

sumably, mercaptoethanol selectively blocks Pd surface sites for activating bicarbonate, thus favoring the transfer of conduction-band electrons to H₂-evolving sites.

A comparison of the selectivity factor can be made between the Pd-TiO₂ systems and the previously examined photosystem²⁹ consisting of the photosensitizer deazariboflavin, dRFI, the electron mediator MV²⁺, the electron donor oxalate, and the catalyst Pd(β -CD, 60 °C) colloids. The best selectivity factor of the Pd-TiO₂ systems (SF = 2.3; see Table I) is larger than that of dRFI/MV²⁺/oxalate/Pd(β -CD, 60 °C) (SF = 0.013), indicating that the former exhibits lower selectivity for HCO₃⁻ reduction with respect to H₂ evolution than the latter. The basis for this difference in selectivity remains to be established, however.

In conclusion, electron transfer from TiO₂ to properly prepared catalytic Pd surface sites promotes the reduction of CO₂/HCO₃⁻

to formate. The selectivity exhibited by the Pd-TiO₂ particle systems is quite noteworthy in relation to other semiconductor-based systems, which generate a broad distribution of products. Specific sites on the Pd surface favor CO₂/HCO₃⁻ reduction over H₂ evolution. The experimental results reported here as well as those of others^{24a} suggest that other metals might exhibit selectivity in catalyzing the reduction of CO₂ to other desirable organic photoproducts.

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Free Energy of a Charge Distribution in a Spheroidal Cavity Surrounded by Concentric Dielectric Continua

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We present a theoretical treatment for the Helmholtz free energy of an arbitrary discrete charge distribution in a central prolate or oblate spheroidal cavity surrounded by two and three concentric dielectric continua of the same symmetry. The electrostatic interaction is accounted for by a multipolar expansion. This model permits us to consider in a simple way nonlinear dielectric effects and the nonsphericity of solute molecules. The results are presented in a suitable form to discuss them in terms of a virtual polarization charge distribution. Also, we give an explicit expression for the contributions coming from the zeroth-order multipole moments for any number of shells.

I. Introduction

Solvent effects can be modeled in three ways. The first, referred to as the continuum approach,¹⁻³ considers the solute localized in an empty cavity embedded in a structureless polarizable dielectric continuous medium. The electrostatic solute-solvent interactions are accounted for by means of reaction field theory⁴ and then incorporated into quantum mechanical formalisms. The second is the supermolecule approach in which the medium is explicitly represented by a finite number of solvent molecules.⁵ The last is a combination of the other two approaches and it is called the "continuum-supermolecule" approach.^{6,7} In the following, we shall center our attention on the continuum models because they give solvation energies with good accuracy maintaining the simplicity of their mathematical formulation and numerical applications.⁷

Continuum models are rooted in the fact that, at larger solute-solvent distances, it is possible to replace the discrete summations of the intermolecular interactions over the solvent molecules with continuous integrals.⁸ On the other hand, they allow the incorporation of temperature-dependent effects.⁹

The earliest analysis was presented in the now classical paper of Born.¹ His work considered a point charge located in the center of a spherical cavity surrounded by a homogeneous continuous medium characterized by the macroscopic dielectric permittivity of the solvent.

This model can be improved in three principal ways. First, the interaction of the homogeneous dielectric continuum with higher

electric moments can be considered. Within this scheme we have the Onsager model in which the solute molecule carries a permanent dipole moment that can be enhanced by the reaction field through an isotropic harmonic polarizability,² and the Kirkwood analysis of the case of discrete point charges inside a spherical cavity employing a multipolar expansion of the charge distribution in the cavity center.⁹ The general case of a polarizable charge distribution was studied later.¹⁰ Quantum mechanical schemes have been derived from these approaches.¹¹⁻¹³

The second improvement takes into account the shape of the cavity. Clearly, spherical cavity models are restricted to physical systems possessing the same symmetry, i.e., spherical ions and molecules. This consideration led to the analysis of spheroidal

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cavities, considering a set of charges in an ellipsoid restricted to dipole polarization when the dipole lies on the interfocal axis.¹⁴ Other publications considered the dipole energy.^{4,15-17} Recently, the general expression for the Helmholtz free energy of a discrete charge distribution in spheroidal cavities was derived.^{18,19} Other cavity shapes have also been considered.²⁰⁻²³

The third improvement considers that, since in the neighborhood of an ion there exist inhomogeneous electric fields of the order of millions of volts/centimeter, the appearance of nonlinear dielectric effects is expected.^{4,24} These effects will produce distance-dependent changes of the medium's permittivity. Therefore, continuum models can be improved by modeling these phenomena. This was done by modifying the Born equation through the introduction of mathematical functions in which the dielectric permittivity of the medium varies continuously with the distance.²⁵⁻²⁹ Nevertheless, the simplest way to consider these effects is to consider a continuum partitioned into concentric shells characterized by different dielectric constants for the spherical case.³⁰⁻³² Following this approach, it has been shown that the partition of the continuum is the best suited to predict solvation energies.^{28,32}

