Path integral's formulation of the molecular solvent effects

Julio Marañón

PROFIMO, Departamento de Física, Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, C.C. 67 (1900) La Plata, Argentina

With the formalism of the path-integral into molecular-orbital theory, we introduce the quatum fluctuation into the molecular ground state. As a consequence, a non-linear formulation of the molecular orbitals is obtained. Then, we connect the non-linear term of the effective Hamiltonian with the solvent effects of the environment surrounding the molecular system, and explain this mechanism.

1. Introduction

When we inmerse a molecular system in a solvent, we are adding Coulombic fields to the system, deforming its electronic structure of the ground state. These fields produce local deformation, which, in turn, manifests an energy and electronic charge shift resulting from ground-state fluctuations. Years ago Yomosa et al. [1] and Tapia et al. [2] showed some theoretical evidence justifying the preceding statement in the molecular-orbital theory. The field acting on the system is characterized as a self-dependent reaction field. Here, the term self-dependent means that the field acting upon the system depends on its electronic structure and geometry. Therefore, the general equation of the state of the molecular system in the self-dependent field can be given by a non-linear Schrödinger equation [1].

Furthermore, a quantum mechanical reaction field theory of the solvent effect has been proposed. As a limit case it contains Onsager's model. It also leads to an effective non-linear Hamiltonian for the molecule in solution, and hence a tool for studying changes of the electronic charge distribution in molecular properties. The approximate solution of the non-linear equation within the molecular-orbital framework is presented; correlation defaults to the Hartree-Fock-like solutions are stated [2].

More recently Tapia [3] has proposed a generalized reaction field theory of surrounding medium effects on the electronic wave function of the solute or the subsystem immersed therein. He explains that the reaction field is given in a compact

functional form factorized into a solute charge density and a reaction field suscept-ibility. It is important to note that the later depends on the geometry and static polarizability distribution of the surrounding medium.

The aim of this paper is to propose a link between the non-linear formulation by the path integral method [4] and the solvent effect. Further, we provide an expla-nation of the surrounding medium induced ground state quantum field fluctuation which produces an energy and electronic shift of the solute and emphasizes its non-linear character.

2. Mathematical outline

In this section we present, in the context of the molecular-orbital theory, a collec-tion of formulae that we have already derived in previous publications in order to introduce quantum fluctuations in the ground state of the electronic molecular sys-tem [5], and a brief version of the theory in the non-linear case [4]. Its basic aspects are outlined here.

Let us consider that the time-independent N-electron molecular Hamiltonian H can be written as

$$H = \sum_{\alpha}^{N} H_{\alpha} + \sum_{\alpha < \beta}^{N} V(r_{\alpha}, r_{\beta}),   \tag{1}$$

where H_{α} is the Hamiltonian of the αth electron in the field of the atomic nucleus and $V(r_{\alpha}, r_{\beta})$ is the electron–electron repulsion.

The multielectronic wave function Ψ is approximated by a Slater determinant D of the molecular orbitals ψ_{α},

$$\Psi \cong D = \sum_{\{P\}} \delta_P \frac{P}{(N)^{1/2}} |\psi_1, \psi_2, \ldots, \psi_N|,   \tag{2}$$

where $\delta_P = (-1)^P$ (P is the permutation operator).

The matrix elements of the evolution operator of the molecular system between the initial state $|D_{t_i}\rangle$ and the final state $\langle D_{t_f}|$ can be written as

$$Z(N) = \langle D_{t_f}|e^{-iH(t_f - t_i)}|D_{t_i}\rangle,   \tag{3}$$

where t_i, t_f are the initial and final times, respectively.

