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Department of Chemistry, University College of Science, Calcutta-9, India

SCF CI Calculation of the electronic spectra of nitroso and nitro benzene

By

Rama Basu (née Bhattacharya)

SCF calculation with CI has been found to give a reasonable value for the longest wavelength π-π^* transition in nitroso and nitro benzene if a sufficient number of configurations are taken into considerations. The applicability of this method to the case of n-π^* transition is, however, of doubtful validity. For the electron density approximation of chemical reactivity simple Hückel calculation may be good enough if the parameters are carefully chosen.

Eine SCF-CI-Berechnung ergab brauchbare Werte für die langwelligsten π-π^*-Übergänge von Nitro- und Nitrosobenzol, wenn genügend Konfigurationen in die Rechnung einbezogen werden. Jedoch ist der Wert der Methode für die Berechnung von n-π^*-Übergängen zweifelhaft. Die Elektronendichte ist nicht wesentlich von der der Hückel-Theorie verschieden, so daß letztere für Fragen der chemischen Reaktivität ausreichend erscheint, wenn die Parameter sorgfältig gewählt werden.

Un calcul SCF donne des énergies raisonnables pour les premières transitions π-π^* de nitroso- et de nitrobenzène, quand on considère un nombre suffisant de configurations. Mais l'application de ce procédé aux transitions n-π^* est douteuse. Si l'on croisit soigneusement les paramètres, la méthode simple de Hückel semble suffir pour le calcul des densités électroniques dans des problèmes de réactivité chimique.

The semiemperical SCF-LCAO-MO method with limited configuration interaction (CI) has given encouraging results in the calculation of electronic spectra of aromatic hydrocarbons as well as of a number of π-electron systems containing hetero atoms like nitrogen or oxygen. In the latter case it has been observed that although the calculation reproduces the π-π^* transition reasonably well, the transition involving the non-bonding electrons on the hetero atom, *i. e.* so called n-π^* transition comes out much higher than the experimental value. Inspite of this discrepancy the calculation of n-π^* transition has been useful in locating this transition with respect to the longest wavelength π-π^* singlet and triplet band.

As far as the author is aware of careful SCF CI calculations have not been made on π-electron systems containing two different hetero atoms. From the experimental point of view these compounds present a problem as to the assignment of their n-π^* band. Further most of the biologically important compounds contain more than one hetero atom and the current lively interest in quantum biology demands that the usefulness of SCF-CI method in the calculation of electronic structure of systems containing more than one hetero atoms must be carefully analysed. With this object in view SCF CI calculations were made on two simple π-electron systems namely nitroso and nitro benzene, containing the two different hetero atoms oxygen and nitrogen. Recently McEwen [*4*] has made some calculations on nitroso and nitro methane and has discussed the theoretical principles underlying the evalution of various molecular integrals using atoms-in-molecule approximation. The same procedure was followed in the present case but attention was focussed mainly on the longest wavelength π-π^* and n-π^* transitions.

The theoretical principles involved in the SCF-CI calculation have been discussed in greater detail by various authors [*6*, *7*]. In the present work a machine computation was done to get complete self consistancy within the framework of this approximation.

Method of Calculation

The machine computation uses the fact that the single electron density matrix $(1/2)P_{\mu\nu}$ is idempotent and that the total energy is a minimum for correct $p_{\mu\nu}$. An initial $p_{\mu\nu}$ usually based on the corresponding Hückel type matrix is brought closer to satisfying the equations for the correct $p_{\mu\nu}$. Then introducing the electron repulsion integrals, iteration procedure was carried out. Usually 10—11 iterations were necessary for self consistency to within 0.0001 e. v.

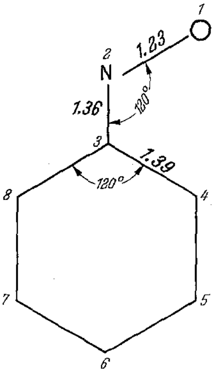
After the self-consistency is obtained for the ground state energy the configurational wave function for the excited states were constructed from the unoccupied orbitals. If we denote ${}^1\chi_{i\to k}$ for the singlet configurational wave function in which one electron is excited from an occupied orbital ψ_i to an unoccupied orbital ψ_k, and the corresponding triplet wave function as ${}^3\chi_{i\to k}$, then the excitation energy corresponding to transition $i\to k$ may be expressed as follows:

$$\begin{aligned} E\,({}^1\chi_{i\to k}) &= ({}^1\chi_{i\to k} \mid H \mid {}^1\chi_{i\to k}) - (\chi_0 \mid H \mid \chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik \mid G \mid ik) + 2\,(ik \mid G \mid ki) \\ E\,({}^3\chi_{i\to k}) &= ({}^3\chi_{i\to k} \mid H \mid {}^3\chi_{i\to k}) - (\chi_0 \mid H \mid \chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik \mid G \mid ik) \end{aligned}$$