Recently, a quantum chemical formalism using the SCF approximation including local dielectric effects via Beveridge and Schnuelle's partition of the continuum model has been proposed.^{33,34} Its application to the calculation of hydration energies for Li⁺, Na⁺, and F⁻ ions in aqueous solution showed very good agreement with experimental results.³⁴

An extension of the usual quantum mechanical studies makes it necessary to modify the spherical cavity in order to consider the real shape of the solute molecule, and the continuum structure the better to describe dielectric saturation and electrostrictive phenomena. Accordingly, we present here the classical derivation of the Helmholtz free energy for an arbitrary discrete charge distribution in a prolate or oblate spheroidal cavity surrounded by one and two concentric dielectric shells of the same symmetry embedded in a bulk dielectric continuum. The notation and development of the cases discussed here are organized so as to correspond to those presented by Beveridge et al.^{18,30}

II. Background

The derivation is based on Laplace's equation in spheroidal coordinates (λ, μ, θ):

$$\nabla^2(\lambda, \mu, \theta) \Phi(\lambda, \mu, \theta) = 0 \quad (1)$$

where ∇^2 is the Laplacian operator and Φ is the potential at all points other than the sites of the point charges in a discrete charge distribution or at all points outside a continuum distribution.

The reaction potential, Φ_R , can be obtained from the potential inside the cavity, Φ_0 , making use of the boundary conditions

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assuring the continuity of the potential across the cavity surface and the continuity of the normal component of the dielectric displacement vector across the boundary ellipsoid.

The interaction energy, A , is given by

$$A = \frac{1}{2} \sum_{l=1}^M q_l \Phi_R(\vec{r}_l) \quad (2)$$

where q_l is the net charge of the l th particle located at \vec{r}_l .

III. The Prolate Case, Including One Dielectric Layer of the Same Symmetry

Laplace's equation in spheroidal prolate coordinates is

$$\left[\frac{\partial}{\partial \lambda} \left[(\lambda^2 - 1) \frac{\partial}{\partial \lambda} \right] + \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial}{\partial \mu} \right] + \frac{\lambda^2 - \mu^2}{(\lambda^2 - 1)(1 - \mu^2)} \frac{\partial^2}{\partial \theta^2} \right] \Phi(\lambda, \mu, \theta) = 0 \quad (3)$$

where λ and μ are defined as

$$\lambda = (r_A + r_B)/2d \quad 1 \leq \lambda < \infty \quad (4)$$

$$\mu = (r_A - r_B)/2d \quad -1 \leq \mu \leq 1 \quad (5)$$

and θ is the azimuthal angle around the semimajor rotation axis ($0 \leq \theta \leq 2\pi$). Here, r_A and r_B are respectively the distances between the point and the two foci separated by $2d$. For the case analyzed here, the general solution of eq 3 is

$$\Phi = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{B}_{nm} d^n P_n^m(\lambda) + \bar{F}_{nm} d^n P_n^m(\lambda) + \frac{\bar{E}_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (6)$$

where P_n^m and Q_n^m are, respectively, the associated Legendre polynomials of the first and second class.^{18,35}

By the application of the boundary conditions we shall obtain the coefficients \bar{B}_{nm} , \bar{F}_{nm} , and \bar{E}_{nm} of eq 6.

For this purpose, it is convenient to define the function $\Gamma_{nm}(\epsilon, \lambda)$ as the generalization of the γ 's introduced by Abbott and Bolton:¹⁶

$$\Gamma_{nm}(\epsilon, \lambda) \equiv \frac{1 - \epsilon}{\epsilon} \left[\frac{P_n^m(\lambda)}{Q_n^m(\lambda)} - \frac{1}{\epsilon} \frac{\dot{P}_n^m(\lambda)}{\dot{Q}_n^m(\lambda)} \right]^{-1} \quad (7)$$

The potential inside the cavity is

$$\Phi_0 = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{B}_{nm} d^n P_n^m(\lambda) + \bar{F}_{nm} d^n P_n^m(\lambda) + \frac{\bar{E}_{nm} Q_n^m}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (8)$$

where ϵ_0 is the dielectric constant of the cavity.

The terms involving $Q_n^m(\lambda)/d^{n+1}$ can be identified with a multipolar expansion of the potential due to the central charge distribution:

$$\sum_{k=1}^M \frac{q_k}{|r - r_k|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \frac{\bar{E}_{nm}}{d^{n+1}} Q_n^m(\lambda) P_n^m(\mu) e^{im\theta} \quad (9)$$

The potential in the local region is

$$\Phi_1 = (1/\epsilon_1) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{F}_{nm} d^n P_n^m(\lambda) + \frac{\bar{G}_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (10)$$

with a dielectric constant ϵ_1 .