One may represent the molecular orbital on a space–time lattice which is gen-erated by breaking the time interval into M time slices of time duration $\tau = (t_f - t_i)/M$. We first factorize the evolution operator into M terms of the form $e^{-i\tau H}$. Hence, eq. (3) reads

$$Z(N) = \prod_{l}^{M} \langle D_{t_f} | D_{t_M} \rangle \langle D_{t_M} | e^{-i\tau H} | D_{t_{M-l}} \rangle \cdots$$

$$\cdots \langle D_{t_{M-l}} | e^{-i\tau H} | D_{t_{M-l-1}} \rangle \cdots \langle D_{t_l} | D_{t_i} . \tag{4}$$

Then, with the above result we arrive, after little algebra, at the following final form of $Z(N)$ [4]:

$$Z(N) = \prod_{j}^{M} \left\{ \prod_{\alpha,\beta}^{N} \int d\psi_{\alpha}^{*}(t_j) \, d\psi_{\beta}(t_j) \, \langle D_{t_f} | D_{t_M} \rangle \langle D_{t_j} | D_{t_i} \rangle \right.$$

$$\times \delta \left[\int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv - \delta_{\alpha,\beta} \right] \Bigg\}$$

$$\times \exp \Bigg\{ -i\tau \left[\sum_{l,j}^{M} \sum_{\alpha,\beta}^{N-1} \left\{ \int dv \, \psi_{\alpha}^{*}(t_l) H_{\beta} \psi_{\alpha}(t_j) \right. \right.$$

$$\left. \left. \left. - \int dv \int dv' \, \psi_{\alpha}^{*}(t_l) \psi_{\beta}^{*}(t_j') V(r_{\alpha}, r_{\beta}') \{ \psi_{\alpha}(t_l) \psi_{\beta}(t_j') - \psi_{\beta}(t_l) \psi_{\alpha}(t_j') \} \right\} \right] \right] \Bigg\},$$

$$\tag{5}$$

where δ, the Dirac function of eq. (5), has the following Fourier integral representation:

$$\delta \left[\int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv - \delta_{\alpha,\beta} \right]$$

$$= \frac{1}{[(2\pi i)^{1/2}]^{N^2}} \int d\epsilon_{\alpha,\beta} \exp \left\{ i\epsilon_{\alpha,\beta} \left[\int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv - \delta_{\alpha,\beta} \right] \right\} . \tag{6}$$

We are now able to introduce the quantum fluctuations into molecular-orbital theory using the Gaussian approximation on the δ-Dirac Fourier integrals equation (6) introduced by Wilson in an Ising model on the lattice [4],

$$\delta \left[\int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv - \delta_{\alpha,\beta} \right] \cong A \int d\epsilon_{\alpha,\beta} \exp \left\{ i \left[U' \left\{ \int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv \right\}^2 \right. \right.$$

$$\left. \left. + \frac{b}{2} \int \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \, dv + \ldots \right] \right\}, \tag{7}$$

where $A = 1/[(2\pi i)^{1/2}]^{N^2}$, $b/2 = -2\epsilon_{\alpha,\beta}\delta_{\alpha,\beta}$, $b = -4U'$, and U' is a positive quantity.

Taking into account the Gaussian approximation (7) in (5), the propagator $Z(N)$ becomes

$$Z(N) = A \prod_{j}^{M} \left\{ \prod_{\alpha,\beta}^{N} \int d\psi_{\alpha}^{*}(t_j) \, d\psi_{\beta}(t_j) \, \langle D_{t_f} | D_{t_M} \rangle \langle D_{t_j} | D_{t_i} \rangle \int d\epsilon_{\alpha,\beta} \right.$$

$$\left. \times \exp\{-i\tau H_{\text{eff}}[\psi_{\alpha}^{*}, \psi_{\beta}, \epsilon]\} \right\}, \tag{8}$$

where the effective Hamiltonian $H_{\text{eff}}[\psi^*, \psi, \epsilon]$ can be cast as

$$H_{\text{eff}}[\psi^*, \psi, \epsilon] = H[\psi^*, \psi] + \sum_{\alpha,\beta}^{N-1} U \left\{ \sum_{j}^{M} \int dv \, \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) \right\}^2$$

$$+ \frac{b}{2} \sum_{j}^{M} \int dv \, \psi_{\alpha}^{*}(t_j) \psi_{\beta}(t_j) + \dots, \tag{9}$$

the constant $U = U'/\tau$ and the functional $H[\psi^*, \psi]$ is given by the expression

$$H[\psi^*, \psi] = \sum_{l,j}^{M} \left\{ \sum_{\alpha,\beta}^{N} \left\{ \int dv \, \psi_{\alpha}^{*}(t_l) H_{\beta} \psi \alpha(t_j) - \int dv \int dv' \, \psi_{\alpha}^{*}(t_l) \psi_{\beta}^{*}(t_j') \right. \right.$$

$$\left. \left. \times V(r_{\alpha}, r_{\beta}) \{ \psi_{\alpha}(t_l) \psi_{\beta}(t_j') - \psi_{\beta}(t_l) \psi_{\alpha}(t_j') \} \right\} \right\}. \tag{10}$$