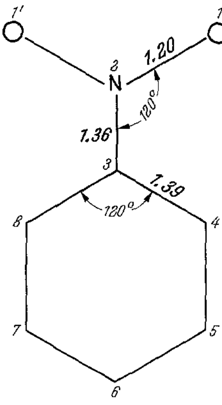
where

$$(pq \mid G \mid rs) = \int \psi_p^*(1)\, \psi_q^*(2)\, (e^2/r_{12})\, \psi_r(1)\, \psi_s(2)\, dv_1\, dv_2$$

and ε_k are orbital energies.



Nitrosobenzene



Nitrobenzene

The interconfigurational matrix elements were obtained in a similar way

$$\begin{aligned} ({}^1\chi_{i\to k} \mid H \mid {}^1\chi_{j\to l}) &= -\,(jk \mid G \mid il) + 2\,(jk \mid G \mid li) \\ ({}^3\chi_{i\to k} \mid H \mid {}^3\chi_{j\to l}) &= -\,(jk \mid G \mid il). \end{aligned}$$

An excited state wave function was approximated by a linear combination of singly excited configuration functions $\chi_{i\to k}$.

Selection of parameters: The α in the core Hamiltonian was calculated from the valency state ionisation energy and two center integrals as suggested by PARISER and PARR [5]. In the Hückel calculation following values of α were used,

$$\alpha_N = \alpha_C + 0.2\,\beta$$
$$\alpha_O = \alpha_C + 1.0\,\beta$$

where α_C is the core Coulomb integral for carbon and β_{CC} the core resonance integral for a C-C bond. The core β was considered as an empirical parameter and the following values were used for the various bonds,

$$\beta_{CC} = -\ 2.39 \text{ e.v.}$$
$$\beta_{CN} = -\ 1.60 \text{ e.v.}$$
$$\beta_{NO} = -\ 3.00 \text{ e.v.}$$
(for nitrosobenzere)
$$\beta_{NO} = -\ 2.90 \text{ e.v.}$$
(for nitrobenzene).

The various mono and bicentric integrals were either taken from the paper of McEWEN [4] or calculated by method suggested by PARISER and PARR [5].

n-π^* transitions

The above formulation holds strictly for π-molecular orbitals and π-π^* transitions. Recently ANNO and SADO [1] have extended the SCF calculation with limited CI to take into account the non-bonding electrons explicitely along with the π-electrons in the calculation of transition energies in p-benzoquinone, formaldehyde and aza-aromatics. The semiemperical calculations of the n-π^* spectra of several molecules containing carbonyl groups has also been performed by SIDMAN [8]. Although the results of these calculations are encouraging the agreement between the experimental and the theoretical n-π^* transition energies is not as satisfactory as is the case with π-π^* transitions. ANNO and SADO [1] have suggested that this discrepancy arises from the fact that doubly excited configurations have been neglected for n-π^* states. In the present case procedure with only singly excited configurations has been performed in order to see if doubly excited configurations are also important in molecules containing two different hetero atoms.

The non-bonding molecular orbitals were built as a linear combination of non-bonding atomic orbitals in a way similar to the calculation of McEWEN. The non-bonding electron on nitrogen was assumed to be in a sp^2 hybridised state while that on oxygen was in a pure p-state. In the calculation of matrix elements of the FOCK Hamiltonian it was assumed that each atom now donates two electrons to the molecular orbital. As n-orbitals and π-orbitals have different symmetry with respect to the molecular plane, only electron interactions involving nearest neighbours were taken into considerations in the calculation of n-π^* transition energies.

Results

In the Tab. 1 the various atomic parameters used in the present calculations are summarised.

