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The Virtual Charge Model of a Polarizable Medium as a Basis for Hückel Calculations with the ω-Technique

Raymond Constanciel

Centre de Mécanique Ondulatoire Appliquée, 23, Rue du Maroc, F-75019 Paris, France, and Université Pierre et Marie Curie, 4, Place Jussieu, F-75230 Paris, France

It is shown that the consideration of a strongly polarizable medium using the Virtual Charge Model (VCM) allows for the possibility of treating independently each electronic subsystem of a molecule by a Hückel-type ω-technique. The case of a finite polarizable environment can be treated by a first-order perturbation calculation.

Key Words: Virtual charge model – Polarizable medium, consideration of ~

1. Introduction

It is a formidable task to account by quantum mechanical methods for the properties of a system containing middle size molecules between which a chemical reaction may occur. Fortunately, the complexity of the theoretical study can be subsequently reduced by the knowledge of the process which governs the chemical reaction [1]. In many cases, the essential step is a bimolecular process so that we may consider only a reduced system containing only one molecule of each of the reactants. However, as the analysis of many experiments has shown, the solvent plays an essential role in chemical reactivity [1] and consequently it must be introduced in the reduced system. In this respect, continuum representations of the solvent effects [2] are of great value since in many cases they allow one to consider explicitly only both the substrate and the reactant. Unfortunately, even in the framework of such an approximation and in spite of the growing development of the computational facilities, it remains evident that the most elaborate methods of quantum chemistry are impracticable.

In fact, since the necessary chemical accuracy (1 kcal/mole ~ 0.04 eV) cannot generally be obtained, one must be satisfied with obtaining qualitative information by means of somewhat crude methods.

Recently, we have proposed a self-consistent procedure [3] which is able to account

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for the mutual reorganization of the charge clouds of a solvated molecule and of the polarization charges induced by it in a surrounding polarizable medium. The "Virtual Charge Model" (VCM) that we have used for simulating the molecular environment is a modification of the "Solvaton Model" [4] proposed earlier by G. Klopman. Within this model, the consideration of polarization effects due to the solvent results from minor corrections of the SCF LCAO MO equations in the CNDO approximation.

In this paper, we show that a kind of decoupling between the different electronic subsystems of a molecule (e.g. σ or π system) may result from the hypothesis of a highly polarizable environment. This provides a justification of calculations restricted to a part of the electron system. In particular, we remark that the VCM equations obtained for strong solvation effects have the essential features of the equations of the Hückel method including ω technique [5]. We point out also that such a simplified calculation can serve as zero-order approximation for a first-order perturbation calculation taking account of the effects of a moderate polarizable medium. The total energy expression obtained in this manner contains various additive terms which have been introduced empirically in some previous works.

2. Theory

2.1. Expression for the Energy of the Solute-Solvent System

If only the electrostatic solvent effects are considered [3], the total energy of a system formed by a molecule immersed in a polarizable environment can be written as a sum of two terms.

1) The first term is the effective energy of the molecule in its environment which we assume entirely characterized by the unique parameter ε (this quantity which can be assimilated to an effective dielectric constant, is a measure of the medium polarizability). This energy is a sum of three parts. The first one is the effective electronic energy E^{el} of the molecule, i.e. the energy of the valence electron system of the molecule in the field of the core and also in the field of the polarization charges induced in the medium. We assume that this contribution is derived within the LCAO MO approximation from a single closed-shell determinant wavefunction: for a well defined value of the parameter ε, it can be expressed as usual [6] as a function of the one-particle density matrix $\boldsymbol{P}$

$$E_{\varepsilon}^{\text{el}}(\boldsymbol{P}) = \operatorname{Tr} \boldsymbol{P}(F_{\varepsilon}(\boldsymbol{P}) - \tfrac{1}{2}G(\boldsymbol{P})) \tag{1}$$

where G is the electron field operator and F_{ε} is an effective Fock operator taking account of the medium polarization.

The second part is the core energy. It is simply the sum of the core charge interactions augmented by the self-energy contributions (that we assume to have a finite well defined value)

$$E^{\text{core}} = \frac{1}{2}\sum_{A}\sum_{B} Z_A Z_B \Gamma_{AB} \tag{2}$$

where Z_A is the core charge on the center A and Γ_{AB} is the two-center core interaction integral.

At last we must add the sum of the core–medium interaction terms $E^{\text{core-med}}$.

2) The second term which must be considered in obtaining the total energy is the medium electrostatic self energy E^{med}.

