

Variable Metric Optimization of Molecular Geometry in Electronically Excited States

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The variable metric (VM) method is used to optimize molecular geometry in electronically excited states. A general expression for the first derivative of energy in the particular excited state is derived, considering configuration interaction of all singly excited configurations. A special expression for the excited states energy derivative is given for calculations with semiempirical methods of CNDO type. The geometry optimizations of a set of molecules in various excited states have been carried out by the CNDO/2 method. The results of computations have been discussed and compared with the available experimental data. A good agreement of the calculated geometries with the experimental ones has been shown in the first excited states and a relatively good agreement in the higher states, with some exceptions. Some special features of the proposed method are discussed.

Key words: Variable metric optimization

1. Introduction

The success of variable metric methods [1–4], introduced into quantum chemistry by several authors [5–8] for optimizing molecular geometry, stimulated the interest to extend the method to geometry optimization also in an arbitrary electronically excited state. Pancíř [7] optimized the molecular geometry in the first excited state using half-electron approximation [9] in the framework of CNDO/2 method. We have shown [10, 11] that the CNDO/2 method, in the original (Pople's) version [12, 13], may be successfully used to study molecular geometry in electronically excited states in a sufficiently large range of molecular types when configuration interaction is included. Gordon *et al.* [14, 15] have found optimal geometries of several alkanes and some other molecules in different excited states from INDO energy hyper-surfaces, using the method of Powell [16] (no use of derivatives).

In this communication, we report the results of our attempt to use the quadratically convergent optimization method for calculating molecular geometries of closed-shell systems in various excited states.

2. Theory

In order to derive the energy expression of the particular electronically excited state v and multiplicity n (1 or 3) we use the interaction wave function

$${}^n\Psi_v = \sum_{ik} A_{v,ik} {}^n\Phi_{ik} \quad (1)$$

where $A_{v,ik}$ are the expansion coefficients, belonging to the transitions $i \rightarrow k$ and ${}^n\Phi_{ik}$ are the corresponding singlet or triplet functions of Slater determinants.

The elements of the H' matrix constructed from the functions ${}^n\Phi_{ik}$, may be written in the form [17]

$$H'_{ik,jl} = (E_0 + \varepsilon_k - \varepsilon_i)\delta_{ij}\delta_{kl} + 2\langle il|g|kj\rangle\delta_{1n} - \langle ik|g|lj\rangle \quad (2)$$

where E_0 is the Hartree-Fock energy expression of the ground state and $\langle ik|g|lj\rangle$ and $\langle il|g|kj\rangle$ are the Coulomb and exchange integrals, respectively, formed from the molecular orbitals ψ_i, ψ_k etc. For the sake of simplicity we assume that the MO's are real. Then $\langle ik|g|lj\rangle = \int \psi_i(1)\psi_k(2)(1/r_{12})\psi_l(1)\psi_j(2) d\tau$ and δ 's are Kronecker δ 's.

The total electronic energy of the excited state v of multiplicity n may then be written in the form

$${}^nE_v = A_v^\dagger H' A_v \quad (3)$$

$$= E_0 + A_v^\dagger H A_v \quad (3a)$$

where H is the matrix with the elements $H_{ik,jl} = H'_{ik,jl} - E_0\delta_{ij}\delta_{kl}$ and A_v is the v th eigenvector.

When we express the ψ_i as the expansions of the basis functions in matrix formulation

$$\psi_i = \mathbf{c}_i^+ \boldsymbol{\phi} \quad (4)$$

with the usual meaning of the notation,¹ we may write

$$\langle ik|g|lj\rangle = \mathbf{c}_i^+ \otimes \mathbf{c}_k^+ (\boldsymbol{\phi} \otimes \boldsymbol{\phi}|g|\boldsymbol{\phi}^+ \otimes \boldsymbol{\phi}^+) \mathbf{c}_l \otimes \mathbf{c}_j \quad (5)$$

where \otimes denotes the direct product [18]. Therefore $\mathbf{c}_i^+ \otimes \mathbf{c}_k^+$ and $\mathbf{c}_l \otimes \mathbf{c}_j$ are the row and column vectors, respectively, of the dimension N^2 , when N is the number of basis functions. $(\boldsymbol{\phi} \otimes \boldsymbol{\phi}|g|\boldsymbol{\phi}^+ \otimes \boldsymbol{\phi}^+) = \mathbf{G}^B$ is the $N^2 \times N^2$ square Hermitian matrix² of two electron integrals, over the basis functions. Similarly it may be expressed $\langle il|g|kj\rangle$.

¹ In the MOLCAO theory [3] the form of the expansion $\boldsymbol{\phi}\mathbf{c}_i$ is used, i.e. $\boldsymbol{\phi}$ and \mathbf{c}_i are row and column vectors, respectively. We use the equivalent form (4) for the purpose of the further procedure.

² In this symbol of the matrix the column row ordering of the vectors indicates in what manner the elements have to be formed using the matrix multiplication rule.