Therefore, we now consider the effective Hamiltonian in a short time slice. Therewith, according to Wilson's algebraic derivation [4] we add and substract appropriate terms in each of the j and $j+1$ sites in order to arrive at the effective Hamiltonian H_{eff} in a site representation. So that, $\Delta\langle\psi_{\alpha}(t_j)| = \langle\psi_{\alpha}(t_{j+1})| - \langle\psi_{\alpha}(t_j)|$ is the increment of $\langle\psi(t_j)|$ in the j-site,

$$(R(\alpha))_j = \frac{b}{2}(H_{\alpha})_{j,j+1} - \frac{(H_{\alpha})_{j,j+1}}{(H_{\alpha})_{j,j+1}} - 1,$$

$$(U(\alpha))_{j,j+1} = \frac{U'}{(H_{\alpha})_{j,j+1}} \quad \text{and} \quad (B(\alpha,\beta))_{j,j+1} = (V(r_{\alpha}, r_{\beta}))_{j,j+1}.$$

Denoting the lattice spacing as a in the space R^d (d = dimension of the real space R) in the continuum limit ($a \Rightarrow 0, M \Rightarrow \infty$), we can switch to the lattice using the correspondence formulae:

$$j \Rightarrow r,$$

$$\sum_{j} \Rightarrow a^{-d}d,$$

$$\sum_j \Delta |\psi_\alpha(t_j)\rangle\langle\psi_\alpha(t_j)| \Rightarrow a^2 \frac{\partial|\psi_\alpha\rangle}{\partial r}\frac{\partial\langle\psi_\alpha|}{\partial r} .$$

Besides, we have changed the scale of the wave product $|\psi_\alpha\rangle\langle\psi_\alpha| \Rightarrow a^{2-d}|\psi_\alpha\rangle\langle\psi_\alpha|$. Thus, making use of the Coulomb and exchange integrals J_β and K_β, namely,

$$J_\beta = \int dr^d \; \psi_\alpha^* B_0(\alpha,\beta)\psi_\alpha , \tag{11}$$

$$K_\beta = \int dr^d \; \psi_\alpha^* B_0(\alpha,\beta)\psi_\beta , \tag{12}$$

where

$$B_0(\alpha,\beta) = a^{d-4}B(\alpha,\beta) , \tag{13}$$

the effective Hamiltonian equation (9) in the continuum takes on its desired form:

$$H_{\text{eff}}[\psi^*,\psi,\epsilon] = \int dr^d \left\{ \sum_\alpha^N \left(-\frac{\partial|\psi_\alpha\rangle}{\partial r}\frac{\partial\langle\psi_\alpha|}{\partial r} - \frac{m_0^2(\alpha)}{2}|\psi_\alpha\rangle\langle\psi_\alpha| \right) \right.$$
$$\left. + \sum_{\alpha<\beta}^N \left\{ [2|\psi_\alpha\rangle J_\beta\langle\psi_\alpha| - |\psi_\alpha\rangle K_\beta\langle\psi_\alpha|] + \frac{U_0(\alpha)}{4!}(|\psi_\alpha\rangle\langle\psi_\beta|)^2 \right\} \right\} , \tag{14}$$

where

$$\frac{m_0^2(\alpha)}{2} = 2R(\alpha)a^{-2} \tag{15}$$

and

$$\frac{U_0(\alpha)}{4!} = 4!2a^{d-4}U(\alpha) . \tag{16}$$

We notice that the corresponding effective potential V_{eff} reads

$$V_{\text{eff}}[\psi^*,\psi,\epsilon] = -\sum_\alpha \frac{m_0^2(\alpha)}{2}|\psi_\alpha\rangle\langle\psi_\alpha| + \sum_{\alpha<\beta}^N \left\{ [2|\psi_\alpha\rangle J_\beta\langle\psi_\alpha| - |\psi_\alpha\rangle K_\beta\langle\psi_\alpha|] \right.$$
$$\left. + \frac{U_0(\alpha)}{4!}(|\psi_\alpha\rangle\langle\psi_\beta|)^2 \right\} \tag{17}$$

and it has one or two minima depending on the sign of the coefficients $U_0(\alpha)$. So, when the $U_0(\alpha)$ vanishes for all particles, expression (14) reduces to the classical effective Hamiltonian of the linear problem [5].