Now, if we use the CNDO/2 approximations [7] in the calculations on the valence electrons, the matrix elements of the free molecule Fock operator $F_1(\boldsymbol{P})$ in the atomic orbital basis are

$$[F_1(\boldsymbol{P})]_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \tfrac{1}{2}(1 - \boldsymbol{P}_{\mu\mu})\gamma_{AA} - \sum_B (Z_B - \boldsymbol{P}_{BB})\gamma_{AB} \tag{3}$$

$$[F_1(\boldsymbol{P})]_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{4}$$

where the various symbols have the usual meaning given by J. A. Pople in his original publications.

In the same way, we have for the electron field operator $G(\boldsymbol{P})$

$$[G(\boldsymbol{P})]_{\mu\mu} = -\tfrac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_B P_{BB}\gamma_{AB} \tag{5}$$

$$[G(\boldsymbol{P})]_{\mu\nu} = -\tfrac{1}{2}P_{\mu\nu}\gamma_{AB}. \tag{6}$$

In the Virtual Charge Model of the environment [3], the effective Fock operator $F_\varepsilon(\boldsymbol{P})$ can be derived from the free molecule one $F_1(\boldsymbol{P})$ by adding to the diagonal elements a term representing the field due to the polarization charges induced in the medium. We assume that for each center in the molecule there is associated a polarization charge defined by

$$Q_B^{\text{pol}}(\boldsymbol{P}) = -\left(1 - \frac{1}{\sqrt{\varepsilon}}\right)(Z_B - P_{BB}) \ . \tag{7}$$

so that we obtain

$$[F_\varepsilon(\boldsymbol{P})]_{\mu\mu} = [F_1(\boldsymbol{P})]_{\mu\mu} - \sum_B Q_B^{\text{pol}}(\boldsymbol{P})\gamma_{AB} \tag{8}$$

or, more explicitly, by using Eq. (3) and Eq. (7)

$$[F_\varepsilon(\boldsymbol{P})]_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \tfrac{1}{2}(1 - P_{\mu\mu})\gamma_{AA} - \frac{1}{\sqrt{\varepsilon}}\sum_B (Z_B - P_{BB})\gamma_{AB}. \tag{9}$$

On the other hand, we have for the core-medium interaction energy

$$E_\varepsilon^{\text{core-med}}(\boldsymbol{P}) = \sum_A \sum_B Z_A Q_B^{\text{pol}}(\boldsymbol{P})\gamma_{AB} = -\left(1 - \frac{1}{\sqrt{\varepsilon}}\right) \sum_A \sum_B Z_A(Z_B - P_{BB})\gamma_{AB} \tag{10}$$

and for the medium self-energy

$$\begin{aligned} E_\varepsilon^{\text{med}}(\boldsymbol{P}) &= \frac{1}{2}\sum_A \sum_B Q_B^{\text{pol}}(\boldsymbol{P}) Q_B^{\text{pol}}(\boldsymbol{P})\gamma_{AB} \\ &= \frac{1}{2}\left(1 - \frac{1}{\sqrt{\varepsilon}}\right)^2 \sum_A \sum_B (Z_A - P_{AA})(Z_B - P_{BB})\gamma_{AB}. \end{aligned} \tag{11}$$

As we have shown elsewhere [3] the optimal value of the energy is obtained by putting $\boldsymbol{P} = \boldsymbol{P}_\varepsilon^{\mathrm{SCF}}$ in the above equations, where $\boldsymbol{P}_\varepsilon^{\mathrm{SCF}}$ is the solvated molecule density matrix derived from the self-consistent solution of the F_ε operator eigenvalue problem and to which is associated a minimum of the effective electronic energy defined in Eq. (1).

2.2. The Case of a Strongly Polarizable Medium

Now, we will examine more particularly what happens when the solvent dielectric constant has a high numerical value or, in other words, when the influence of the environment must be introduced self-consistently in the calculation in consideration of the important modifications that it induces on the electronic charge distribution of the free molecule.

Under these conditions, an examination of the diagonal elements of the operator $F_\varepsilon(\boldsymbol{P})$ as given in Eq. (9) shows that the term depending on the dielectric constant is small; it can be reasonably neglected in the density matrix optimization process and introduced only as a perturbative correction to the energy.