Then it may be written

$$\begin{aligned} 2\langle il|g|kj\rangle\delta_{1n} - \langle ik|g|lj\rangle &= 2\mathbf{c}_i^+ \otimes \mathbf{c}_l^+ \mathbf{G}^B \mathbf{c}_k \otimes \mathbf{c}_j \delta_{1n} - \mathbf{c}_i^+ \otimes \mathbf{c}_k^+ \mathbf{G}^B \mathbf{c}_l \otimes \mathbf{c}_j \\ &= \{2\mathbf{c}_i^+ \otimes \mathbf{c}_l^+ [\mathbf{c}_k^+ \otimes \mathbf{c}_j^+ \delta_{1n} - \mathbf{c}_i^+ \otimes \mathbf{c}_k^+ [\mathbf{c}_l^+ \otimes \mathbf{c}_j^+] \mathbf{G}^B]^+\}. \end{aligned} \quad (6)$$

The brackets $[\]^+$ indicate the factors which have to be multiplied and, after the multiplication has been carried out, the resulting row vectors have to be transposed. Further, we substitute ε_k by

$$\varepsilon_k = \mathbf{c}_k^+ \mathbf{F} \mathbf{c}_k \quad (7)$$

and similarly ε_i . The Fock matrix \mathbf{F} is built up from the basis functions and \mathbf{c}_k is the k th eigenvector. Then we realize that

$$\begin{aligned} \varepsilon_k - \varepsilon_i &= \mathbf{c}_k^+ \mathbf{F} \mathbf{c}_k - \mathbf{c}_i^+ \mathbf{F} \mathbf{c}_i \\ &= (\mathbf{c}_k^+ [\mathbf{c}_k^+ - \mathbf{c}_i^+ [\mathbf{c}_i^+] \mathbf{F}]^+ \end{aligned} \quad (8)$$

where again the brackets $[\]^+$ have the same meaning as those mentioned above, we get the expression for the energy gradient component with respect to the coordinate q_x in the following form

$$\begin{aligned} \frac{\partial^n E_v}{\partial q_x} &= \frac{\partial E_0}{\partial q_x} + A_v^+ \frac{\partial}{\partial q_x} \mathbf{H} A_v \\ &= \frac{\partial E_0}{\partial q_x} + A_v^+ \left\{ \mathbf{H}^D \frac{\partial}{\partial q_x} \mathbf{F} \right\}^+ + \mathbf{H}^G \frac{\partial}{\partial q_x} \mathbf{G}^B \right\}^+ + \left(\frac{\partial}{\partial q_x} \mathbf{H}^G \right) \mathbf{G}^B \right\}^+ A_v. \end{aligned} \quad (9)$$

In (9) \mathbf{H}^D (diagonal) and \mathbf{H}^G are the supermatrices of the same order as \mathbf{H} with the elements

$$\begin{aligned} \mathbf{H}_{ik}^D &= \mathbf{c}_k^+ [\mathbf{c}_k^+ - \mathbf{c}_i^+ [\mathbf{c}_i^+] \\ \mathbf{H}_{ik,jl}^G &= 2\mathbf{c}_i^+ \otimes \mathbf{c}_l^+ [\mathbf{c}_k^+ \otimes \mathbf{c}_j^+ \delta_{1n} - \mathbf{c}_i^+ \otimes \mathbf{c}_k^+ [\mathbf{c}_l^+ \otimes \mathbf{c}_j^+] \end{aligned} \quad (9a)$$

and their multiplication by the factors, which are matrices, has to be understood as the multiplication of each element of the respective supermatrix by these factors (directly). The form of the gradient component in (9) is convenient since the parts containing variation parameters are separated from the parts containing integrals. The supermatrix \mathbf{H}^D composed of the Fock matrix eigenvectors may be kept constant in the first derivative of energy [5, 19, 20] because $\partial\varepsilon/\partial c = 0$. The supermatrix \mathbf{H}^G , also composed of the eigenvectors of the same matrix, must be differentiated. The matrix \mathbf{F} , besides the integrals, contains the density matrix \mathbf{D} . Due to the requirement that \mathbf{D} must be idempotent [5], \mathbf{D} in \mathbf{F} must also be differentiated. The same holds for the derivative of the ground state energy E_0 which as the explicit formula is given in [5]. Obviously, in this formula the derivative of the \mathbf{F} matrix is also included. Another form of $\partial E_0/\partial q_x$ is given in [21, 22].

It may be assumed that the expression (9) will be useful in some minimization problems in excited states although only singly excited configurations in the CI wave function are included. This is established by some *ab initio* calculations of molecular geometry in electronically excited states in which only singly excited configurations also are used [23, 24].

3. Method of Calculation

We use all singly excited configurations in a CI treatment. With respect to the ZDO approximation, the two-electron integrals in the CI matrix may be written in the explicit form

$$\langle ik|g|lj\rangle = \sum_{\mu,\nu} c_{i\mu}c_{l\mu}c_{k\nu}c_{j\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu}^A c_{i\mu}c_{l\mu}c_{k\nu}c_{j\nu}\gamma_{AA} + \sum_{\mu,\nu}^{AB} c_{i\mu}c_{l\mu}c_{k\nu}c_{j\nu}\gamma_{AB} \quad (10)$$

where $\gamma_{\mu\nu}$, γ_{AA} and γ_{AB} have the well-known meaning of repulsion integrals [12], the superscripts *A* and *AB* on the sums denote one- and two-atomic parts and $c_{i\mu}, \dots$ are the respective components of the Fock matrix eigenvectors.