When we wanted to know the energy of the state produced by CI from a configuration i, all configurations lying more than 10 e.v. above the configuration i

were neglected. This led to the mixing of $\chi^{3,5}$ with $\chi^{4,6}$ for the calculation of long wavelength π-π^* transitions. For the n-π^* transitions $\chi^{n,5}$ and $\chi^{n,6}$ configurations

Table 1. *Atomic parameters in e.v. for nitroso and nitro benzene*

		Nitrose	Nitro
Ionisation energy	$I_O(\pi)$	17.21	17.21
	$I_N(\pi)$	14,63	14.16
	$I_C(\pi)$	11.22	11.22
	$I_O(n)$	17.21	17.21
	$I_N(n)$	14.32	—
Monocentric integrals	$(O_\pi O_\pi/O_\pi O_\pi)$	14.52	14.52
	$(N_\pi N_\pi/N_\pi N_\pi)$	12.27	12.81
	$(C_\pi C_\pi/C_\pi C_\pi)$	10.53	10.52
	$(O_n O_n/O_n O_n)$	14.52	14.52
	$(N_n N_n/N_n N_n)$	12.74	—
Bicentric integrals	$(O_\pi O_\pi/N_\pi N_\pi)$	9.06	8.88
	$(O_\pi O_\pi/C_{\pi 3} C_{\pi 3})$	5.95	5.95
	$(O_\pi O_\pi/C_{\pi 4} C_{\pi 4})$	5,04	5.15
	$(O_\pi O_\pi/C_{\pi 5} C_{\pi 5})$	3.50	3.54
	$(O_\pi O_\pi/C_{\pi 6} C_{\pi 6})$	3.34	3.35
	$(O_\pi O_\pi/C_{\pi 7} C_{\pi 7})$	3.33	3.33
	$(O_\pi O_\pi/C_{\pi 8} C_{\pi 8})$	4.10	4.10
	$(N_\pi N_\pi/C_{\pi 3} C_{\pi 3})$	7.68	7.68
$(N_\pi N_\pi/C_{\pi 4} C_{\pi 4}) =$	$(N_\pi N_\pi/C_{\pi 8} C_{\pi 8})$	5.60	5.60
$(N_\pi N_\pi/C_{\pi 5} C_{\pi 5}) =$	$(N_\pi N_\pi/C_{\pi 7} C_{\pi 7})$	2.84	2.84
	$(N_\pi N_\pi/C_{\pi 6} C_{\pi 6})$	2.65	2.65
$(C_{\pi 3} C_{\pi 3}/C_{\pi 4} C_{\pi 4}) =$	$(C_{\pi 3} C_{\pi 3}/C_{\pi 8} C_{\pi 8})$	7.30	7.30
$(C_{\pi 3} C\mathrm{s}_3/C_{\pi 5} C_{\pi 5}) =$	$(C_{\pi 3} C_{\pi 3}/C_{\pi 7} C_{\pi 7})$	5.46	5.46
	$(C_{\pi 3} C_{\pi 3}/C_{\pi 6} C_{\pi 6})$	4.90	4.90
	$(O_\pi O_\pi/O_{\pi'} O_{\pi'})$	—	6.58
	$(O_n O_n/N_n N_n)$	13.65	—
	$(O_\pi O_\pi/O_n O_n)$	12.76	12.76
	$(N_\pi N_\pi/O_n O_n)$	9.46	9.46
	$(N_\pi N_\pi/N_n N_n)$	11.31	—
	$(N_n N_n/O_\pi O_\pi)$	10.85	—

Table 2. *Calculated and experimental transition energies for nitroso and nitro benzene*

		Calc. (e. v.)	Obs. (e. v.)[2]
Nitroso	π-π^* singlet (4,6)	5.188	4.710
	π-π^* singlet (3,5)	5.165	4.506
	π-π^* triplet (4,6)	4.363	—
	π-π^* triplet (3,5)	4.099	—
	n-π^* singlet (n,5)	0.006	—
	n-π^* singlet (n,6)	1.461	1.560
Nitro	π-π^* singlet (5,7)	4.780	4.420
	π-π^* singlet (4,6)	5.900	4.782
	π-π^* triplet (5,7)	4.263	—
	π-π^* triplet (4,6)	4.323	—
	n-π^* singlet (n,6)	3.691	3.752

(Experimental data on triplet transitions were not available for comparison.)

were mixed. The results of these calculations are summarised in Tab. 2. The experimental data on the triplet transitions were not available for comparison.

Discussion

A number of interesting conclusions may be drawn from the results of the above calculation. The calculated π-π* singlet appears at a higher energy than the experimental value. The introduction of extensive configuration interaction will bring the calculated value close to the experimental transition. For the *n*-π* transition, however, the calculated transition energies are consistently lower than the observed values. Taking more configurations into account will not correct this error in calculation .This error may arise from the fact that (1) the state of hybridisation of the non-bonding electrons has not been correctly assessed and (2) the atoms-in-molecule approximation is not very well justified in the calculation of various two center integrals involving non-bonding and π-electrons.

