

CCA-663

539.19:541

Note

Variational Approach to the Correlation Problem in the Molecules

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Received December 21, 1970

The aim of this work is to apply the variational approach as introduced by Da Providencia¹ to the correlation problem. We are interested not only in the calculation of the ground state energy, but, even more, in the excitation transition of the treated systems.

Da Providencia¹ and Čížek² have written the exact wave function in the form:

$$\Psi = (\exp iS) \cdot \Phi$$

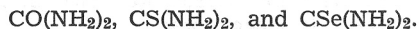
where Φ is some appropriate approximation to Ψ and

$$S = \sum_{mi} c_{mi} a_m^+ a_i + \frac{1}{2} \sum_{mnij} c_{mnij} a_m^+ a_n^+ a_j a_i$$

where C_{mi} , C_{mnij} are determined from

$$\langle \Psi | H | \Psi \rangle = \min.$$

In our study Φ was taken as a Slater determinant with molecular orbitals determined with the semiempirical SCF-PPP method. The studied systems are



The previous calculation³ proved that the single — excited states contributions are negligible ($C_{mi} = 0$). Only C_{mnij} were taken in S and were determined from the inhomogeneous system of equations. The calculated energies of the ground states are in Table I.

In the nonheterogenous atom system the doubly — excited states contribution is the largest one but this is not *a priori* true for heterogeneous one. This fast explains perhaps why the differences E (variational) — E (HF)

TABLE I
Ground State Energies (eV)

	H—F	this work
CO(NH ₂) ₂	— 106.775	— 106.814
CS(NH ₂) ₂	— 103.494	— 103.527
CSe(NH ₂) ₂	— 101.597	— 101.642

are so small. The variational method is very suitable for the calculation of the excitation transitions. With the transformation $H' = e^{-iS} H e^{iS}$ in

$$E = \langle \Phi | e^{-iS} H e^{iS} | \Phi \rangle$$

we have tried to eliminate the ground state correlation implicit in H . The excitations can be deduced from the transformed Hamiltonian with the time-dependent variational principle. The system of equation is¹

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \epsilon \begin{pmatrix} X \\ Y \end{pmatrix}$$

and corresponds formally to the system of the Random-Phase-Approximation (RPA). The difference between both methods is fundamental. While RPA uses Φ as a ground state wave function, the variational method takes $(\exp S)$. The results of both methods are presented in Table II. Both methods

TABLE II
Transition Energies (eV)

	RPA	this work
CO(NH ₂) ₂	6.70	6.60
CS(NH ₂) ₂	4.93	4.92
CSe(NH ₂) ₂	4.07	4.07

give almost identical results. This is another consequence of the fact that doubly — excited states (in part also quadruply excited) are not involved in Ψ to any large extent.

REFERENCES

1. J. Da Providencia, *Nuclear Physics* **61** (1965) 871.
2. J. Čížek, *J. Chem. Phys.* **45** (1966) 4256.
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IZVLEČEK

Variacijska metoda določevanja korelacijske energije molekul

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Variacijsko metodo¹ smo uporabili za določitev energije osnovnega stanja molekul. Metoda je zelo primerna za račun eksitacij, če je doprinos dvojno vzbujenih stanj k osnovnemu stanju znaten.

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ODDELEK ZA KEMIJO
UNIVERZA V LJUBLJANI

Sprejeto 21. prosinca 1970