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Note

Variational Approach to the Correlation Problem in the Molecules

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The aim of this work is to apply the variational approach as introduced by Da Providencia[1] 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 Providencia[1] and Čižek[2] 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

$$CO(NH_2)_2,\ CS(NH_2)_2,\ \text{and}\ CSe(NH_2)_2.$$

The previous calculation[3] 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 $H' = e^{-iS}He^{iS}$ 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 is[1]

$$\begin{pmatrix} A & B \\ B^{x} & A^{x} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \varepsilon \begin{pmatrix} X \\ Y \end{pmatrix}$$

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). Φ. The results of both methods are presented in Table II. Both methods 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.

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

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IZVLEČEK

Variacijska metoda določevanja korelacijske energije molekul

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Variacijsko metodo[1] 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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