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Electronic Structure of Hydrazinium (2⁺) Ion. A Semiempirical MO Treatment

J. Zupan and M. Drofenik

Nuclear Institute »Jožef Stefan«, Ljubljana, Slovenia, Yugoslavia

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A simple semiempirical MO treatment of the electronic structure of hydrazinium (2⁺) ion was carried out on the basis of an extended Hückel method. The electronic population analysis for nitrogen and hydrogen atoms in this ion was calculated to be (1s)² (2s)^{1.127} (2p_x)^{1.360} (2p_y)^{1.360} (2p_z)^{0.986} and (1s)^{0.722}, respectively.

For the calculation of the magnetic susceptibility of the hydrazinium (2⁺) ion¹ the electronic structure and energy levels data are necessary, and for this purpose approximate evaluation of the energy levels and the charge distribution was carried out. The basic set of AO considered of Slater orbitals of 2s and 2p types from each nitrogen and 1s types from each hydrogen atom. The following values for the Coulomb integrals were calculated² (p. 118) or taken from tables² (p. 122). $H_{ii}(\text{H } a) = -18.80$ eV, $H_{ii}(\text{H } e) = -7.49$ eV, $H_{ii}(\text{N } 2s) = -25.50$ eV and $H_{ii}(\text{N } 2p) = -13.15$ eV. The off diagonal matrix elements H_{ij} were taken as $H_{ij} = 2G_{ij}(H'_{ii} \cdot H'_{jj})^{1/2}$, where H'_{ii} are noncorrected Coulomb integrals². The overlap integrals G_{ij} were evaluated using the Slater type atomic orbitals. The bond distances were taken from R. Liminga³ (N-N distance 1.43 Å, N-H distance 1.03 Å and N-N-H angle about 109°). The hydrazinium (2⁺) ion was supposed to belong to the point group D_{3d} (Fig. 1).

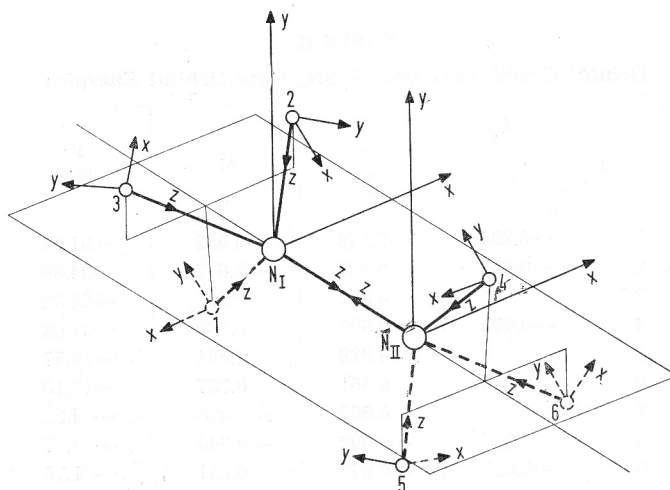


Fig. 1. The MO coordinate system of hydrazinium (2⁺) ion $\text{N}_2\text{H}_6^{2+}$. The symmetry belongs to the point group D_{3d} .

TABLE I
MO Combinations for Hydrazinium (2+) Ion According to Point Group D_{3d}

Reprez.	Ψ_{AO}^s	Ψ_{AO}^k	Φ_{lig}^k	k
A_{1g}	$2^{-1/2}[(2s)_I + (2s)_{II}]$	$2^{-1/2}[(2p_z)_I + (2p_z)_{II}]$	$2^{-1/2}[\varphi_{lig I}^z + \varphi_{lig II}^z]$	z
A_{2u}	$2^{-1/2}[(2s)_I - (2s)_{II}]$	$2^{-1/2}[(2p_z)_I - (2p_z)_{II}]$	$2^{-1/2}[\varphi_{lig I}^z - \varphi_{lig II}^z]$	z
E_u		$2^{-1/2}[(2p_x)_I + (2p_x)_{II}]$	$2^{-1/2}[\varphi_{lig II}^x - \varphi_{lig I}^x]$	x
		$2^{-1/2}[(2p_y)_I + (2p_y)_{II}]$	$2^{-1/2}[\varphi_{lig I}^y - \varphi_{lig II}^y]$	y
E_g		$2^{-1/2}[(2p_x)_I - (2p_x)_{II}]$	$2^{-1/2}[\varphi_{lig I}^x + \varphi_{lig II}^x]$	x
		$2^{-1/2}[(2p_y)_I - (2p_y)_{II}]$	$2^{-1/2}[\varphi_{lig I}^y + \varphi_{lig II}^y]$	y

$$\varphi_{lig I}^x = 2^{-1/2}[(1s)_2 - (1s)_3]$$

$$\varphi_{lig I}^y = (2/3)^{1/2}\{(1s)_1 - (1/2)[(1s)_2 + (1s)_3]\}$$

$$\varphi_{lig I}^z = 3^{-1/2}[(1s)_1 + (1s)_2 + (1s)_3]$$

$\varphi_{lig II}^k$ were obtained by replacing indexes 1, 2, 3 by 4, 5, 6, respectively.