We substitute the orbital energies $\varepsilon_k, \varepsilon_i$ which occur in the diagonal elements of the CI matrix, by the expressions

$$\varepsilon_k = \sum_{\mu,\nu} c_{k\mu}c_{k\nu}F_{\mu\nu} = \sum_{\mu} c_{k\mu}^2 F_{\mu\mu} + \sum_{\substack{\mu,\nu \\ (\mu \neq \nu)}} c_{k\mu}c_{k\nu}F_{\mu\nu}. \quad (11)$$

We use the Fock matrix elements $F_{\mu\mu}, F_{\mu\nu}$ according to Pople [13]. Then, introducing the expressions (10) and (11) into the CI matrix (3) we get the first derivative of energy ${}^n E_v$, in the framework of the CNDO type methods, in the following form:

$$\begin{aligned} \frac{\partial {}^n E_v}{\partial q_x} &= \frac{\partial E'_0}{\partial q_x} + \sum_{ik,jl} C_{v,ik} C_{v,jl} \\ &\cdot \left\{ \left[\sum_{\mu} (c_{k\mu}^2 - c_{i\mu}^2) \cdot \sum_{B(\neq A)} (P_{BB} - Z_B) \frac{\partial \gamma_{AB}}{\partial q_x} + \sum_{\substack{\mu,\nu \\ (\mu \neq \nu)}} (c_{i\mu}c_{k\nu} - c_{i\mu}c_{i\nu}) \right. \right. \\ &\quad \cdot \left. \left(\beta_{AB}^0 \frac{\partial S_{\mu\nu}}{\partial q_x} - \frac{1}{2} P_{\mu\nu} \frac{\partial \gamma_{AB}}{\partial q_x} \right) \right] \delta_{ij} \delta_{kl} \\ &\quad \left. + \sum_{\mu,\nu}^{AB} [(2c_{i\mu}c_{k\mu}c_{l\nu}c_{j\nu})\delta_{1n} - c_{i\mu}c_{j\mu}c_{k\nu}c_{l\nu}] \frac{\partial \gamma_{AB}}{\partial q_x} \right\}. \quad (12) \end{aligned}$$

The notation of the quantities in (12) is well known and is given in the cited paper [12]. The term $\partial E_0/\partial q_x$ in the CNDO type approximation was published by Pančič [7]. The prime over E_0 means the total energy of the molecule, i.e. the sum of the electronic and repulsion energy of the cores. The terms $(\partial {}^n E_v/\partial c) \cdot (\partial c/\partial q_x)$ are very small and therefore neglected in (12).

We used the CNDO/2 method with standard parametrization [13] and we calculated the derivatives of $\gamma_{\mu\nu}$ integrals from the integral expansions used in the same method. We took over the overlap integrals as well as their derivatives from McIver and Komornicki [25]. The convergence of SCF calculations was ensured by the procedure of Flurry [26].

The optimization procedure is based on iteration steps in which the coordinate vector \mathbf{q} is changed according to the formula

$$\mathbf{q}_i = \mathbf{q}_{i-1} - \alpha \mathbf{H}_{i-1}^{-1} \mathbf{g}_{i-1} \quad (13)$$

where α is a scalar so chosen that the term $E(\mathbf{q}_{i-1} + \alpha \mathbf{H}_i^{-1} \mathbf{g}_{i-1})$ is minimal, \mathbf{H} is the Hessian matrix and \mathbf{g} the energy gradient vector. The inverse \mathbf{H}^{-1} was calculated according to the formula [3].

$$\begin{aligned} \mathbf{H}_i^{-1} &= \mathbf{H}_{i-1}^{-1} + (\mathbf{p}^+ \mathbf{p} - \mathbf{p}^+ \mathbf{z} - \mathbf{z}^+ \mathbf{p} + \mathbf{z}^+ \mathbf{z}) / (c_1 - c_2) \\ \mathbf{p} &= \mathbf{q}_i - \mathbf{q}_{i-1}, \quad \mathbf{z} = (\mathbf{H}_{i-1}^{-1})^+ \mathbf{y}, \quad c_1 = \mathbf{y}^+ \mathbf{p}, \quad c_2 = \mathbf{y}^+ \mathbf{z} \\ \mathbf{y} &= \mathbf{g}_i - \mathbf{g}_{i-1} \end{aligned} \quad (14)$$

starting from the unit matrix. Further, the matrix was successively formed as the calculation proceeded. To follow the way to the energy minimum we used the simplified technique, without double iteration [6], choosing $\alpha = 1$, and this value was only diminished when the energy increased (the overstep). For the other parameters [4, 27] the values $\varepsilon = 10^{-6}$, $\theta = 10^{-3}$, $\gamma = 10^{-8}$ were used.

The whole procedure consists of the following successive steps: 1) Full SCF calculation on the imposed molecular geometry of the respective species and configuration interaction treatment, including all singly excited configurations, 2) calculation of the gradient vector for the chosen state v and multiplicity n , 3) calculation of the Hessian matrix inverse, 4) calculation of the new coordinates. The process is then repeated until the gradient vector components decrease below the accuracy stated, or until the bond lengths (in Å) do not change on the third decimal place. Therefore, the accuracy of the calculated bond lengths introduced in Table 1 is ± 0.0005 Å and in the cases of a worse convergence in the vicinity of the limit, otherwise seldom in our calculations (e.g. formaldehyde) about ± 0.005 Å. The limit for the gradient norm value was 0.001 (in a.u.); after this value had been achieved the calculation was stopped.