Thus a satisfactory zero-order approximation $(\boldsymbol{P}_\varepsilon^{\mathrm{SCF}})^0$ of $\boldsymbol{P}_\varepsilon^{\mathrm{SCF}}$ will be obtained as usual, after self-consistency has been reached, from the eigenvectors of the following operator

$$H = \lim_{\varepsilon \to \infty} F_\varepsilon \tag{12}$$

which is the limit of the operator F_ε when ε increases infinitely. More explicitly, we have from Eq. (9)

$$[H(\boldsymbol{P})]_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \tfrac{1}{2}(1 - P_{\mu\mu})\gamma_{AA} \tag{13}$$

$$[H(\boldsymbol{P})]_{\mu\nu} = [F_1(\boldsymbol{P})]_{\mu\nu}. \tag{14}$$

On the other hand, a first-order approximation of the optimal value of the energy is obtained by putting $\boldsymbol{P} = (\boldsymbol{P}_\varepsilon^{\mathrm{SCF}})^0$ in Eqs. (1–11) where, according to Eq. (12),

$$(\boldsymbol{P}_\varepsilon^{\mathrm{SCF}})^0 = \lim_{\varepsilon \to \infty} \boldsymbol{P}_\varepsilon^{\mathrm{SCF}} \tag{15}$$

is the same for all ε values and will be denoted hereafter by $(\boldsymbol{P}^{\mathrm{SCF}})^0$.

From a formal point of view it is interesting that a simpler expression of the energy can be obtained by introducing explicitly the operator H in Eq. (1): we have

$$E_\varepsilon^{\mathrm{el}}(\boldsymbol{P}) = Tr\boldsymbol{P}H(\boldsymbol{P}) - \frac{1}{\sqrt{\varepsilon}} \sum_A \sum_B P_{AA} Q_B(\boldsymbol{P}) \gamma_{AB} + \frac{1}{4} \sum_A \sum_\mu^{\mathrm{A}} \sum_B \sum_\upsilon^{\mathrm{B}} P_{\mu\upsilon}^2 \gamma_{AB} - \frac{1}{2} \sum_A \sum_B P_{AA} \boldsymbol{P}_{BB} \gamma_{AB} \tag{16}$$

where the usual notation

$$Q_B(\boldsymbol{P}) = Z_B - P_{BB} \tag{17}$$

has been used for designing the net charge on the center B. Some terms of the effective electronic energy (16) can be recombined with the core repulsions (2), the core medium (10) and the medium self-energy (11) terms so that we obtain for the total energy the very simple expression

$$E_\varepsilon(P) = \mathrm{Tr}\boldsymbol{P}\overline{H}(\boldsymbol{P}) + \frac{1}{2\varepsilon}\sum_A\sum_B Q_A(\boldsymbol{P})Q_B(\boldsymbol{P})\gamma_{AB} + \frac{1}{2}\sum_A\sum_B Z_A Z_B(\Gamma_{AB} - \gamma_{AB}). \tag{18}$$

The first term of the right-hand side is defined as

$$\mathrm{Tr}\boldsymbol{P}\overline{H}(\boldsymbol{P}) = \mathrm{Tr}\boldsymbol{P}H(\boldsymbol{P}) + \frac{1}{4}\sum_A\sum_\mu^A\sum_B\sum_\nu^B P_{\mu\nu}^2\gamma_{AB} \tag{19}$$

where the operator $\overline{H}(\boldsymbol{P})$, the matrix elements of which are given by

$$[\overline{H}(\boldsymbol{P})]_{\mu\mu} = [H(\boldsymbol{P})]_{\mu\mu} + \tfrac{1}{4}P_{\mu\mu}\gamma_{AA} \tag{20}$$

$$[\overline{H}(\boldsymbol{P})]_{\mu\nu} = [H(\boldsymbol{P})]_{\mu\nu} + \tfrac{1}{4}P_{\mu\nu}\gamma_{AB} \tag{21}$$

can be related to $H(\boldsymbol{P})$ by the Harris formula [8]

$$[H(\boldsymbol{P})]_{\mu\nu} = [\overline{H}(\boldsymbol{P})]_{\mu\nu} + \sum_{\alpha\beta} P_{\alpha\beta}\frac{\partial[\overline{H}(\boldsymbol{P})]_{\alpha\beta}}{\partial P_{\mu\nu}} \tag{22}$$

3. Discussion

We have shown that the electronic structure of a molecule immersed in an extremely polarizable medium ($\varepsilon \to \infty$) can be studied in a somewhat simplified way by comparison with the usual SCF CNDO calculation on the free molecule. The simplifications arise essentially from the modification of the diagonal elements of the Fock operator $F_1(\boldsymbol{P})$, and the main features of the results obtained by using the operator H of Eq. (12) can be deduced by comparing both Eqs. (3) and (13).