The potential outside the cavity is

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$$\Phi_2 = (1/\epsilon_2) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \frac{\bar{C}_{nm}}{d^{n+1}} Q_n^m(\lambda) P_n^m(\mu) e^{im\theta} \quad (11)$$

ϵ_2 being the bulk dielectric constant.

Inside the cavity, the reaction potential can be written as

$$\Phi_R = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} [\bar{B}_{nm} d^n P_n^m(\lambda) + \bar{F}_{nm} d^n P_n^m(\lambda)] P_n^m(\mu) e^{im\theta} \quad (12)$$

The boundary conditions assuring the continuity of the potential across the surfaces $\lambda = \lambda_0$ and $\lambda = \lambda_1$ are

$$\Phi_0(\lambda_0, \mu, \theta) = \Phi_1(\lambda_0, \mu, \theta) \quad (13)$$

$$\Phi_1(\lambda_1, \mu, \theta) = \Phi_2(\lambda_1, \mu, \theta) \quad (14)$$

and the boundary conditions assuring the continuity of the normal component of the dielectric displacement vector across these surfaces are

$$\epsilon_0 \frac{\partial \Phi_0(\lambda, \mu, \theta)}{\partial \lambda} \Big|_{\lambda=\lambda_0} = \epsilon_1 \frac{\partial \Phi_1(\lambda, \mu, \theta)}{\partial \lambda} \Big|_{\lambda=\lambda_0} \quad (15)$$

$$\epsilon_1 \frac{\partial \Phi_1(\lambda, \mu, \theta)}{\partial \lambda} \Big|_{\lambda=\lambda_1} = \epsilon_2 \frac{\partial \Phi_2(\lambda, \mu, \theta)}{\partial \lambda} \Big|_{\lambda=\lambda_1} \quad (16)$$

where the parameters $\lambda_0 = \lambda_1$ are defined by

$$\lambda_0 = a_0/d \quad \text{and} \quad \lambda_1 = a_1/d \quad (17)$$

a_0 and a_1 being the semimajor axis of the cavity and the layer, respectively.

Since the Legendre polynomials constitute a linearly independent set of functions, the boundary conditions can be applied term by term to Φ_0 , Φ_1 , and Φ_2 , leading respectively to

$$(1/\epsilon_0) \left[\bar{B}_{nm} d^n P_n^m(\lambda_0) + \bar{F}_{nm} d^n P_n^m(\lambda_0) + \frac{\bar{E}_{nm}}{d^{n+1}} Q_n^m(\lambda_0) \right] = (1/\epsilon_1) \left[\frac{\bar{G}_{nm}}{d^{n+1}} Q_n^m(\lambda_0) + (1/\epsilon_1) \bar{F}_{nm} d^n P_n^m(\lambda_0) \right] \quad (18)$$

$$(1/\epsilon_1) \left[\bar{F}_{nm} d^n P_n^m(\lambda_1) + \frac{\bar{G}_{nm}}{d^{n+1}} Q_n^m(\lambda_1) \right] = (1/\epsilon_2) \frac{\bar{C}_{nm}}{d^{n+1}} Q_n^m(\lambda_1) \quad (19)$$

$$\bar{B}_{nm} d^n \dot{P}_n^m(\lambda_0) + \frac{\bar{E}_{nm}}{d^{n+1}} \dot{Q}_n^m(\lambda_0) = \frac{\bar{G}_{nm}}{d^{n+1}} \dot{Q}_n^m(\lambda_0) \quad (20)$$

$$\bar{F}_{nm} d^n \dot{P}_n^m(\lambda_1) + \frac{\bar{G}_{nm}}{d^{n+1}} \dot{Q}_n^m(\lambda_1) = \frac{\bar{C}_{nm}}{d^{n+1}} \dot{Q}_n^m(\lambda_1) \quad (21)$$

Starting from eqs 19 and 21 and carrying out a little algebra, we obtain

$$\bar{F}_{nm} = \frac{\Gamma_{nm}(\epsilon_{a_1}, \lambda_1) \bar{G}_{nm}}{d^{2n+1}} \quad (22)$$

where ϵ_{a_1} is defined as

$$\epsilon_{a_1} = \epsilon_2/\epsilon_1 \quad (23)$$

and $\Gamma_{nm}(\epsilon_{a_1}, \lambda_1)$ is given by eq 7.