Before we discuss our experiences with the proposed method and the special features of VM calculation in the range of excited states, we have to mention some significant properties of our gradient. According to the Walsh rules [28] the strain in a molecule, caused by electronic excitation, is relaxed by the change of symmetry. As a consequence of this fact the potential energy hypersurface will be changed during this relaxation process. Therefore, our gradient in VM calculation leads to the excited species which possess the geometry belonging to a symmetry group different from that of the ground state. However, this property is not general and in some cases the symmetry is conserved, which is dependent on the properties of the energy hypersurface in the particular state.

4. Results and Discussion

In order to verify the suitability of the proposed optimization method, we chose a set of species (Table 1) which represent different structural types of small molecules. We performed the geometry optimizations in the first and second excited singlet states and some calculations concerning the higher singlet and the lowest triplet states. The initial geometries were always either those of the ground state, or any which sufficiently differed from the expected ones. The results have then been compared with the experimental ones [29]. Unfortunately, there is a very small amount of experimental data for the higher excited states and for triplet states.

Table 1

Species	Excited state	Geometry		Experimental	E [eV] ^a	Transition energy [eV]		
		Symmetry group and character of state				Calculated	Exp.	
		Starting	Calculated					vert. ^b
NH ₃	Singlet: 1st	D_{3h}	D_{3h}, A_2'' $R_{NH} = 1.101^c$	D_{3h}, A_2'' $R_{NH} = 1.08$	-370.8223	6.01	7.03	5.72
		C_{3v}	D_{3h}, A_2'' $R_{NH} = 1.104$		0.0033	6.01	7.04	
	2nd	D_{3h}	C_{2v}, B_1 $R_{NH'} = 1.178, R_{NH''} = 1.063$ $\angle H'NH'' = 107^\circ, \angle H''NH'' = 146^\circ$	D_{3h}, E'' $R_{NH} = 1.027$	-368.9537	7.23	8.90	7.34
		C_{3v}	C_{2v}, B_2 $R_{NH'} = 1.053, R_{NH''} = 1.122$ $\angle H'NH'' = 131.6^\circ, \angle H''NH'' = 94^\circ$		0.0510	7.50	8.95	
	3rd	D_{3h}	D_{3h}, A_2'' $R_{NH} = 1.096$	D_{3h}, A_1'	-368.4176	8.52	9.44	8.64
		D_{3h}	C_s $R_{NH'} = 1.146, R_{NH''} = 1.126, R_{NH'''} = 1.135$ $\angle H'NH'' = 153.5^\circ, \angle H''NH'' = 73.7^\circ$	D_{3h}	-365.3948	9.21	12.46	
	5th	D_{3h}	C_s $R_{NH'} = 1.139, R_{NH''} = 1.132, R_{NH'''} = 1.121^d$	D_{3h}	-362.5012	13.91	15.35	
		D_{3h}	D_{3h} $R_{NH} = 1.126$		-360.7553	15.74	17.10	
	7th	D_{3h}	C_s $R_{NH'} = 1.110, R_{NH''} = 1.133, R_{NH'''} = 1.122^d$		-359.4009	16.53	18.45	
		D_{3h}	C_s $R_{NH'} = 1.127, R_{NH''} = 1.126, R_{NH'''} = 1.119^d$		-359.0710	17.46	18.78	
	9th	D_{3h}	D_{3h} $R_{NH} = 1.109$		-357.1780	19.59	20.68	

HCN	Singlet: 1st	C_s, A'' $R_{CN} = 1.260, R_{CH} = 1.127$ $\angle HCN = 133^\circ$	-513.5037	5.94	7.65	6.48
		C_s, A'' $R_{CN} = 1.284$ $R_{CH} = 1.146$ $\angle HCN = 132.5^\circ$	0.4285	5.87	8.07	
2nd	$C_{\infty v}, \Sigma^+$ $R_{CN} = 1.294, R_{CH} = 1.089$ C_s, A'' $R_{CN} = 1.288, R_{CH} = 1.148$ $\angle HCN = 128.2^\circ$	-512.5494	7.19	8.60	6.77*	
	C_s, A'' $R_{CN} = 1.334$ $R_{CH} = 1.14$ $\angle HCN = 114.5^\circ$	-513.1004	5.64	8.05		
3rd	C_s, A'' $R_{CN} = 1.259, R_{CH} = 1.142$ $\angle HCN = 134.1^\circ$	0.1578	6.51	8.21		
	$C_{\infty v}, \Sigma^+$ $R_{CN} = 1.294, R_{CH} = 1.089$ $\angle HCN = 180^\circ$	0.5510	7.19	8.60		
4th	C_s $R_{CN} = 1.290, R_{CH} = 1.077$ $\angle HCN = 124^\circ$	-511.6939	9.17	9.46	8.13	
	$C_{\infty v}, \Sigma^+$ $R_{CN} = 1.294, R_{CH} = 1.089$ $\angle HCN = 180^\circ$	-512.5490	9.17	8.60		
10th	C_s, A' $R_{CN} = 1.236, R_{CH} = 1.161$ $\angle HCN = 139.3^\circ$	-510.1796	9.67	10.98	8.88	
	$C_{\infty v}$ $R_{CN} = 1.281, R_{CH} = 1.111$ $\angle HCN = 180^\circ$	-502.9005	17.10	18.25		

