Theoret. Chim. Acta (Berl.) 47, 171–174 (1978)

THEORETICA CHIMICA ACTA

Short Communication

Environmental Effects on Second Order Perturbation Energy

O. Tapia, E. Poulain* and F. Sussman*

Centre de Mécanique Ondulatoire Appliquée, 23, rue du Maroc, F-75019 Paris, France

A perturbative analysis of the selfconsistent reaction field electronic wave function allows for the establishment of a simple formula to describe the variation of the second-order perturbation energy with the solute–solvent coupling parameter. A numerical test is given.

Key words: Solvent effect – Dispersion forces

1. Introduction

The London–Van der Waals dispersion effects contribute to the stability of the H-bonded as well as to the donor–acceptor (charge transfer) molecular complexes. The interaction between the two partners depends on the medium in which they exist [1]. While the exact corrections to the interaction energy are very difficult to obtain, it would be of interest to have approximate tools to estimate the medium effect upon the dispersion forces or quantities related to them.

Within the supermolecule approach to the calculation of intermolecular forces and potentials, the second order perturbation (SOP) energy (E_{SOP}) calculated as a correction to the self-consistent field energy is related to the London–Van der Waals forces. We have already shown [2, 3] that this quantity is affected by the presence of a given polarizable medium. The solute-medium coupling is described within the self-consistent reaction field (SCRF) theory of solvent effects [4], which is appropriate in this connection.

---

* *Permanent Addresses:* F. S.: Chemical Physics Department, The Weizmann Institute of Science, P.O.B. 26, Rehovot, Israël; E.P.: Quantum Chemistry Group, Uppsala University, Box 518, 75120 Uppsala, Sweden.

0040–5744/78/0047/0171/$01.00

New calculations have been carried out on a formaldehyde-water, an acetone-water, several water dimers corresponding to different geometrical conformations, and a tetrahedrally arranged water trimer. For all cases studied the E_{SOP} behaves similarly, it depends both on the reaction field strength (RFS) and upon the reaction field direction with respect to the direction of the dipole moment. For a reaction field making an angle with the zero order dipole moment $\boldsymbol{M}_0$ smaller than $\pi/2$, i.e., for positive g-values [3], the SOP energy diminishes as the RFS increases. The opposite behaviour is found in the negative g-values regime [3]. All systems studied display the same results. The autonomy shown by the trends concerning E_{SOP} from the nature of the particular system studied is in agreement with the universal character of both the SOP effect and the reaction field polarization effect in dipolar systems. The aim of this note is to put forward in a mathematical fashion the actual dependence of E_{SOP} with respect to the reaction field (RF).

A general analysis of the SOP energy formula via a perturbative development of the SCRF wavefunction is sketched. An approximate formula is obtained which describes qualitatively and semi-quantitatively the numerical results found so far. This result is believed to give also a useful information about the medium effect on dispersion forces in donor–acceptor complexes.

2. Second Order Perturbation Energy: A Perturbative Analysis of ψ_{SCRF}

The second order perturbation energy is given by the formula:

$$-E_{\mathrm{SOP}}=\sum_{i,j}^{\mathrm{occ.}}\sum_{\mu,\nu}^{\mathrm{unocc.}}\frac{\langle\psi_{\mathrm{SCRF}}|V|\psi_{ij}^{\mu\nu}\rangle\langle\psi_{ij}^{\mu\nu}|V|\psi_{\mathrm{SCRF}}\rangle}{\varepsilon_\mu+\varepsilon_\nu-\varepsilon_i-\varepsilon_j}\equiv\langle\psi_{\mathrm{SCRF}}|V\tilde{T}_0V|\psi_{\mathrm{SCRF}}\rangle \tag{1}$$

where V is the Coulomb repulsive interaction among the electrons; ψ_{SCRF} is the Slater determinant build up with the n spin orbitals of lower energy (basic configuration) which come out as solutions of the SCRF-MO equation [4, 5]; $\psi_{ij}^{\mu\nu}$ are Slater determinant(s) forming an eigenfunction of S^2 with $S=0$, they are issued from a replacement of the orbitals ϕ_i, ϕ_j present in ψ_{SCRF} by the orbitals ϕ_μ, ϕ_ν belonging to the orthogonal complement to the basic configuration; ε_k is the k'th molecular orbital energy.

The analysis of (1) can be done once ψ_{SCRF} is written down on the basis formed by the isolated system wave functions. Bearing in mind that at the end of the self-consistent procedure the RF can be taken as a constant quantity, the ψ_{SCRF} is developed up to first order in it,

$$|\psi_{\mathrm{SCRF}}\rangle=|0\rangle+\sum_{K\neq 0}\frac{|K\rangle\langle K|\boldsymbol{\mu}|0\rangle}{E_K^0-E_0^0}\cdot\boldsymbol{R}\equiv|0\rangle+T_0\boldsymbol{\mu}|0\rangle\cdot\boldsymbol{R} \tag{2}$$

where $|0\rangle$ and $|K\rangle$ are eigenfunctions of H_0 with $H_0|K\rangle=E_{\mathrm{K}}^0|\boldsymbol{\mu}\rangle$.