$$\Psi_i(A_{1g}) = c_{i1} \Psi_{AO}^s + c_{i2} \Psi_{AO}^z + \lambda_i \Phi_{lig}^z \quad i = 1, 4, 6$$

$$\Psi_i(A_{2u}) = c_{i1} \Psi_{AO}^s + c_{i2} \Psi_{AO}^z + \lambda_i \Phi_{lig}^z \quad i = 2, 8, 9$$

$$\Psi_i(E_u) = c_{i2} \Psi_{AO}^x + \lambda_i \Phi_{lig}^x \quad i = 3, 7$$

$$\Psi_i(E_u) = c_{i2} \Psi_{AO}^y + \lambda_i \Phi_{lig}^y \quad i = 3, 7$$

$$\Psi_i(E_g) = c_{i2} \Psi_{AO}^x + \lambda_i \Phi_{lig}^x \quad i = 5, 10$$

$$\Psi_i(E_g) = c_{i2} \Psi_{AO}^y + \lambda_i \Phi_{lig}^y \quad i = 5, 10$$

TABLE II
Orbital Coefficients and Appropriate Orbital Energies

i	C_{ij}		λ_i	E_i (ev)
	j			
	1	2		
1	-0.834	-0.148	-0.532	-51.04
2	-0.652	0.339	-0.677	-24.86
3		0.823	-0.567	-22.82
4	-0.079	-0.921	0.380	-21.63
5		0.826	-0.564	-13.57
6	-0.546	0.361	0.757	-12.15
7		-0.567	-0.823	-4.22
8	0.308	-0.699	-0.646	-3.47
9	-0.693	-0.629	0.351	-1.75
10		0.564	0.826	-0.67

MO combinations derived according to standard group theoretical operations are listed in Table I. MOs are transforming in the point group D_{3d} as follows:

$$A_{1g}: \Psi_1, \Psi_4, \Psi_6$$

$$A_{2u}: \Psi_2, \Psi_8, \Psi_9$$

$$E_g: \Psi_5, \Psi_{10}$$

$$E_u: \Psi_3, \Psi_7$$

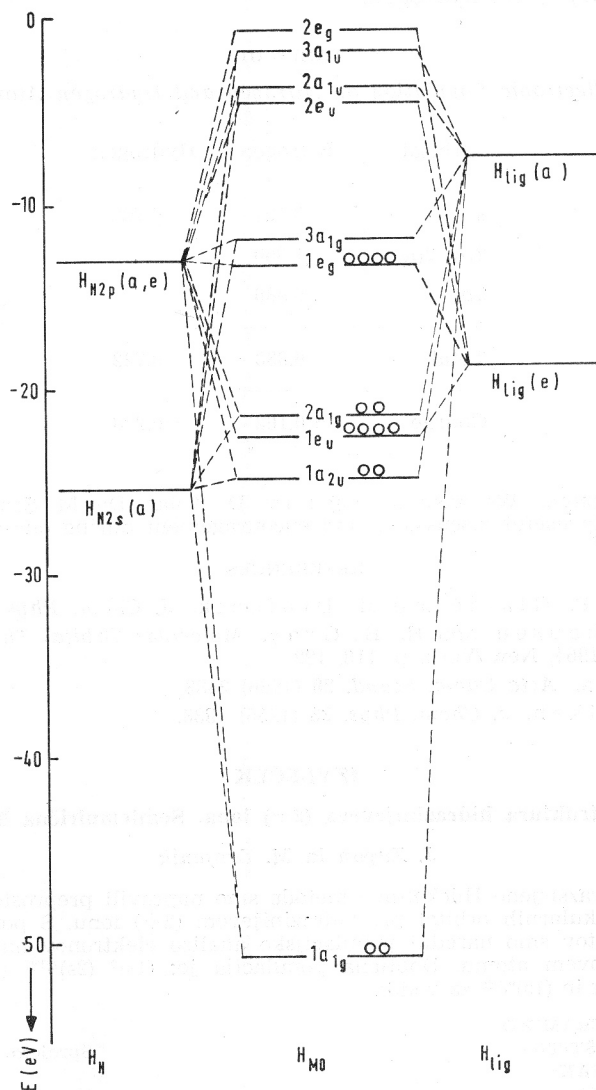
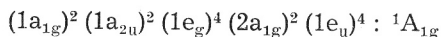


Fig. 2. Orbital energies of hydrazinium (2+) ion.

The MO energies and the LCAO coefficients obtained by this method are listed in Table II. This calculation leads to the ground state configuration (listed in the order of increasing energy):



The ground state is a singlet one. (Fig. 2).

The LCAO coefficients form the basis for the electronic population analysis after Mulliken⁴. The results of this calculation are summarised in Table III which can be expressed as follows: $(1s)^2 (2s)^{1.127} (2p_x)^{3.360} (2p_y)^{1.360} (2p_z)^{0.986}$ for nitrogen and $(1s)^{0.722}$ for hydrogen.

TABLE III
Electronic Population on Nitrogen and Hydrogen Atoms

Orbital	Nitrogen	Hydrogen
s	3.127	0.722
2p _x , 2p _y	1.360	
2p _z	0.986	
Total	6.833	0.722
Charge	+0.162	+0.278

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IZVLEČEK

Elektronska struktura hidrazinijevega (2+) iona. Semiempirična MO obravnava

J. Zupan in M. Drofienik

Na osnovi razširjene Hückel-ove metode smo napravili preprosto semiempirično obravnavo molekularnih orbital pri hidrazinijevem (2+) ionu. S pomočjo dobljenih LCAO koeficientov smo naredili populacijsko analizo elektronov na dušikovem ozioroma na vodikovem atomu. Dobljena populacija je: $(1s)^2 (2s)^{1.127} (2p_x)^{3.360} (2p_y)^{1.360} (2p_z)^{0.986}$ za dušik in $(1s)^{0.722}$ za vodik.

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NUKLEARNI INŠTITUT
»JOŽEF STEFAN«
LJUBLJANA

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