continued

Table 1—continued

Species	Excited state	Geometry Symmetry group and character of state		E [eV] ^a	Transition energy [eV]	
		Starting	Calculated		Calculated	Exp.
HCN	Singlet: 20th	C_s		-475.1260	42.36	46.02
		\times HCN = 140°	$C_{s, A'}$ $R_{CN} = 1.250, R_{CH} = 1.136$ \times HCN = 176.7°			
HNO	Singlet: 1st	C_s		-834.2907	1.82	2.01
		\times HNO = 140°	$C_{s, A''}$ $R_{NO} = 1.187, R_{NH} = 1.076$ \times HNO = 123.1°			
			$C_{s, A''}$ $R_{NO} = 1.241$ $R_{NH} = 1.036$ \times HNO = 116.3°			
	2nd	C_s		0.0011	1.82	2.01
		(Ground State. Geom.)	$C_{s, A''}$ $R_{NO} = 1.187, R_{NH} = 1.076$ \times HNO = 123.7°			
	10th	C_s		-828.6390	7.25	7.66
		C_s	$C_{s, A''}$ $R_{NO} = 1.233, R_{NH} = 1.087$ \times HNO = 103.1°			
		C_s		-819.0479	16.74	17.25
		C_s	$R_{NO} = 1.220, R_{NH} = 1.135$ \times HNO = 97.9°			

CH ₂	Singlet: 1st	C _{2v}	C _{2v} , B ₁	-220.0470	0.80	1.563	0.92 ^f
			R _{CH} = 1.095				
			∠HCH = 142.8°				
	2nd	C _{2v}	D _{∞h} , Σ _g ⁻	-214.6703	4.82	6.94	
			R _{CH} = 1.161				
			∠HCH = 180°				
	9th	C _{2v}	C _s	-196.0493	23.46	25.56	
			R _{CH'} = 1.276, R _{CH''} = 1.314				
			∠H'CH'' = 99.5°				
HCF	Singlet: 1st	C _s	C _s , A''	-955.2717	1.91	2.51	2.14
			R _{CH} = 1.104, R _{CF} = 1.290				
			∠HCF = 131°				
	2nd	C _s	C _s , A'	-951.3710	2.75	6.42	
			R _{CH} = 1.265, R _{CF} = 1.276				
			∠HCF = 153.6°				
CF ₂	Singlet: 1st	C _{2v}	C _{2v} , B ₁	-1689.8694	3.61	4.17	4.67
			∠FCF = 120°				
			R _{CF} = 1.299, ∠FCF = 123.7°				
	2nd	C _{2v}	C _{2v} , B ₁	0.0994	2.92	4.27	
			∠FCF = 150°				
			R _{CF} = 1.299, ∠FCF = 134.8°				
CO ₂	Singlet: 1st	C _{2v}	C _{2v} , B ₂	-1181.5277	3.62	5.78	
			R _{CO} = 1.267, ∠OCO = 125.4°				
			R _{CO} = 1.246				
			∠OCO = 122° ± 2°				

continued

Table 1—continued

Species	Excited state	Geometry Symmetry group and character of state		E [eV] ^a	Transition energy [eV]	
		Starting	Calculated		Experimental	Calculated
CH ₄	Singlet: 1st	D_{4h}	D_{4h}, B_{2u} $R_{CH} = 1.143$	-266.5002	0.41	8.7
		T_d	C_{3v}, A_1 $R_{CH'} = 1.225, R_{CH''} = 1.141^*$ $\angle H'CH'' = 82^\circ$	4.3811	10.22	13.08
C ₂ H ₂	Singlet: 1st	C_{2v}	C_{2v}, B_1 $R_{CC} = 1.299, R_{CH} = 1.118$ $\angle CCH = 152^\circ$	-408.0003	7.28	9.44
		C_{2h}	C_{2h}, A_u $R_{CC} = 1.335, R_{CH} = 1.108$ $\angle CCH = 131.3^\circ$	0.0056	5.99	9.45
		$D_{\infty h}, \Sigma^+$	C_{2h}, A_u $R_{CC} = 1.388$ $R_{CH} = 1.058$ $\angle CCH = 120^\circ$			5.23
C ₂ H ₄	Singlet: 1st	$D_{\infty h}$	$R_{CC} = 1.322, R_{CH} = 1.090$ $\angle CCH = 180^\circ$	0.2571	8.72	9.70
		C_{2h}	C_{2h} $R_{CC} = 1.318, R_{CH} = 1.099$ $\angle CCH = 153.8^\circ$	-407.2775	8.31	10.16
	2nd				8.31	10.16
						8.15

H ₂ CO	Singlet:							
	1st	C _s	C _s , A'' R _{CO} = 1.267, R _{CH} = 1.138 ∠α ^b = 36.5°, ∠HCH = 99.6°	-725.7640	3.41	4.36	3.49	C _s , A'' R _{CO} = 1.312 R _{CH} = 1.093 ∠HCH = 119° ∠α = 31° ^c
	2nd	C _{2v}	C _{2v} , B ₁ R _{CO} = 1.303, R _{CH} = 1.113 ∠HCH = 84°	-721.5616	8.11	8.55		
	Triplet:							
	1st	C _s	C _s , A'' R _{CO} = 1.263, R _{CH} = 1.149 ∠α = 50.2°	-726.0114	2.53	3.12	C _s , A'' R _{CO} = 1.312 ∠α = 35°	

^a For the higher values only the differences from the lowest are given.