Working eqs 18 and 22, we find

$$\bar{G}_{nm} = \epsilon'_{a_0} \left[\bar{B}_{nm} d^{2n+1} \frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)} + \bar{E}_{nm} \right] \quad (24)$$

where ϵ'_{a_0} is defined as

$$\epsilon'_{a_0} = \epsilon_{a_0} \left[1 + (1 - \epsilon_{a_0}) \Gamma_{nm}(\epsilon_{a_1}, \lambda_1) \frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \right]^{-1} \quad (25)$$

and

$$\epsilon_{a_0} = \epsilon_1/\epsilon_0 \quad (26)$$

Eliminating \bar{G}_{nm} from eqs 20 and 24, we get

$$\bar{B}_{nm} = \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\bar{E}_{nm}}{d^{2n+1}} \quad (27)$$

By substituting eqs 24 and 27 into eq 22, and noting that

$$\epsilon \left[1 + \Gamma_{nm}(\epsilon, \lambda) \frac{P_n^m(\lambda)}{Q_n^m(\lambda)} \right] = 1 + \Gamma_{nm}(\epsilon, \lambda) \frac{\dot{P}_n^m(\lambda)}{\dot{Q}_n^m(\lambda)} \quad (28)$$

we get for the coefficients \bar{F}_{nm} :

$$\bar{F}_{nm} = \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{\dot{Q}_n^m(\lambda_0)} \right] \frac{\Gamma_{nm}(\epsilon_{a_1}, \lambda_1)}{d^{2n+1}} \bar{E}_{nm} \quad (29)$$

By inserting expressions 27 and 29 in the reaction potential (eq 12), we obtain

$$\Phi_R = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) + \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{\dot{Q}_n^m(\lambda_0)} \right] \Gamma_{nm}(\epsilon_{a_1}, \lambda_1) \right] \frac{\bar{E}_{nm}}{d^{n+1}} P_n^m(\lambda) P_n^m(\mu) e^{im\theta} \quad (30)$$

It is possible to define the constants \bar{E}_{nm} in terms of the ones published for the concentric spheres³⁰ in order that the formulas derived here reduce properly to the expressions for the spherical case when the eccentricity of the ellipsoids approaches zero. These definitions are

$$\bar{E}_{nm} = (-1)^m (2n+1) \left[\frac{(n-m)!}{(n+m)!} \right]^2 d^n \sum_{k=1}^M q_k P_n^m(\lambda_k) P_n^m(\mu_k) e^{-im\theta_k} \quad (31)$$

By using the expression for the Helmholtz free energy (eq 2) and eqs 30 and 31, we obtain

$$A = (1/2\epsilon_0) \sum_{n=0}^{\infty} \frac{2n+1}{d} \sum_{k=1}^M \sum_{l=1}^M q_k q_l \sum_{m=-n}^{+n} (-1)^m \times \left[\frac{(n-m)!}{(n+m)!} \right]^2 \left[\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) + \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{\dot{Q}_n^m(\lambda_0)} \right] \Gamma_{nm}(\epsilon_{a_1}, \lambda_1) \right] P_n^m(\lambda_1) P_n^m(\mu_1) P_n^m(\lambda_k) \times P_n^m(\mu_k) e^{im(\theta_l - \theta_k)} \quad (32)$$

The verification of this equation can be carried out in two ways. The first one consists in taking the limit when d approaches zero, the case in which the eccentricity of the spheroids tends to zero (i.e., the spheroids tend to spheres). The mathematical work is based on eqs 27–36 of Beveridge's paper¹⁸ and permits one to obtain the expression for the Helmholtz free energy for a charge distribution in a spherical cavity surrounded by a local dielectric continuum of equal symmetry embedded in a dielectric continuum (ref 30, eq 40).

The second procedure permits us to recuperate the expression of the Helmholtz free energy previously obtained for a discrete charge distribution in a prolate spheroidal cavity embedded in a single continuum dielectric (ref 18, eq 26). This can be carried out by taking the limit case when ϵ_1 tends to ϵ_0 or to ϵ_2 . For example, let us consider the last situation. In this case ϵ_{a_1} in eq 23 tends to 1 and $\Gamma_{nm}(\epsilon_{a_1}, \lambda_1)$ (eq 7) tends to zero. Introducing this result into eq 25, we can see that ϵ'_{a_0} tends to ϵ_{a_0} and ϵ_{a_0} tends to ϵ_2/ϵ_0 (eq 26). If we introduce this limit in $\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0)$, we get eq 23 of ref 18. This last result, coupled to the result when $\Gamma_{nm}(\epsilon_{a_1}, \lambda_1)$ tends to zero in eq 32, allows us to recuperate eq 26 of ref 18.

