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 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 Čižek² have written the exact wave function in the form:

$$\Psi = (\exp \mathbf{S}) \cdot \Phi$$

where $\Phi$ is some appropriate approximation to $\Psi$ and

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

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

$$\langle \Psi | \mathbf{H} | \Psi \rangle = \text{min.}$$

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

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

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>
<thead>
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<th>TABLE I</th>
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<tr>
<td><strong>Ground State Energies (eV)</strong></td>
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<tr>
<td>$\text{CO(NH}_2\text{)}_2$</td>
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<td>$\text{CS(NH}_2\text{)}_2$</td>
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<td>$\text{CSe(NH}_2\text{)}_2$</td>
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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

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

and corresponds formally to the system of the Random-Phase-Approximation (RPA). The difference between both methods is fundamental. While RPA uses $\Phi$ as a ground state wave function, the variational method takes $\langle \exp S \rangle$. 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 $\Psi$ to any large extent.

**REFERENCES**