^b Emission.

^c The bond lengths are given in Å.

^d The angles HNH are slightly different from 120°.

^e Refers to DCN.

^f Ref. [40].

^g Three equivalent CH bonds.

^h The angle between C=O and the plane HCN.

ⁱ Ref. [47].

Regarding the results concerning the first singlet states of all species studied (Table 1), the geometry parameters agree quite well with the experimental data measured by Herzberg *et al.* [29]. The differences in the bond lengths are in the second decimal places. Acceptable values were obtained also for the valence angles. The differences from the experimental values amount to several degrees. Comparing the calculated and experimental adiabatic excitation energies, introduced in Table 1, it is seen that the differences between them amount to about 10–25% related to the experimental ones (most of them amount to about 20%). Besides these values, we give in Table 1 the corresponding emission vertical energies, i.e. the differences between the excited states energy minima and the corresponding Franck–Condon ground states. Namely, these values are very close to the experimental adiabatic excitation energies and the differences amount to about 2–10% with respect to the latter (except carbenes and the triplet states). We think that in spite of the different physical meaning of these two quantities, the emission vertical energies would be a good measure of the experimental adiabatic values and the calculation by this method would represent a manner of providing the right adiabatic values.

The geometry of the ammonia molecule in the first excited state is of the symmetry D_{3h} , i.e. planar. We obtained two forms of the same symmetry D_{3h} whether we started from the planar form or from the pyramidal ground state geometry. These two forms differ only very slightly in energy and in the bond lengths. In general it is a special feature of the method that, also in the higher states, there are several local minima which differ slightly in energy, and in most cases the starting geometry has been shown to be decisive for this phenomenon³. It would be a consequence of the approximative character of the CNDO/2 method, but we assume that it corresponds to several transitions of a lower probability, by which the most probable transition is always accompanied. We calculated also the methane molecule. This molecule is isoelectronic with ammonia and therefore we could expect it would be planar at least in the first excited state. However, there is no experimental evidence for the existence of the planar form. Herzberg did not determine the geometry in the excited state since the band in the far ultraviolet is too broad, the transitions are of Rydberg type and moreover above the lowest dissociation limit [29]. The more recent measurements by Sandorfy *et al.* [31] show the allowed band at 9.705 eV and by Koch and Skibowski [32] two bands at 9.6 and 10.4 eV. Barring this, the calculations [33] indicate the only moderate partition of Rydberg states in the first excited state of methane. In calculations on the semiempirical level by RCNDO method in which Rydberg orbitals are included, Salahub and Sandorfy [33] considered the vertical transitions in the methane molecule and obtained for the first allowed bands the energies 9.49 and 12.88 eV, respectively. Montagnani *et al.* [34] obtained for these transitions by *ab initio* calculations the values 9.73 and 10.7 eV. Hoffmann [35] assumes the planar form as the most stable in the first excited state. Gordon *et al.* [14] calculated some optimal forms of methane in several excited states and they did not consider the planar form. The result of our calculation is

³ We only assume that all these stationary points are relative minima. We did not examine in more detail their actual nature.

also here very interesting. When we started from the planar form of the symmetry D_{4h} we obtained the optimized form of the same symmetry. But starting from the tetrahedral form, we obtained the “umbrella” form of the C_{3v} symmetry. The emission vertical energy of the latter form is 10.22 eV, which is close to both the already mentioned measured and calculated vertical excitation energies of methane. This resemblance is striking even when we realize the different physical meaning of the two quantities. We optimized HCN using three initial geometries. Thus starting from C_s symmetry with the angle $\angle\text{HCN} = 140^\circ$ we obtained the form of the same symmetry and an excellent agreement with the experimental data. However, starting from the geometry with $\angle\text{HCN} = 110^\circ$, there results the form with nearly the same bond angle but with different bond lengths and especially with the lower energy of about 0.5 eV. When we started from the $C_{\infty v}$ symmetry we obtained the species of the same symmetry but with a higher energy about 1 eV. Here the symmetry was conserved. For HNO we obtained practically the same geometry, whether we started from the ground state or from any different geometry with the changed valence angle. The calculation of formaldehyde in the first excited singlet state conserves the symmetry. Therefore, the bent form which is lower in energy had to be used as the starting one. Our calculated emission vertical energy of 3.41 is again quite close to the experimental adiabatic [29] value of 3.49 and also, obviously as a special case, to the exactly calculated [36] vertical value of 3.43 eV. The bending angle calculated by us is larger by 6° while the INDO value [14] is smaller by 10° than the experimental one [29]. In acetylene the symmetry is also conserved and thus the three possible geometries have been taken as initial ones. The C_{2v} form arises as the most stable, while the C_{2h} form for which experimental data are available, is higher in the total energy but with the lower excitation energy. The differences between the calculated values and experimental ones are acceptable. The highest in energy is the linear form. The calculated geometry of carbene in the first excited singlet state 1B_1 agrees quite well with the experimental one. The CO_2 molecule is bent in the first excited state. Since the symmetry is conserved in this case, we optimized separately the bent and linear forms. The calculated geometry of the bent form agrees quite well with the experimental one. However, we must note that the separation between the hypersurfaces of both bent and linear forms is very small in the surroundings of equilibrium geometry and consequently the convergence of VM calculation is not quite good in this region. Therefore, the accuracy of the bond length is only 0.01 Å. The linear form is higher in energy, but near the limit the energy difference becomes small. Also the bond length difference of the two forms is small.