With reference to the $Z(N)$ propagator, eq. (5) in the continuum [4] reads

$$Z(N) = \int \mathcal{D}[\psi^*]\mathcal{D}[\psi] \prod_{\alpha,\beta}^N \int d\epsilon_{\alpha,\beta} \exp\left(-i \int_{t_i}^{t_f} dt \; H_{\text{eff}}[\psi^*,\psi,\epsilon] \right) , \tag{18}$$

where the path integral measure $\mathcal{D}[\psi^*]\mathcal{D}[\psi]$ is given as

$$\mathcal{D}[\psi^*]\mathcal{D}[\psi] = \lim_{M \to \infty; \tau \to 0} \mathcal{A} \prod_j^M \left\{ \prod_{\alpha,\beta}^N \int d\psi_\alpha^*(t_j) \, d\psi_\beta(t_j) \, \langle D_{t_f}|D_{t_M}\rangle\langle D_{t_j}|D_{t_i}\rangle \right\}.$$

(19)

3. Solvents effect

The non-linear Schrödinger equations arising from the Hamiltonian equation (14) can be used to describe quantum-mechanical systems that interact with their surroundings. Through its wave function, the molecular system interacts with its environment by inducing a net field which then acts back on the system itself.

Thus, the self-consistent reaction field theory of solvent effects is used as an adequate framework to calculate an effective electronic wave function and the electronic energy of a molecule immersed in an environment, where homogeneous and heterogeneous reaction fields in the modelled, surrounding medium effects are involved [6].

We are now ready to link the above-developed formalism of the path integral with the solvent effects. Thus, if we split the effective Hamiltonian equation (14), after a partial integration, into the Hartree–Fock part

$$H_{\text{H–F}}[\psi^*, \psi, \epsilon] = \int dr^d \left\{ \sum_\alpha -|\psi_\alpha\rangle \left[\frac{\partial}{\partial r} + \frac{m_0^2(\alpha)}{2} - \sum_{\alpha \neq \beta}(2J_\beta - K_\beta) \right] \langle \psi_\alpha| \right\}$$

(20)

plus the interaction part

$$H_{\text{I}}[\psi_*, \psi, \epsilon] = \sum_\alpha \frac{U_0(\alpha)}{4!} \int dr^d \, (|\psi_\alpha\rangle\langle\psi_\alpha|)^2$$

$$= \sum_\alpha \frac{\bar{U}_0(\alpha)}{4!} \Lambda^\omega V[\psi^*, \psi]$$

(21)

then, the propagator $Z(N)$ equation (18), by using the eqs. (20) and (21) in expression (14), may be rewritten as

$$Z(N) = \int \mathcal{D}[\psi^*]\mathcal{D}[\psi] \prod_{\alpha,\beta}^N \int d\epsilon_{\alpha,\beta}$$

$$\times \exp\left(-\mathrm{i} \int_{t_i}^{t_f} dt \, [H_{\text{H–F}}[\psi^*, \psi, \epsilon] + H_{\text{I}}[\psi^*, \psi, \epsilon]] \right)$$

$$= Z_{\text{H–F}}[\psi^*, \psi, \epsilon] Z_{\text{I}}[\psi^*, \psi, \epsilon].$$

(22)

We can observe that the potential $V[\psi^*, \psi]$ of the Hamiltonian interaction part in eq. (21) is a function of the ψ^* and ψ. This result is in agreement with Sanhueza et al. [7], where they show that it would be well represented by a power series of the first order density. The potential function appears by applying quantum fluctuations to the molecular system, which is produced by surrounding a molecule by a dielectric environment as in the SCRF theories of solvent effects [1,2]. Thus, the parameter $U_0(\alpha)/4!$ could describe the solute–solvent interaction, which depends upon the mean dielectric constant of the environment.