Table 3. *SCF charge and bond-order matrix for nitroso benzene*

	1	2	3	4	5	6	7	8
1	1.1815	0.9653	—0.0737	—0.1417	0.0066	0.0955	0.0114	—0.1334
2	0.9563	0.8604	0.2334	0.0672	—0.0152	—0.0475	—0.0241	0.0630
3	—0.0737	0.2334	1.0137	0.6479	—0.0031	—0.3237	—0.0143	0.6443
4	—0.1417	0.0672	0.6479	0.9918	0.6679	0.0234	—0.3279	—0.0384
5	0.0066	—0.0152	—0.0031	0.6679	0.9813	0.6662	0.0193	—0.3302
6	0.0955	—0.0475	—0.3237	0.0234	0.6662	0.9828	0.6623	0.0208
7	0.0114	—0.0241	—0.0134	—0.3279	0.0193	0.6623	0.9779	0.6723
8	—0.1334	0.0630	0.6443	—0.0384	—0.3302	0.0208	0.6723	1.0106

Table 4. HÜCKEL *and SCF charge and bond-order matric for nitro benzene*

HÜCKEL

	1	2	3	4	5	6	7	8	1′
1	1.6654	0.6199	—0.0592	—0.1480	0.0125	0.1155	0.0125	—0.1480	—0.3346
2	0.6199	0.7733	0.3833	0.1019	—0.0451	—0.0909	0,0451	—0.1019	—0.6199
3	—0.0592	0.3833	1.0188	0.6139	—0.0051	—0.3030	—0.0051	0.6139	—0.0592
4	—0.1480	0.1019	0.6139	0.9559	0.6780	0.0404	—0.3220	—0.0441	—0.1480
5	0.0125	—0.0451	—0.0051	0.6780	1.0014	0.6590	0.0014	—0.3220	0.0125
6	0.1155	—0.0909	—0.3030	0.0404	0.6590	0.9624	0.6590	0.0404	0.1155
7	0.0125	—0.0451	—0.0051	—0.3220	0.0014	0.6590	1.0014	0.6780	0.0125
8	—0.1480	0.1019	0.6139	—0.0441	—0.3220	0.0404	0.6780	0.9559	—0.1480
1’	—0.3346	0.6199	—0.0592	—0.1480	0.0125	0.1155	0.0125	—0.1480	1.6654
					SCF				
1	1.5925	0.6841	0.0251	—0.0807	—0.0011	0.0510	—0.0098	—0.0715	—0.4073
2	0.6841	0.8125	0.1675	0.0156	—0.0109	—0.0063	—0.0109	0.0156	0.6841
3	0.0251	0.1675	0.8516	0.6483	0.0239	—0.3268	0.0239	0.6483	0.0251
4	—0.0807	0.0156	0.6483	1.0296	0.6709	—0.0522	—0.3277	0.0816	—0.0715
5	—0.0011	—0.0109	0.0239	0.6709	1.0243	0.6636	—0.0277	—0.3277	—0.0098
6	0.0510	—0.0063	—0.3268	—0.0522	0.6636	1.0430	0.6636	—0.0522	0.0510
7	—0.0098	—0.0109	—0.0239	—0.3277	—0.0277	0.6636	1.0243	0.6709	—0.0011
8	—0.0715	0.0156	0.6483	0.0816	—0.3277	—0.0522	0.6709	1.0296	—0.0807
1’	—0.4073	0.6841	0.0251	—0.0715	—0.0098	0.0510	—0.0011	—0.0807	1.5925

In the case of nitroso benzene it has often been asked if in the *n*-π* transition the non-bonding electrons come from nitrogen or oxygen lone pairs (3). In the non-bonding molecular orbital the two lone pair atomic orbitals make almost equal contributions. So in this formulation of SCF calculation we can not speak in terms of nitrogen or oxygen electrons separately.

We may conclude that SCF calculation with CI is quite good for the calculation of π-π^* electronic spectra of molecules containing two different hetero atoms provided sufficient number of configurations are taken into account. For the calculation of n-π^* transitions, however, applicability of the method is of doubtful validity.

In the Tab. 3 and 4 the SCF charge and bond-order matrix for nitroso and nitro benzene are reproduced. A comparison of the Hückel charge and bond-order matrix with the SCF one for nitro benzene shows that in the qualitative interpretation of chemical reactivity in terms of electron density simple Hückel calculation with proper parameters may be good enough.

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