We can state that the Walsh rules hold in all calculated molecules. All the other geometries of the species which are not in agreement with Walsh rules are higher in energy. Also the characters of the state agree quite well with the experimental ones although the experimental characters of the state include the Rydberg states.

For the higher excited states there are experimental data only for ammonia, cyanohydrogen and partially for acetylene. Thus Herzberg [29] gives the whole geometry for the second excited state of ammonia and only symmetries for the third, fourth and fifth excited states. It should be noted that our results for the second excited

state do not agree with the experimental ones. For ammonia we obtained two planar forms of the symmetry C_{2v} with a small difference in energy but with quite different bond lengths. Again, the form resulting from the pyramidal initial geometry is higher in energy. Consequently also the character of state disagrees. On the other hand for the third excited state we obtained the form of the symmetry D_{3h} which agrees with the Herzberg statement. However, for the fourth and fifth states we obtained planar forms but with the symmetries C_s even when we started from D_{3h} form. This again disagrees with the experimental D_{3h} symmetry. For the second excited state of HCN, we obtained quite good agreement with the experimental bond lengths, the angle of the bent form is greater by ca. 14° than the experimental one. For the second state, we obtained two further forms. One of these differs only slightly from the optimal one. The second, starting from the linear form, results as the linear. In these cases the symmetry was again conserved. There are partial experimental data also for the third excited state of HCN [29]. The calculated CH bond length and valence angle differ slightly from the experimental ones (lack of experimental CN bond length). However, there is another form with a lower energy, but linear, although we started from the bent form also in this case. For the fourth excited state of HCN only the experimental excitation energy is available. There is a large difference between this value and the calculated emission vertical energy. However, since the comparison of the geometry data is not possible and the fourth state has the same character as the third, we assume that the observed energy may be assigned to one of the local minima of the third state, the calculated energy value of which is close to the experimental one. Also for the second excited state of acetylene only the experimental excitation energy is given. In this case, our emission energy is again close to the experimental adiabatic one. In the first excited triplet state, we only calculated carbene, formaldehyde and difluorocarbene. However, the carbene first excited triplet arises by the CNDO/2 method degenerated with the first excited singlet. Therefore we used the INDO method for which the gradient is the same. By INDO the first excited triplet is lower than the singlet ground state, with the bent structure and character 3B_1 , which is in agreement with the observations [37–40] and exact calculations [41–42]. For $\angle\text{HCN}$ and R_{CH} we obtained 140.6° and 1.098 \AA which is close to the observed [37–39, 43] $136 \pm 5^\circ$, 1.05 \AA and calculated [41, 42, 44] values. However, also by the INDO method we get the first excited triplet 3B_1 degenerated with the excited singlet 1B_1 . Similarly, by the CNDO/2 method we get the first excited triplet of difluorocarbene degenerated with the first excited singlet 1B_1 . The calculated data for the triplet state of formaldehyde are quite satisfactory, the CO bond length agrees quite well with the experimental one (experimental CH bond lengths are not given). The deviation angle of the CO group from the plane is by 15° greater than the measured one.

We also carried out some calculations in the highest singlet excited states in order to prove the convergence of the method. Thus in ammonia we calculated the ninth state and at the cyanohydrogen the twentieth. We can state that the convergence of the method also in these states was relatively good and the equilibrium geometry was achieved. However, the value of the gradient norm was of the order 10^{-1} even when the bond lengths were already stabilized to the third decimal places. Obviously,

this is due to a more complicated form of the energy hypersurface in the higher states and its sharper curvature in the surroundings of the equilibrium geometry.

It seems to be necessary to discuss still some general features of the full geometry optimization procedure. Originally in our procedure we used the integrals of Roothaan [45, 46] and their derivatives used in the procedure of Pancíř [7]. However, we must state that, in spite of our good experience with the Pancíř program DERIVAL, which we used for optimizations of ground state geometries and conformations, the Roothaan integrals and their derivatives used in his program, have been shown as not suitable for optimization of excited state geometries. With these integrals, we did not obtain correct bond lengths (e.g. in acetylene 1.15 Å). Only when we used the expansions of the integrals used in the original Pople's version of the CNDO/2 method, which are slightly modified by fitting on bond lengths (option for cut-off of the series), we obtained the agreement with the experimental bond lengths. The program was written in FORTRAN IV language and the calculations were performed by the computer Siemens 4004.

We also use a similar procedure as in the present paper, suitable for open shells, for geometry optimization of radicals in excited states. The work is now in a state of elaboration.