Therefore, the potential interaction could be expressed as $V[\psi^*, \psi]\langle\psi_\alpha|\boldsymbol{\mu}^T|\psi_\alpha\rangle$ $\cdot\,\mathbf{g}\cdot\langle\psi_\alpha|\boldsymbol{\mu}^T|\psi_\alpha\rangle$, where $\mathbf{g}$ is a coupling tensor, $\boldsymbol{\mu}$ is the total dipolar moment operator and the superscript T designates the transpose of a matrix.

Then, in the case of the real space, the space dimension $d = 3$, $Z_I[\psi^*, \psi, \epsilon]$ can be expressed similar to Onsager's reaction fields approach [2] by

$$
Z_I[\psi^*, \psi, \epsilon] = \int \mathcal{D}[\psi^*]\mathcal{D}[\psi] \prod_{\alpha,\beta}^{N} \int d\epsilon_{\alpha,\beta} \exp\left(-i\int_{t_i}^{t_f} dt \sum_\alpha \frac{\bar{U}_0(\alpha)}{4!} V[\psi_\alpha^*, \psi_\alpha]\right)
$$

$$
= \int \mathcal{D}[\psi^*]\mathcal{D}[\psi] \prod_{\alpha,\beta}^{N} \int d\epsilon_{\alpha,\beta}
$$

$$
\times \exp\left(-i\int_{t_i}^{t_f} dt \sum_\alpha \frac{\bar{U}_0(\alpha)}{4!} \langle\psi_\alpha|\boldsymbol{\mu}^T|\psi_\alpha\rangle \cdot \mathbf{g} \cdot \langle\psi_\alpha|\boldsymbol{\mu}^T|\psi_\alpha\rangle\right).
$$

$$(23)$$

From the above results, we can obtain the Roothaan equation with the solvent effects involved. In the semiempirical approximations (CNDO/2) (see Villar et al. [8]) we can realize calculations of the molecular electronic structure with solvent effects using the dielectric constant as imput data.

The above calculations are only approximate, there are other ways of evaluating the path integral $Z_I[\psi^*, \psi, \epsilon]$: the Monte Carlo algorithm [9] and perturbedly like an ω-expressium technique in critical phenomena [10].

Our procedure would be an alternative treatment of the influence of the solvent in the chemical bond by the Monte Carlo path integral formalism [11], but then using it in the molecular orbital theory framework. This means that we use like coordinates the coefficients of the atomic orbitals representations. In relation to this, but in physical space, we also mention the considerable effort made on new methods of Monte Carlo path integral calculations [12,13].

References

[1] S. Yomosa, J. Phys. Soc. Jpn. 35 (1973) 1738.

[2] O. Tapia, O. Goscinsky, Mol. Phys. 6 (1975) 1653;
O. Tapia, Theor. Chim. Acta (Berl.) 47 (1978) 157.

[3] O. Tapia, J. Mol. Struc. (Theochem) 226 (1991) 59.

[4] J. Marañón, In. J. Quant. Chem. 48 (1993) 151.

[5] J. Marañón, Phys. Lett. A104 (1984) 459; Phys. Rev. A36 (1987) 5530; In. J. Quant. Chem. 33 (1988) 491.

[6] See, for example, O. Tapia and G. Johannin, J. Chem. Phys. 75 (1981) 3624.

[7] See eq. (14) of J.E. Sanhueza, O. Tapia, W.G. Laidlaw and M. Trsic, J. Chem. Phys. 70 (1979) 3096.

[8] P.H. Villar, E.A. Castro and F.M. Fernandez, Chem. Scripta 22 (1982) 49.

[9] Y. Avishai and J. Richert, Phys. Rev. Lett. 50 (1983) 1175.

[10] D.J. Amit, *Field Theory, the Renormalization Groups, and Critical Phenomena* (MacGraw-Hill, New York, 1978).

[11] R.A. Chiles, G.A. Jongeward, M.A. Bolton and P.G. Wolynes, J. Chem. Phys. 87 (1984) 2039.

[12] J. Chang and W.H. Miller, J. Chem. Phys. 87 (1987) 1648.

[13] J.D. Doll, D. Coalson and D.L. Freeman, J. Chem. Phys. 87 (1987) 1641.