IV. The Oblate Case, Including One Dielectric Layer of the Same Symmetry

Laplace's equation in a spherical oblate coordinates is

$$\left[\frac{\partial}{\partial \lambda} \left[(1 + \lambda^2) \frac{\partial}{\partial \lambda} \right] + \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial}{\partial \mu} \right] + \frac{\lambda^2 + \mu^2}{(1 - \mu^2)(1 + \lambda^2)} \frac{\partial^2}{\partial \theta^2} \right] \Phi(\lambda, \mu, \theta) = 0 \quad (33)$$

where λ and μ are defined as

$$(\lambda^2 + 1)^{1/2} = (r_A + r_B)/2d \quad 1 \leq \lambda < \infty \quad (34)$$

$$(1 - \mu^2)^{1/2} = (r_A - r_B)/2d \quad 0 \leq \mu \leq 1 \quad (35)$$

θ being the azimuthal angle around the semiminor rotation axis with values between 0 and 2π , and r_A , r_B , and d are defined as in the prolate case.

The resolution and verification of this problem follows an identical line as in the prolate case with the only difference that we need to work in the complex plane by replacing λ and d everywhere by $i\lambda$ and d/i , respectively (ref 35 and Appendix of ref 18).

The final equations are

$$A = (1/2\epsilon_0) \sum_{n=0}^{\infty} \frac{2n+1}{d} \sum_{k=1}^M \sum_{l=1}^M q_k q_l \sum_{m=-n}^{+n} (-1)^m \times \left[\frac{(n-m)!}{(n+m)!} \right]^2 \left[\Gamma_{nm}(\epsilon'_{a_0}, i\lambda_0) + \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, i\lambda_0) \frac{\dot{P}_n^m(i\lambda_0)}{Q_n^m(i\lambda_0)} \right] \Gamma_{nm}(\epsilon_{a_1}, i\lambda_1) \right] P_n^m(i\lambda_k) P_n^m(i\lambda_k) \times P_n^m(\mu_l) P_n^m(\mu_k) e^{im(\theta - \theta_k)} \quad (36)$$

where $\Gamma_{nm}(\epsilon'_{a_0}, i\lambda_0)$, $\Gamma_{nm}(\epsilon_{a_1}, i\lambda_1)$ and ϵ'_{a_0} differ from the ones for the prolate case only in that the arguments of the Legendre polynomials are complex in eqs 7 and 25.

V. The Prolate Case, Including Two Dielectric Layers of the Same Symmetry

The general solution of Laplace's equation (eq 1) for this problem is

$$\Phi = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{B}_{nm} d^n P_n^m(\lambda) + \bar{F}_{nm} d^n P_n^m(\lambda) + \bar{G}_{nm} d^n P_n^m(\lambda) + \frac{\bar{E}_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (37)$$

with d , λ , μ , and θ being the same as in section III.

The potential inside the cavity is

$$\Phi_0 = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{B}_{nm} d^n P_n^m(\lambda) + \bar{F}_{nm} d^n P_n^m(\lambda) + \bar{G}_{nm} d^n P_n^m(\lambda) + \frac{\bar{E}_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (38)$$

The potential in the internal local region is

$$\Phi_1 = (1/\epsilon_1) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{F}_{nm} d^n P_n^m(\lambda) + \bar{G}_{nm} d^n P_n^m(\lambda) + \frac{\bar{K}_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (39)$$

The potential in the external local region is

$$\Phi_2 = (1/\epsilon_2) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\bar{G}_{nm} d^n P_n^m(\lambda) + \frac{L_{nm}}{d^{n+1}} Q_n^m(\lambda) \right] P_n^m(\mu) e^{im\theta} \quad (40)$$

The external potential is

$$\Phi_3 = (1/\epsilon_3) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \bar{M}_{nm} Q_n^m(\lambda) P_n^m(\mu) e^{im\theta} \quad (41)$$

The reaction potential inside the cavity is

$$\Phi_R = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} [\bar{B}_{nm} d^n + \bar{F}_{nm} d^n + \bar{G}_{nm} d^n] P_n^m(\lambda) P_n^m(\mu) e^{im\theta} \quad (42)$$

The application of the boundary conditions for this case, the resolution of the resulting set of equations, and the use of eq 31 lead to the following expression for the reaction potential:

$$\Phi_R = (1/\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) + \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \times \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \right] + \Gamma_{nm}(\epsilon_{a_2}, \lambda_2) \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \right] \right] \left[1 + \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \frac{\dot{P}_n^m(\lambda_1)}{Q_n^m(\lambda_1)} \right] \frac{P_n^m(\lambda)}{d^{n+1}} \bar{E}_{nm} P_n^m(\mu) e^{im\theta} \quad (43)$$

with the definitions

$$\lambda_0 = a_0/d, \quad \lambda_1 = a_1/d, \quad \lambda_2 = a_2/d \quad (44)$$

$$\epsilon_{a_0} = \epsilon_1/\epsilon_0, \quad \epsilon_{a_1} = \epsilon_2/\epsilon_1, \quad \epsilon_{a_2} = \epsilon_3/\epsilon_2 \quad (45)$$

