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ALL-VALENCE LCAO MO SCF INDO METHOD FOR GROUND AND EXCITED STATE PROPERTIES*

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Applying the theoretical Linderberg-Seamans relation to the resonance integral an all-valence LCAO MO SCF INDO method reproducing ground and excited state properties is proposed. The ground state results as well as the spectral properties are in good agreement with relevant experimental studies for chemically different isolated molecules and molecular complexes. In general, ground and excited state properties are better reproduced than in any other semiempirical approach known so far.

1. Introduction

It has been found that the all-valence semiempirical methods are able to reproduce only some physical or chemical properties fairly well. In general, it is possible to classify parametrizations into two distinct groups, i.e. one for a ground state and another for an excited state. Therefore, it is still interesting whether it is possible to find a unique set of parameters to reproduce both the ground and excited state properties for chemically different compounds.

On the other hand, in all quantum chemical calculations based on the all-valence semiempirical LCAO MO scheme a number of non-physical parameters are introduced [1]. For spectral properties, different parameters were used even for matrix elements between the σ and π atomic orbitals [2]. We contend that in every semiempirical approach some of the free and unjustified parameters should be reduced, i.e. non-physical parameters ought to be substituted with approximate but grounded relations.

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* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

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2. *Method and parametrization*

In this paper the LCAO MO method at the INDO level [1] has been chosen as a model for an all-valence method where the Hartree-Fock-Roothaan matrix elements are expressed by the following relationships

$$F_{ii} = U_{ii} + \sum_{j\in A} P_{jj}[(ii|jj) - 1/2(ij|ij)] + \sum_{B\neq A} (P_{BB} - Z_B)\gamma_{AB},$$

$$F_{ij} = 1/2P_{ij}[3(ij|ij) - (ii|jj)]; \quad i, j \in A,$$

$$F_{ij} = H_{ij} - 1/2P_{ij}\gamma_{AB}; \quad i \in A,\ j \in B. \tag{1}$$

The one-center U_{ii}, $(ii|ii)$, $(ii|jj)$, and $(ij|ij)$ integrals (Table I) are those evaluated from the respective atomic terms by Hanazaki and Nagakura [3], whereas two-center Coulomb integrals γ_{AB} were approximated by the relation

$$\gamma_{AB} = \gamma_{AB}^{\mathrm{th}} - V_{AB}^{\mathrm{corr}}, \tag{2}$$

TABLE I

Atomic parameters [eV] used in our calculations [3]

Parameter	H	C	N	O
U_{ss}	−13.605	−50.15	−73.98	−99.01
U_{pp}		−38.94	−59.54	−79.65
$(ss\|ss)$		11.88	13.85	15.49
$(pp\|pp)$		10.49	13.27	14.95
$(ss\|\bar{p}\bar{p})$		11.00	13.22	14.70
$(pp\|\bar{p}\bar{p})$		9.24	11.51	12.70
$(sp\|sp)$		2.56	3.29	3.84
$(p\bar{p}\|p\bar{p})$		0.63	0.91	1.08

where $\gamma_{AB}^{\mathrm{th}}$ is the $(S_AS_A|S_BS_B)$ Coulomb integral calculated with Slater type orbitals. V_{AB}^{corr} denotes here a "correlation energy" of the $A-B$ bond evaluated as the arithmetic mean

$$V_{AB}^{\mathrm{corr}} = \tfrac{1}{2}S_{AB}(V_{AA}^{\mathrm{corr}} + V_{BB}^{\mathrm{corr}}) \tag{3}$$

of "correlation energies" of the valence electron pairs of the A and B atoms times the overlap integral between ns atomic orbitals centered on A and B.

V_{AA}^{corr} and V_{BB}^{corr} were calculated from the relationship

$$V_{AA}^{\mathrm{corr}} = \gamma_{AA}^{\mathrm{th}} - \gamma_{AA} \tag{4}$$

with the Coulomb integral γ_{AA} evaluated from the extended Sichel and Whitehead [4] equation

$$\gamma_{AA} = 1/16[(ss|ss) + 6(ss|pp) + 3(pp|pp) + 6(pp|\bar{p}\bar{p}) - 3(sp|sp) - 3(p\bar{p}|p\bar{p})]. \tag{5}$$

A crucial point in every semiempirical all-valence scheme is the approximation of the H_{ij} resonance integral. A theoretical [5] relation for the H_{ij} integral appearing in the Pariser-Parr-Pople method made it possible to reproduce with good accuracy the electronic states of a number of aromatic systems [6]. Recently, relations for resonance integrals of the all-valence level have been derived by Linderberg and Seamans [7] using the Heisenberg equation of motion and the second quantization formalism. Therefore, it seemed interesting to investigate the role these relations at the semiempirical all-valence level in accordance with the possibility of eliminating empirical parameters occurring in the interatomic matrix elements.