More precisely, we observe in Eq. (9) that the inclusion of environment effects by the VCM approximation produces a screening of the net charge terms which appeared in $[F_1(\boldsymbol{P})]_{\mu\mu}$. The screening is complete when the polarizability parameter ε is infinitely high; thus the diagonal elements $[H(\boldsymbol{P})]_{\mu\mu}$ are functions of the electronic charge $P_{\mu\mu}$ in the μ orbital only.

As a result, if we consider the case of a system described by a separable $\sigma - \pi$ wave function (planar conjugated molecule), we see that the electronic distribution relative to the π orbitals does not depend on the σ electronic structure. In other words, the mutual $\sigma - \pi$ polarization effects, the consideration of which have made all-valence electrons treatments superior to the π approximation [9], vanish identically in that case. The same deduction can be extended to other cases of separability; thus the valence bonds would have electronic properties depending on their nature only and not on their neighbourhood. Therefore we conclude that the procedure of reducing the electron system to one of its parts [10] can be justified by considering strong environment effects by the VCM approximation.

Moreover, restricting ourselves to the study of π systems, we observe that the expression (13) of $[H(\boldsymbol{P})]_{\mu\mu}$ can be compared with the following relationship [5] used in the Hückel ω technique:

$$\alpha_\mu(\boldsymbol{P}) = \alpha_\mu^0 + \omega\beta Q_\mu(\boldsymbol{P}) \tag{23}$$

where α_μ^0 is the value of the Coulomb integral for an atom having no net charge ($Q_\mu(\boldsymbol{P}) = 0$), ω is a constant determined empirically and β is the reference bond integral taken as an energy unit. By assuming $[H(\boldsymbol{P})]_{\mu\mu} = \alpha_\mu^{\mathrm{VCM}}(\boldsymbol{P})$ we find

$$\alpha_\mu^0 = -\tfrac{1}{2}(I_\mu + A_\mu) + \tfrac{1}{2}(1 - n_\mu)\gamma_{\mu\mu} \tag{24}$$

a formula previously used by G. Berthier *et al.* [11] where n_μ is the number of electrons contributed by the μ orbital,

$$Q_\mu(\boldsymbol{P}) = n_\mu - P_{\mu\mu} \tag{25}$$

and

$$(\omega^{\mathrm{VCM}})\beta = \tfrac{1}{2}\gamma_{\mu\mu}. \tag{26}$$

This interpretation of the quantity α_μ^0 and $Q_\mu(\boldsymbol{P})$ agrees with that previously given by A. Streitwieser [12] or I. Fisher-Hjalmars [13]; however the sign of the ω^{VCM} parameter is opposite to that they found.

This discrepancy can be explained by the fact that these authors define a Coulomb integral $\alpha_\mu(\boldsymbol{P})$ by the relation

$$[F_1(\boldsymbol{P})]_{\mu\mu} = \alpha_\mu(\boldsymbol{P}) - \sum_{v \neq \mu} Q_v(\boldsymbol{P})\gamma_{\mu v} \tag{27}$$

although we have assumed following Eqs. (3) and (13)

$$[F_1(\boldsymbol{P})]_{\mu\mu} = \alpha_\mu^{\mathrm{VCM}}(\boldsymbol{P}) - \sum_{v} Q_v(\boldsymbol{P})\gamma_{\mu v}. \tag{28}$$

Comparing both Eqs. (27) and (28) we see that the two α integrals are related by

$$\alpha_\mu^{\mathrm{VCM}}(\boldsymbol{P}) - \alpha_\mu(\boldsymbol{P}) = Q_\mu(\boldsymbol{P})\gamma_{\mu\mu} = 2\omega^{\mathrm{VCM}}\beta Q_\mu(\boldsymbol{P}). \tag{29}$$