a_0 , a_1 , and a_2 being respectively the semimajor axis of the internal to external surfaces limiting the different dielectrics, and

$$\epsilon'_{a_1} = \epsilon_{a_1} \left[1 + (1 - \epsilon_{a_1}) \Gamma_{nm}(\epsilon_{a_2}, \lambda_2) \frac{P_n^m(\lambda_1)}{Q_n^m(\lambda_1)} \right]^{-1} \quad (46)$$

$$\epsilon'_{a_0} = \epsilon_{a_0} \left[1 + (1 - \epsilon_{a_0}) \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \right]^{-1} \quad (47)$$

$$\epsilon''_{a_0} = \epsilon'_{a_0} \left[1 + \frac{\epsilon'_{a_0}}{\epsilon_{a_0}} (1 - \epsilon_{a_0}) \frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \left[1 + \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \frac{\dot{P}_n^m(\lambda_1)}{Q_n^m(\lambda_1)} \right] \Gamma_{nm}(\epsilon_{a_2}, \lambda_2) \right]^{-1} \quad (48)$$

In an analogous way to the case of the prolate with one layer, we obtain for the Helmholtz free energy:

$$A = (1/2\epsilon_0) \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \left[\frac{2n+1}{d} \right] \sum_{k=1}^M \sum_{l=1}^M q_k q_l \sum_{m=-n}^{+n} (-1)^m \times \left[\frac{(n-m)!}{(n+m)!} \right]^2 \left[\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) + \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \times \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_1)}{Q_n^m(\lambda_1)} \right] + \Gamma_{nm}(\epsilon_{a_2}, \lambda_2) \times \left[1 + \Gamma_{nm}(\epsilon'_{a_1}, \lambda_1) \frac{\dot{P}_n^m(\lambda_1)}{Q_n^m(\lambda_1)} \right] \right] \left[1 + \Gamma_{nm}(\epsilon'_{a_0}, \lambda_0) \frac{\dot{P}_n^m(\lambda_0)}{Q_n^m(\lambda_0)} \right] \times P_n^m(\lambda_k) P_n^m(\lambda_l) P_n^m(\mu_k) P_n^m(\mu_l) e^{im(\theta - \theta_k)} \quad (49)$$

The verification of eq 49 can be carried out in an analogous way to eq 32, i.e., by taking the limiting case when two neighborhood dielectrics become identical in their permittivity properties. This work leads to eq 32.

Starting from eqs 43 and 49 we may obtain directly the reaction potential and the Helmholtz free energy for a charge distribution contained in an oblate spheroidal cavity surrounded by two layers of different dielectric constant and embedded in a dielectric continuum.

VI. Discussion

Equations 32, 36, and 49 are the general expressions for the interaction energy of an arbitrary discrete charge distribution embedded in a spheroidal cavity surrounded by two and three concentric dielectric continua. This energy can be assimilated to the reversible work necessary to transfer isothermally a non-polarizable assembly of charges from the vacuum to the cavitated polarizable solvent. Therefore, it corresponds to a Helmholtz free energy and represents the electrostatic contribution to the solvation free energy. The insertion process induces a polarization of the medium that acts back over the solute by generating the reaction potential given by eqs 30 and 43.

Each value of n appearing in the summations of eqs 32, 36, 49, 39, and 43 corresponds to the contributions to the polarization energies and to the reaction potential coming from the multipoles of n th order. Thus, the first term in eqs 32 and 49 (i.e., $n = 0$) is the prolate spheroidal analogue of the Born charging energy in a layered medium, and the second one (i.e., $n = 1$) the Onsager dipole polarization energy analogue.

In eq 32, the first term between the double brackets (i.e., $\Gamma_{nm}(\epsilon'_{a_0}, \lambda_0)$) corresponds to a weighting factor accounting for the multipole-polarized local region interaction. The second one arises from the long-range polarization of the external region. Both terms play the role of reaction field coefficients. These factors are dependent on the cavity shapes, through λ_0 and λ_1 , and of the dielectric properties of the whole solvent. For example, ϵ'_{a_0} in eq 25 is a relative measure of the effects of the rising of the dielectric constant from the local to the external region, combined with the thickness of the local region. If we consider the rest of the terms appearing in this equation, with the exception of $(1/2\epsilon_0)$ and of the summations of n and m , we can see that they can be identified with the square of the ellipsoidal multiple moments.^{19,35} The depend only on the nuclear geometry, atomic net charges of the solute, and interfocal separation. The physical meaning of the terms appearing in eqs 30 and 43 is similar.

For the one-layer prolate case, the contribution to the Helmholtz free energy from the term with $n = 0$ is (see eq 32)

$$A_0 = \frac{1}{4} \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_0} \right] \frac{q_0^2}{d} \ln \left[\frac{\lambda_0 + 1}{\lambda_0 - 1} \right] + \frac{1}{4} \left[\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right] \frac{q_0^2}{d} \ln \left[\frac{\lambda_1 + 1}{\lambda_1 - 1} \right] \quad (50)$$

q_0 being the net charge of the distribution.