Under these circumstances the non-diagonal core Hamiltonian matrix elements were calculated from the relationship

$$H_{ij} = K\beta_{ij} \tag{6}$$

with the constant parameter $K = 1.2$ fitted only to give -3.0 eV for the $H_{\pi\pi}$ integral of the ethylene molecule. It should be noted that reasonable results are also obtained when $H_{ij} = \beta_{ij}$. According to the Linderberg-Seamans theory [7] β_{ij} integrals (in atomic units) were evaluated from the following relations

$$\beta_{ss}^{HA} = 1/R\,\frac{dS_{ss}}{dR}, \quad \beta_{s\sigma}^{AB} = -1/\mu_A\,\frac{dS_{\pi\pi}}{dR}, \quad \beta_{s\sigma}^{HA} = \frac{d(S_{s\sigma}/R)}{dR}, \quad \beta_{\sigma s}^{AB} = 1/\mu_B\,\frac{dS_{\pi\pi}}{dR},$$

$$\beta_{ss}^{AB} = -\frac{S_{\pi\pi}}{\mu_A\mu_B}, \quad \beta_{\sigma\sigma}^{AB} = \frac{d^2S_{\pi\pi}}{dR^2}, \quad \beta_{\pi\pi}^{AB} = 1/R\,\frac{dS_{\pi\pi}}{dR}, \tag{7}$$

where the S_{ij} denotes the respective overlap integral, and the μ_A, μ_B are the transition moment integrals given by

$$\mu_k = \frac{n_k+1/2}{\sqrt{3}\,\xi_k} \tag{8}$$

with the Slater orbital exponent ξ_k. The indispensable expressions for the first and second derivative of the overlap integral are

$$\frac{dS}{dR} = 1/R[aS(n_A, n_B)-b(n_A)S(n_A+1, n_B)-b(n_B)S(n_A, n_B+1)], \tag{9}$$

$$\frac{d^2S}{dR^2} = 1/R^2\{a(a-1)S(n_A, n_B)+2[b(n_A)b(n_B)S(n_A+1, n_B+1)-ab(n_A)S(n_A+1, n_B)$$
$$-ab(n_B)S(n_A, n_B+1)]+b(n_A)c(n_A)S(n_A+2, n_B)+b(n_B)c(n_B)S(n_A, n_B+2)\}, \tag{10}$$

where

$$a = n_A+n_B+1, \quad b(n_k) = [(n_k+1)\,(n_k+1/2)]^{1/2}, \quad c(n_k) = [(n_k+3/2)\,(n_k+2)]^{1/2},$$

and n_k denotes the principal atomic quantum number.

The total energy has been evaluated as the sum of the standard electronic term and the internuclear repulsion energy

$$E^{\text{core}} = \sum_{A}\sum_{B>A}\left[Z_A Z_B\left(V_{AB}^{\text{th}}+V_{BA}^{\text{th}}-\gamma_{AB}^{\text{th}}\right)\gamma_{AB}/\gamma_{AB}^{\text{th}}\right], \tag{11}$$

where γ_{AB} is the two-center Coulomb repulsion integral defined by (2), and V_{AB}^{th}, V_{BA}^{th} denote the respective theoretical nuclear attraction integrals.

3. *Results and discussion*

In a number of numerical calculations performed for chemically different molecular systems, generally good agreement of theoretical ground state as well as excited state properties with experimental results has been found. The first ionization energies are within the limits of an experimental error and the type of higher ionization energies is also correctly reproduced. The dipole moments, evaluated as a sum of the point charge distribution and hybridization terms, (Table II), including their orientation, are given in our approach with the accuracy similar to the CNDO/INDO methods [1].

TABLE II

Theoretical and experimental dipole moments [D] for some representative systems

Molecule	Calc.	Exp.	Molecule	Calc.	Exp.
Water	2.17	1.88[a]	Pyrrole	2.00	1.80[a]
Ammonia	2.16	1.47[a]	Imidazole	4.19	4.02[b]
Formaldehyde	3.14	2.34[a]	Pyridine	2.15	2.15[a]
Hydrogen cyanide	2.85	2.99[a]	Pyrazole	2.45	2.21[c]

[a] R. D. Brown, F. R. Burden, *Theor. Chim. Acta* **12**, 95 (1968).

[b] O. A. Osipov, A. M. Simonov, V. I. Minkin, A. D. Garnoskii, *Dokl. Akad. Nauk SSSR* **137**, 1374 (1961).

[c] W. H. Kirchhof, *J. Am. Chem. Soc.* **89**, 1312 (1967).