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References

1. Davidon, W. C.: Variable metric method for minimization, A.E.C. Research and Development Report ANL 5990 (Rev) (1959)
2. Fletcher, R., Powell, M. J. D.: *Comp. J.* **6**, 163 (1963)
3. Murtagh, B. A., Sargent, R. W. H.: A constrained minimization method with quadratic convergence, Joint Conference on Optimization. Univ. of Keele, March 1968
4. Murtagh, B. A., Sargent, R. W. H.: *Computer J.* **13**, 185 (1970)
5. Pulay, P.: *Mol. Phys.* **17**, 197 (1969)
6. McIver, J. W., Jr., Komornicki, A.: *Chem. Phys. Letters* **10**, 303 (1971)
7. Pancíř, J.: *Theoret. Chim. Acta (Berl.)* **29**, 21 (1973)
8. Pulay, P., Török, F.: *Mol. Phys.* **25**, 1153 (1973)
9. Ellison, F. O., Matheu, F. M.: *Chem. Phys. Letters* **10**, 322 (1971)
10. Zahradník, P., Leška, J.: *Chem. Phys. Letters* **41**, 293 (1976)
11. Zahradník, P., Leška, J.: *Coll. Czech. Chem. Commun.* **42**, 2060 (1977)
12. Pople, J. A., Santry, D. P., Segal, G. A.: *J. Chem. Phys.* **43**, 129 (1965)
13. Pople, J. A., Segal, G. A.: *J. Chem. Phys.* **44**, 3289 (1966)
14. Saatzer, P. M., Koob, R. D., Gordon, M. S.: *J. Chem. Soc. Faraday Trans. II* **6**, 829 (1977)
15. Gordon, M. S.: *Chem. Phys. Letters* **37**, 593 (1976)
16. Pople, J. A.: QCPE, Program No. 60
17. Pople, J. A.: *Proc. Phys. Soc. A* **68**, 81 (1955)
18. Roothaan, C. C. J.: *Rev. Mod. Phys.* **23**, 69 (1951)
19. Hellmann, J.: *Einführung in die Quantenchemie*. Leipzig: Franz Deulicke 1937
20. Feynman, R. P.: *Phys. Rev.* **56**, 340 (1939)
21. Geratt, J., Mills, I. M.: *J. Chem. Phys.* **49**, 1719 (1968)
22. Moccia, R.: *Theoret. Chim. Acta (Berl.)* **8**, 8 (1967)

23. Del Bene, J. E.: *J. Am. Chem. Soc.* **3713** (1972)
24. Ditchfield, R., Del Bene, J. E., Pople, J. A.: *J. Am. Chem. Soc.* **94**, 4806 (1972)
25. McIver, J. W. Jr., Komornicki, A.: program received from the authors
26. Howland, J. C., Flurry, K. L.: *Theoret. Chim. Acta (Berl.)* **26**, 157, (1972)
27. Pancíř, J.: *Coll. Czech. Chem. Commun.* **40**, 2726 (1975)
28. Walsh, A. D.: *J. Chem. Soc.* **1953**, 2260, 2266, 2288, 2296, 2301, 2306, 2318, 2321, 2325 2330
29. Herzberg, G.: *Molecular spectra and molecular structure*. London-Toronto-Melbourne: Van Nostrand-Reinhold Company 1966
30. Vinogradov, S. N., Linnell, R. H.: *Hydrogen bonding*, p. 109. London: Van Nostrand-Reinhold Company 1971
31. Lombos, B. A., Sauvagean, P., Sandorfy, C.: *J. Mol. Spectry.* **24**, 253 (1967)
32. Koch, E. E., Skibowski, M.: *Chem. Phys. Letters* **9**, 429 (1971)
33. Salahub, D. R., Sandorfy, C.: *Theoret. Chim. Acta (Berl.)* **20**, 227 (1971)
34. Montagnani, R., Pierluigi, R., Salvetti, O.: *Theoret. Chim. Acta (Berl.)* **32**, 161 (1973)
35. Hoffmann, R.: *Pure Appl. Chem.* **24**, 567 (1970)
36. Buenker, R. J., Peyerimhoff, S. D.: *J. Chem. Phys.* **53**, 1368 (1970)
37. Wasserman, E., Yager, W. A., Kuck, V. J.: *Chem. Phys. Letters* **7**, 409 (1970)
38. Bernheim, R. A., Bernard, H. W., Wang, P. S., Wood, L. S., Skell, P. S.: *J. Chem. Phys.* **53**, 1280 (1970)
39. Herzberg, G.: *Proc. Roy. Soc. A* **262**, 211 (1961)
40. Herzberg, G., Johns, J. W. C.: *Proc. Roy. Soc. A* **295**, 107 (1966)
41. Del Bene, J. E.: *Chem. Phys. Letters* **9**, 68 (1971)
42. Harrison, J. F., Allen, I. C.: *J. Am. Chem. Soc.* **91**, 807 (1969)
43. Herzberg, G., Johns, J. W. C.: *J. Chem. Phys.* **54**, 2276 (1971)
44. Bauschlicher Jr., Ch. W., Schaefer III, H. F., Bagus, P. S.: *J. Am. Chem. Soc.* **99**, 7106 (1977)
45. Roothaan, C. C. J.: *J. Chem. Phys.* **19**, 1445 (1951)
46. Roothaan, C. C. J., Ruedenberg, K.: *J. Chem. Phys.* **22**, 765 (1954)
47. Ditchfield, R., Del Bene, J., Pople, J. A.: *J. Am. Chem. Soc.* **94**, 4806 (1972)

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