By using eq 2 for a single particle, we may rewrite eq 50 as

$$A_0 = \frac{1}{2} q_0 \Phi_r^0 \quad (51)$$

where

$$\Phi_r^0 = \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_0} \right] \frac{q}{2d} \ln \left[\frac{\lambda_0 + 1}{\lambda_0 - 1} \right] + \left[\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right] \frac{q}{2d} \ln \left[\frac{\lambda_1 + 1}{\lambda_1 - 1} \right] \quad (52)$$

In a similar way to the case of a spherical cavity embedded in concentric shells,³⁴ we may consider that the polarization of the concentric dielectric continua is reduced to the creation of two sets of fictitious polarization charges:

$$q_i^{\text{pol}} = \left[\frac{1}{\epsilon_{i+1}} - \frac{1}{\epsilon_i} \right] q_0, \quad i = 0 \text{ or } 1 \quad (53)$$

By inserting eqs 53 into eq 52 we get

$$\Phi_r^0 = \frac{q_0^{\text{pol}}}{2d} \ln \left[\frac{\lambda_0 + 1}{\lambda_0 - 1} \right] + \left[\frac{q_1^{\text{pol}}}{2d} \right] \ln \left[\frac{\lambda_1 + 1}{\lambda_1 - 1} \right] \quad (54)$$

In eq 54, the first term represents the electrostatic potential at the surface $\lambda = \lambda_0$ due to an uniform line charge with a total charge of q_0^{pol} , distributed between the foci of the cavity. The second term is the potential generated at $\lambda = \lambda_1$ by the linear

distribution with a charge of q_1^{pol} . The other cases can be analyzed in a similar form.

This study permits the generalization for any number of concentric shells. For example, in the prolate case with p local layers we have that the monopole contribution to the polarization energy is

$$A_0 = \frac{q_0^2}{4d} \sum_{l=0}^p \left[\frac{1}{\epsilon_{l+1}} - \frac{1}{\epsilon_l} \right] \ln \left[\frac{\lambda_l + 1}{\lambda_l - 1} \right] \quad (55)$$

where ϵ_{p+1} is the bulk dielectric constant.

By using the appropriate series expansion we have

$$A_0 = \frac{q_0^2}{2d} \sum_{l=0}^p \left[\frac{1}{\epsilon_{l+1}} - \frac{1}{\epsilon_l} \right] \sum_{t=0}^{\infty} \left[\frac{\lambda_l^{-2t-1}}{2t+1} \right] \quad (56)$$

Remembering that $\lambda_l = a_l/d$, we get the following expression for the case in which $p = 0$ and $t = 0$:

$$A_0 = \frac{q_0^2}{2} \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_0} \right] \frac{1}{a_0} \quad (57)$$

expression corresponding to the Born equation.

From eqs 55 and 56, we can see that A_0 is dependent on the net charge. If the eccentricity e_l remains constant, A_0 is inversely proportional to the interfocal distance. Given that $\lambda_l = e_l^{-1}$, it is possible to see from eq 56 that the minimum response is attained when e_l tends to zero. However, even though this is mathematically true, it is not necessarily correct in real cases given that a lowering of d increases the linear charge density of the virtual line charge, and the nonlinear dielectric effects become more pronounced, affecting the term $(\epsilon_{l+1}^{-1} - \epsilon_l^{-1})$. In the limiting case, in which the spheroid tends to a sphere, A_0 is given by eq 56 with $t = 0$. On the other hand, with a fixed d and when λ_l tends to infinity, the logarithmic function of eq 55 vanishes. This means that the contribution to A_0 of distance layers is negligible. This last behavior is accentuated by the asymptotic behavior of ϵ .

The partition of the solvent in diverse regions constitutes a simple form of modeling nonlinear dielectric effects. For example, in the case of ionic aqueous solutions, it is generally accepted that the medium consists of three main regions.^{28,29,36} The first one corresponds to the first solvation layer in which the highly oriented water molecules strongly decrease the medium's permittivity. The thickness of this layer is approximately a water molecule diameter. The second region extends from one to three solvent molecule diameters. Here, the dielectric constant increases abruptly to its macroscopic value. The third region is the bulk region. These effects can be modeled through eq 49. Obviously, the quality of the results will depend on the correct choice for the thickness and dielectric constants of the layers. A good selection should be based on a good understanding of the nonlinear dielectric effects for a given solute-solvent couple. This selection is particularly important for the inner layer, from which the most important contributions to the electrostatic free energy arise.^{6,28,29}

It is considered that nonlinear dielectric effects induced by neutral dipolar molecules are negligible. These cases can be modeled through eqs 26 and 47 and ref 18, for approximately spheroidal molecules. However, it should be expected that for charged solutes or highly dipolar species such as zwitterions, an appropriate continuum partition will give a better description of the solvation energetic.