Electronically excited states for different systems have been calculated with singly excited configurations taken into account (Table III). The orders and excitation energies of the first and third $\pi-\pi^*$ electronic states are in good agreement with observations but the second electronic transitions appear at slightly higher energies than the relevant experimental results. In all cases the S_1-T_1 splitting is also in satisfactory agreement with experimental values, however, the $n-\pi^*$ electronic transitions are too low by ca. 0.5 – 1.0 eV. We were able to avoid this disagreement by introducing optimized Slater orbital exponents in the SCF iterative process according to the relation $\xi = \xi^0 + kQ$ were ξ^0 denotes the orbital exponent of the neutral atom and Q is the total atomic charge. With this modification and the parameter k resulting from the Slater rules our calculation gives for the $n-\pi^*$ transitions 4.02 and 4.37 eV for formaldehyde and pyridine, respectively. No essential change in other theoretical properties has been found in this case.

TABLE III

Excitation energies ΔE [in eV] and the respective oscillator strengths f for some isolated molecules

	Calculated		Observed	
	E	f	E	f
Water				
$^1B_1(n-\sigma^*)$	7.11	0.004	7.04[a]	0.04[b]
$^1A_2(n-\sigma^*)$	9.73	0.000	9.75[b]	
Formaldehyde				
$^1A_2(n-\pi^*)$	3.51	0.000	3.52–5.39[c]	
$^1B_2(n-\sigma^*)$	6.90	0.059	7.1[c]	0.04[c]
$^1B_1(\sigma-\pi^*)$	6.98	0.006		
$^1A_1(\pi-\pi^*)$	8.26	0.155	8.0[c]	0.1[c]
$^3A_2(n-\pi^*)$	2.91		3.02[c]	
Ethylene				
$^1B_{2u}(\pi-\pi^*)$	7.41	0.425	7.6[c]	0.29[c]
$^3B_{2u}(\pi-\pi^*)$	4.38		4.6[c]	
Trans-butadiene				
$^1B_u(\pi-\pi^*)$	5.56	1.14	5.7[d]	
$^1A_g(\pi-\pi^*)$	7.48	0.000	7.25[d]	
$^3B_u(\pi-\pi^*)$	2.63		2.58[d]	
Pyridine				
$^1B_1(n-\pi^*)$	3.63	0.002	4.31[e]	0.03[f]
$^1A_2(n-\pi^*)$	4.75	0.000	5.0[e]	0.040[f]
$^1B_2(\pi-\pi^*)$	5.25	0.059		
$^1A_1(\pi-\pi^*)$	5.89	0.001	6.2[e]	0.010[f]
$^1B_2(\pi-\pi^*)$	7.32	0.945	7.15[e]	1.3[f]
$^1A_1(\pi-\pi^*)$	7.58	1.224	7.25[e]	
$^3B_1(n-\pi^*)$	2.88		3.68[d]	

[a] K. Dressler, O. Schnepp, *J. Chem. Phys.* **33**, 270 (1960).

[b] J. C. Ho, G. A. Segal, H. S. Taylor, *J. Chem. Phys.* **56**, 1520 (1972).

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[d] S. P. McGlynn, T. Azumi, M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Prentice Hall, New Jersey 1969.

[e] S. Lunnell, P. Lindner, *Phys. Scr.* **10**, 337 (1974).

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It should be noted that the proposed method makes it possible also to simulate the potential energy curves for charge-transfer and hydrogen bonded complexes as well as for charge-transfer-to-solvent addition compounds. Furthermore, within the supermolecule

TABLE IV

Equilibrium interatomic distances (R) of main atoms and heats of formation ($-\Delta H$) for representative molecular complexes calculated in this paper and obtained from ab initio studies (in parentheses)

Complex	R [Å]	$-\Delta H$ [kcal/mole]
H_2O dimer	3.00 (2.92[a])	5.53 (6.05[a])
NH_3 dimer	3.30 (3.49[c])	1.00 (2.7[b])
$[H_2OF]^-$	2.46 (2.52[c])	23.76 (22.18[c])
$[H_2OCl]^-$	2.98 (3.28[c])	16.5 (13.1[c])
$H_2O \cdot Cl_2$	3.0–3.3 (2.9[d])	0.50 (0.75[d])

[a] G. H. F. Diercksen, W. P. Kraemer, B. O. Roos, *Theor. Chim. Acta* **36**, 249 (1975).
[b] P. A. Kollman, L. C. Allen, *J. Am. Chem. Soc.* **93**, 4991 (1971).
[c] H. Kistenmacher, H. Popkie, E. Clementi, *J. Chem. Phys.* **59**, 5842 (1973).
[d] G. L. Leroy, G. Louterman-Leloup, *J. Mol. Struct.* **28**, 33 (1975).

model the above method is able to reproduce heats of formation and equilibrium geometries (Table IV) and electronic spectra of chemically different molecular complexes [8].

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