	3.61	3.77	
6.40 (0.729)	6.48 (0.890)	6.40 (0.510)	x	x	3.95	3.99	
6.59 (1.064)	6.61 (1.101)	6.88 (0.570)	y	y	4.84	4.75	
7.65 (0.295)	7.48 (0.166)	7.87 (0.68)	x	x	5.42	5.63	
Quinoline ($D = 3.5$ eV)							
3.97 (0.052)	3.98 (0.018)	3.96^e	175°	6°	2.75	2.75	—
4.47 (0.170)	4.51 (0.179)	4.59	87°	94°	3.43	3.53	
5.29 (0.583)	5.34 (0.499)		1°	2°	3.60	3.57	
5.64 (0.194)	5.62 (0.627)		7°	4°	3.90	3.93	
5.78 (1.034)	5.71 (0.803)	5.51	1°	177°	4.08	4.08	
5.88 (0.187)	5.88 (0.071)		134°	102°	4.48	4.32	
6.17 (0.691)	6.11 (0.664)		88°	90°	5.49	5.44	
6.95 (0.002)	6.99 (0.002)		177°	173°	5.82	5.85	
Isoquinoline ($D = 3.5$ eV)							
3.97 (0.051)	4.00 (0.018)	3.91^e	111°	108°	2.70	2.71	—
4.52 (0.180)	4.51 (0.205)	4.66	77°	81°	3.39	3.41	
5.31 (0.059)	5.37 (0.011)		137°	75°	3.58	3.64	
5.50 (1.132)	5.52 (0.914)	5.71	177°	175°	3.83	3.91	
5.66 (0.257)	5.63 (0.793)		14°	1°	4.26	4.24	
5.80 (0.475)	5.78 (0.195)		0°	173°	4.45	4.30	
6.18 (0.568)	6.16 (0.612)		89°	86°	5.42	5.41	
6.96 (0.001)	7.01 (0.003)		172°	158°	5.72	5.75	
α-Naphthylamine ($D = 3.5$ eV)							
3.79 (0.039)	3.84 (0.023)	3.73^f (0.13)	171°	5°	2.36	2.48	—
4.09 (0.263)	4.18 (0.248)	3.90	77°	82°	3.25	3.32	
5.06 (0.460)	5.12 (0.447)	5.11 (0.34)	0°	0°	3.34	3.42	
5.18 (0.027)	5.26 (0.040)		119°	150°	3.87	3.87	
5.49 (0.146)	5.52 (0.738)		14°	3°	4.09	4.09	
5.57 (1.027)	5.57 (0.512)	5.88 (0.82)	178°	176°	4.36	4.27	
6.09 (0.682)	6.07 (0.673)		88°	88°	5.21	5.25	
6.53 (0.120)	6.65 (0.073)		171°	169°	5.34	5.42	

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* Numerical value gives the angle between the transition moment vector and the x-axis of the module.

[a] Ref. [11]; [b] Ref. [14]; [c] Ref. [6]; [d] Ref. [7]; [e] Ref. [3];

[f] Baba, H., and S. Suzuki: Bull. chem. Soc. Japan **34**, 82 (1961).

Table 3 (Continued)

Singlet					Triplet		
Transition energy and (Oscillator strength)			Polarization*		Transition energy		
A	B	Obs.	A	B	A	B	Obs.
β-Naphthylamine ($D = 3.5$ eV)							
3.74 (0.065)	3.80 (0.035)	3.56 (0.033)^{f}	125°	120°	2.53	2.61	—
4.36 (0.153)	4.38 (0.165)	4.44 (0.10)	128°	118°	3.21	3.30	
5.06 (0.138)	5.15 (0.103)		178°	174°	3.48	3.51	
5.25 (1.334)	5.31 (1.327)	5.25 (0.86)	20°	16°	3.58	3.72	
5.51 (0.319)	5.51 (0.420)		167°	175°	4.02	4.02	
5.65 (0.203)	5.68 (0.136)		27°	30°	4.28	4.22	
5.85 (0.588)	5.86 (0.619)	5.84	121°	114°	5.11	5.19	

facts tell us that as usual the intensity is very sensitive to a change of the wavefunction, but the energy is rather insensitive. Comparing the results of the aniline spectra given in the previous [10] and the present papers, we can see that an extensive configuration interaction varies considerably the triplet energies, but very slightly the singlet energies. The reason may be that SCF MO's for closed shells are suitable for singlet states. For triplet states, we must carry out the SCF MO calculation for open shells.

Concerning the polarizations of electronic transitions, they are practically unchanged by core energy variations. It is interesting to note that the nature of naphthalene the ^1L_b species, i.e. the direction of polarization, is entirely altered by a substituent at the β-position or by a replacement of $=$CH$-$ by $=$N$-$ at the 2-position, which has been emphasized in a previous paper [8].

The effects of variation in valence state energies for amino derivatives should be common to all other aromatic derivatives having electron donating substituents.

In conclusion, although the core energy variation has a rather small effect on the electronic structure of a neutral molecule, it brings a very characteristic change in charge distributions and bond orders, depending on the type of the hetero-atoms. In amino derivatives, the nitrogen atoms act as electron donors, whereas in N-heterocycles, they behave as electron acceptors. In this paper, only the π-electron distribution is taken into account. However, it is proper that we must consider the σ-electron distribution too. This will be our next interesting problem.

Added in Proof: When the correction term coming from a ionic configuration is taken as $1/2\,\gamma_{\mu\mu}$, Eq. (3) should be rewritten as

$$E_\mu = q_\mu(F^\circ_{\mu\mu} - 1/2\cdot\gamma_{\mu\mu}) = q_\mu(U_\mu + 1/2\cdot\gamma_{\mu\mu}(q_\mu - 1))\,. \tag{3'}$$

This leads to a fixed core approximation, $U_\mu = -I_\mu$. In a next paper, we will discuss various parameterizations in detail.

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