The incorporation of this model into quantum-mechanical formalisms constitutes an easy way to take into account solvent effects, specially in large molecules. However, when molecular size increases, there is an increase of the cavitation energy, and theoretical deviations are expected (for the solvation energetic, see refs 6, 7, 32, and 37). To evaluate this contribution, we may employ Monte Carlo calculations,³⁸ scaled particle theory,³⁹ or

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surface tension measurements.^{40,41} On the other hand, continuum models are valid when only Columbic forces are present. If short-range interactions are important, a good selection is to use the continuum + supermolecule approach.

Finally, the selection of the cavity's geometrical parameters may start by considering the barycenter of the nuclear charges and the molecular volume.^{19,42,43}

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In the next related contribution, we shall present a quantum-mechanical scheme including the models developed here, together with numerical results for comparison with current methodologies.

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Exact Solution to the One- and Two-Dimensional Models of the Binary Lattice with Nearest-Neighbor Interactions

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The "extended sequential construction method", which is newly introduced in this paper, is used for an exact solution to the binary lattice model in the closed form. In section I, this method is applied to a one-dimensional model and a two-dimensional model of a square lattice, for the cases where the fractions of species are not equal ($f \neq 0.5$), and the special case ($f = 0.5$) is being considered in section II. Application of this method to other two-dimensional, and all three-dimensional, models seems to be straightforward. In the cases where $f \neq 0.5$, no first-order phase transition has been found, which is in agreement with the fact that this transition may occur only when $f = 0.5$. However, in the case where $f = 0.5$, the results of our calculations show that no first-order phase transition occurs in the case of a one-dimensional model, and the configurational heat capacity (against temperature) goes through a maximum continuously. For the case of a two-dimensional model (of the square lattice), when $f = 0.5$, first-order phase-transition phenomenon occurs, and the critical temperature is located roughly at the point $x_c = 0.41$, where $x_c = \exp(\epsilon/kT_c)$. A simple exact expression is also obtained for the heat capacity of the one-dimensional model when $f = 0.5$.

Introduction

One may see the terms "binary alloy model", "Ising model", and "lattice gas model" in the literature, all of which may physically be related to the same problem. In these simplified ideal models, the interactions between nearest-neighbors are only considered. These terms are used to explain the nature of different interactions, such as the interactions between different pairs (AA, AB, and BB), in the binary lattice; spins, in Ising model; the atoms that are located on the nearest-neighbor sites, in the lattice gas model. These models have been used in the study of different phenomena in solids, such as adsorption (in the one- and two-dimensional (1D and 2D) lattice gas model), absorption (in the three-dimensional (3D) lattice gas model), ferromagnetism and antiferromagnetism, order-disorder, phase transition, and critical temperature.

Recently, the sequential construction method, SCM,¹ and the modified sequential construction method, MSCM,² were introduced for statistical mechanical studies of special models, specifically Andersen and Mazo's model³ for the feldspar minerals. The main approximation in these methods is that the identical sites of "solid" and "nonsolid" are treated nonidentically, in view of the order of the distribution of atoms among sites. Unlike most other cases, the site energies are more important than the interaction energies in feldspar minerals. The main points of this work are then (1) to take the interaction energies, instead of site energies, into account and (2) to eliminate the nonidentical treatment of the solid and nonsolid sites when we distribute atoms among sites. The elimination of discriminations among equivalent sites of solid and nonsolid, in SCM and MSCM, leads to the exact solution.

The first exact solution to the one-dimensional problem was given by Ising,⁴ who used a combinatorial argument. A matrix method was introduced later by Kramer.⁵ The matrix method was used by Onsager⁶ who, after a very long and sophisticated argument, was able to obtain the solution to a 2D square lattice in closed form, for only the case in which $f = 0.5$. In a later effort, Kaufman⁷ succeeded in cutting the algebra to a great extent. As far as we know, no exact solution is given for the 3D model. The only available solutions for this model are in the form of a series expansions.⁸ More information on this matter can be obtained from ref 9.

Although, the problem of the one-dimensional model has been solved by some approaches, the extended sequential construction method, ESCM, for the one-dimensional model will be considered first because of its simple presentation.

I. General Cases

Application of ESCM to One-Dimensional Model. We consider a binary lattice with N sites that are located along a straight line. Each site is only occupied by one atom, A, or B. We also assume an interaction energy between the nearest-neighbor atoms, which is denoted by ϵ_{AA} , ϵ_{AB} , and ϵ_{BB} , respectively for AA, AB, and BB pairs. Now, we show how to calculate the exact com-

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