This is, of course, a pseudo first order expansion. In fact, $\boldsymbol{R}$ contains infinite order contribution due to its self-consistent nature. The expansion is, nevertheless, adequate so far as the energy contribution derived from this field is only a small percentage of the total zero order electronic energy. Proceeding now to introduce (2) into (1), the following formula is obtained if one neglects the term of second order in **R**

$$-E_{\mathrm{SOP}} \simeq \langle 0|V\tilde{T}_0 V|0\rangle + 2\langle 0|V\tilde{T}_0 V T_0 \boldsymbol{\mu}|0\rangle \cdot \boldsymbol{R} \tag{3}$$

which by means of the closure relationship (Unsöld approximation) applied to T_0 leads to

$$-E_{\mathrm{SOP}} \simeq \langle 0|V\tilde{T}_0 V|0\rangle + (2/Y)\langle 0|V\tilde{T}_0 V \boldsymbol{\mu}|0\rangle \cdot \boldsymbol{R} - (2/Y)\langle 0|V\tilde{T}_0 V|0\rangle\langle 0|\boldsymbol{\mu}|0\rangle \cdot \boldsymbol{R} \tag{4}$$

where Y is a constant positive quantity.

This formula displays a term, the last one, which depends upon the RF direction with respect to the dipole moment of the isolated complex. The negative sign makes this term partially cancel the contribution of the first term. The second term may have either sign.

It follows that the variation of the SOP energy with the surrounding coupling will depend both on the RFS and the RF direction. Thus, our calculations have only elicited the dependency displayed in (4).

Neglecting the second term of (4) the following approximate formula is obtained

$$\frac{\Delta E_{\mathrm{SOP}}(g)}{E_{\mathrm{SOP}}(0)} \equiv \delta(g) = A\boldsymbol{M}_0 \cdot \boldsymbol{R} = gA\boldsymbol{M}_0 \cdot \boldsymbol{M} \tag{5}$$

where $\Delta E_{\mathrm{SOP}}(g) = E_{\mathrm{SOP}}(g) - E_{\mathrm{SOP}}(0)$. While this formula displays explicitly the g-dependence of the numerical results, there is no theoretical foundation to sustain it. Hopefully there would be an error cancellation involved such that (5) would be useful to describe the numerical results found by actual calculations.

3. Results and Discussion

First, it should be noticed that (5) qualitatively summarizes the results already found. In fact, since A is a positive quantity and the RF is taken along $\boldsymbol{M}_0$, an increment of g would lead to a negative $\Delta E_{\mathrm{SOP}}(g)$ due to the fact that $E_{\mathrm{SOP}}(0)$ is itself a negative quantity this means that $-E_{\mathrm{SOP}}(g)$ ought to be a decreasing function of g, and that $|E_{\mathrm{SOP}}(0)| > |E_{\mathrm{SOP}}(g)|$. The formula (5) predicts the opposite trend in the negative g-regime. In this case the RF direction with respect to $\boldsymbol{M}_0$ makes an angle greater than 90°.

Besides this qualitative behaviour a quantitative test can be made on (3). All terms but A in (5) can be either calculated or be fixed quantities. Therefore, if (5) is fulfilled within the range taken up for g, the ratio $\delta(g)/\boldsymbol{M}_0 \cdot \boldsymbol{R}$ should be constant throughout.

The system $H_2C{=}O \cdots H{-}OH$ is used to illustrate the type of results obtained (see Table 1). In the last column the calculated ratio is displayed. Within a reasonable approximation they can be roughly rounded off to 1.0 in the negative g-range and

1.2 in the positive range. Similar results are found for the other systems. These numerical tests seem to confirm the adequacy of this formula to describe the behaviour of the SOP energy under the effect of a reaction field.

Table 1. Selfconsistent reaction field energy (E_{SCRF}), total energy $E = E_{\mathrm{SCRF}} + E_{\mathrm{SOP}}$, where E_{SOP} represents the second order perturbation energy in hartrees, total dipole moment M in debyes and the constant A defined by the Eq. (5) (see text) as a function of the solute–solvent coupling parameter g

g [bohr^{-3}]	$-E_{\mathrm{SCRF}}$ [a.u.]	$-E$ [a.u.]	M [D]	A
−0.010	46.711533	46.820077	3.68	0.95
−0.005	46.721871	46.829359	3.94	1.01
−0.001	46.731736	46.838131	4.19	1.02
0.0	46.734474	46.840569	4.25	—
0.001	46.737321	46.843068	4.31	1.16
0.005	46.750055	46.854295	4.59	1.16
0.010	46.769787	46.871538	5.02	1.24

These results may be extended to the donor–acceptor complexes as well. The results depend only upon the presence of a reaction field. Formula (5) may be useful to obtain new results once E_{SOP} is calculated for $g = 0$ and some other value $g \neq 0$. The calculation of the constant A leads to a semiquantitative estimation of the variation of E_{SOP} with the solute-medium coupling parameter g.

Finally, it should be noticed that the solvent effect upon the SOP energy (c.f. Eq. (3)) acquires the structure of a third order correction in perturbation theory. This is in agreement with other treatments of the same effect [1]. The advantage here is that a polar solute in a polar solvent can also be considered.

References

1. Kestner, N. R., Sinanoğlu, O.: J. Chem. Phys. **38**, 1730 (1963)
2. Tapia, O., Poulain, E., Sussman, F.: Chem. Phys. Letters **33**, 65 (1975)
3. Tapia, O., Poulain, E.: Intern. J. Quantum Chem. **11**, 473 (1977)
4. Tapia, O., Goscinsky, O.: Mol. Phys. **29**, 1653 (1975)
5. Tapia, O.: Theoret. Chim. Acta (Berl.) 47, 157–169 (1978)

Received June 6, 1977