This equation combined with the following

$$\alpha_\mu^{\mathrm{VCM}}(\boldsymbol{P}) - \alpha_\mu(\boldsymbol{P}) = (\omega^{\mathrm{VCM}} - \omega)\beta Q_\mu(\boldsymbol{P}) \tag{30}$$

which results from the definition (23), gives immediately

$$\omega^{\mathrm{VCM}} = -\omega. \tag{31}$$

In other words, these authors wanted to justify the recourse to the simple Hückel ω technique for treating the free molecules whereas we suggest that this procedure (with an appropriate value ω^{VCM} of the parameter ω) is able to account for the electronic properties of strongly solvated molecules. Concerning the relative merits of both interpretations we think that the last is more satisfactory for it can be derived without an additional hypothesis from the basic CNDO equations including solvation by VCM approximation: the disappearance of the neighbour terms in $\alpha_\mu^{\mathrm{VCM}}(\boldsymbol{P})$ results simply from physical effects and is not obtained at the expense of so severe an approximation as the neglect of the $\gamma_{\mu v}$ repulsion integrals in Eq. (27). However the necessary hypothesis concerning the relative constancy of the off-diagonal elements $[F_1(\boldsymbol{P})]_{\mu v}$ [13, 14] is involved in both approaches.

Also, as it appears clearly in Eq. (3), $H(\boldsymbol{P})$ is a convenient approximation of the Fock operator $F_1(\boldsymbol{P})$ when one is dealing with weakly polar molecules ($Q(\boldsymbol{P}) \to 0$). In this case, the electronic charges $P_{\mu\mu}$ are nearly equal and each of them screens almost completely the corresponding core charge $Z_\mu(\boldsymbol{P} \to \boldsymbol{Z})$. Under these conditions, we have

$$\lim_{Q(\boldsymbol{P})\to 0} F_1(\boldsymbol{P}) = \lim_{\boldsymbol{P}\to \boldsymbol{Z}} H(\boldsymbol{P}). \tag{32}$$

Thus the use of H is irrelevant only for charged or highly polar compounds in the gas phase or imbedded in a weakly polarizable medium.

As far as the energy is concerned, Eq. (18) shows that in both cases ($\varepsilon \to \infty$ or $Q(\boldsymbol{P}) \to 0$) an estimation of the total energy is given by Tr $\boldsymbol{P}\bar{H}(\boldsymbol{P})$ (in which the density matrix $\boldsymbol{P}$ has to be replaced by the zero order SCF solution $(\boldsymbol{P}^{\mathrm{SCF}})^0$) and not simply by Tr $\boldsymbol{P}H(\boldsymbol{P})$ as in the simple Hückel method: this duality between both operators H and $\bar{H}$ is a particular case of a general feature of the SCF theory which has been discussed by many authors [8, 15, 16]. This predominant term has to be corrected only by a small core charge interaction contribution which vanishes identically if we assume the relation $\Gamma_{AB} = \gamma_{AB}$, as it has been frequently done [17]. Let us remark that the simplification of the energy expression comes out in part from the introduction of self-energy contributions in Eq. (2) which are customarily ignored in regard to their invariance under electronic excitation or geometrical transformation of the molecule.

When the medium is characterized by a finite value of the parameter ε, an ε depending term must be added to obtain an estimation of the energy which agrees with an usual CNDO calculation. This "desolvation" correction can also be viewed as the sum of a net charge [18] and of a solvation corrective term [19]

$$\begin{aligned}\frac{1}{2\varepsilon}\sum_A\sum_B Q_A(\boldsymbol{P})Q_B(\boldsymbol{P})\gamma_{AB} &= \frac{1}{2}\sum_A\sum_B Q_A(\boldsymbol{P})Q_B(\boldsymbol{P})\gamma_{AB}\\ &\quad -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_A\sum_B Q_A(\boldsymbol{P})Q_B(\boldsymbol{P})\gamma_{AB}\end{aligned} \tag{33}$$

which have been considered earlier by many authors. The expression of the left-hand side of Eq. (33) is particularly adapted to the case where $\varepsilon \to \infty$ whereas the other side corresponds naturally to the situation where $Q(\boldsymbol{P}) \to 0$. This last possibility has already been investigated by us in a previous work [20] where the two corrections just cited were introduced in order to explain some ambident reactivity problems through simple Hückel calculations. This preliminary theoretical study was incomplete however for it did not define clearly the conditions under which the simplified calculations were justified.

4. Conclusion

The consideration of strong environment effects through the Virtual Charge Model leads to substantial simplification of the SCF procedure in the CNDO approximation which works as the Hückel method including ω technique for each separate electronic subsystem of the molecule. Energy calculations by this simplified procedure with first order "desolvation" correction seems promising for the treatment of middle-size molecules reactivity for which the use of elaborate methods of quantum chemistry are prohibitive. Some recent applications of the VCM approximation show that it provides a satisfactory qualitative agreement with experimental facts [21]; thus the main results of this theoretical study can be accepted as giving general trends which would be corrected only in detail by more elaborate calculations.

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