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Annotationes

Solvent Interaction within the Hartree-Fock SCF Molecular Orbital Formalism

Additional Comment

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A theoretical model for introducing solvent effects into the Hartree-Fock (H-F) SCF MO formalism was recently discussed [1]. The model represented the solvent as a number of induced charges or solvatons. One solvaton was associated with each atomic center and contained a charge equal to the negative Mulliken net charge [2] of the associated atomic center. Solvaton-electron and solvaton-nuclei interaction energies were assumed to be a function of the solvent dielectric constant. The original article [1] gave no details concerning the Fock operator used in the study; however, continued work has made the author aware that clarification concerning the derivation of this operator may be desirable. The following outlines the derivation of the Fock operator used in the study.

The Hamiltonian of the M-electron, N nuclei molecular system in solution is given by

$$\begin{aligned} H = \sum_{i}^{M} H_i + \tfrac{1}{2} \sum_{i}^{M} \sum_{\substack{j \\ i \neq j}}^{M} \frac{1}{r_{ij}} + \tfrac{1}{2} \sum_{k}^{N} \sum_{\substack{l \\ k \neq l}}^{N} \frac{Z_k Z_l}{r_{kl}} \\ + \frac{(\varepsilon - 1)}{2\varepsilon} \left[\sum_{i}^{M} \sum_{s}^{N} \frac{Q_s}{r_{si}} - \sum_{k}^{N} \sum_{s}^{N} \frac{Q_s Z_k}{r_{sk}} \right] \end{aligned} \tag{1}$$

where Q_s is the induced solvent (solvaton) charge, r_{si} and r_{sk} are the solvaton-electron and solvaton-nuclei distances, respectively, and $(\varepsilon - 1/2\varepsilon)$ is the function relating the solute-solvent interaction to the solvent dielectric constant. Other symbols have their usual meaning [3]. Using Roothaan's matrix notation [3], the LCAO approximation of the MO's, ϕ_i, is given by

$$\phi_i = \underline{\psi}\, \underline{C}_i \tag{2}$$

$\underline{\psi}$ being the matrix of AO's and $\underline{C}_i$ the matrix of coefficients. The total energy of the closed-shell molecular system in solution is then given by

$$\begin{aligned} E_T = 2 \sum_{i}^{M/2} \underline{C}_i^* \underline{H}\, \underline{C}_i + \sum_{i}^{M/2} \sum_{j}^{M/2} \underline{C}_i^* (2\underline{J}_j - \underline{K}_j)\, \underline{C}_i + \tfrac{1}{2} \sum_{k}^{N} \sum_{\substack{l \\ k \neq l}}^{N} \frac{Z_k Z_l}{r_{kl}} \\ + \frac{\varepsilon - 1}{2\varepsilon} \left[2 \sum_{i}^{M/2} \underline{C}_i^* \underline{D}\, \underline{C}_i - \sum_{k}^{N} \sum_{s}^{M} \frac{Q_s Z_k}{r_{sk}} \right] \end{aligned} \tag{3}$$

where the elements of the solvent interaction matrix $\underline{D}$ are given by

$$D_{ij} = \int \psi_i \left[\sum_{s}^{N} \frac{Q_s}{r_{s1}} \right] \psi_j \, d\tau(1) . \tag{4}$$

The usual variational treatment [3] of E_T yields the following expression for the Fock operator:

$$\underline{F} = \underline{H} + \sum_{j}^{M/2} (2\underline{J}_j - \underline{K}_j) + \left(\frac{\varepsilon - 1}{2\varepsilon} \right) \underline{D} . \tag{5}$$

The above derivation treats the Q_s as constants in the variational process and reflects the intended view of the solvent interaction model. That is, the solvent model is basically a set of temporarily unspecified induced charges and for purposes of obtaining testable quantitative results, these induced charges were ultimately assigned a charge equal but opposite to the Mulliken net charge [2] of an associated atomic center.

On the other hand, if the use of the Mulliken definition of the net atomic charge [2]

$$q_s = Z_s - 2 \sum_{i \in s}^{\text{AO's}} \sum_{j}^{\text{AO's}} \sum_{k}^{M/2} C_{ik} C_{jk} S_{ij} \tag{6}$$

had been considered as the basic premise of the model, the definition of Eq. (6) should have been initially substituted into Eq. (4) and, consequently, into Eq. (3) for the total energy. (S_{ij} is the overlap integral and the first summation, $i \in s$, includes only AO's on the S^{th} atomic center.) Elements of the solvent interaction matrix, $\underline{D}$, would be functions of the MO coefficients and contain, in part, certain unusual molecular integrals related but not identical to the integrals of $\underline{J}_j$ and $\underline{K}_j$. The variational treatment [3] would then result in a Fock operator somewhat different from Eq. (4). This second approach was not taken because the intent of the work was to develop a simple model for incorporating solvent effects into H-F SCF MO calculations. The latter approach would add considerable complexity while, nevertheless, retaining all the conceptual deficiencies of the model.

References

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