C. 3

MAR 4 1997

SAND97-8230 • UC-411
Unlimited Release
Printed January 1997

Single-and Double-Layer Coupling of Schrödinger and Poisson-Boltzmann Equations

(To be published in Chemical Physics Letters)

W. D. Wilson, C. M. Schaldach, W. L. Bourcier

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.

SF2900Q(8-81)

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.
NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of the contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors or subcontractors.

SAND 97-8230
Unlimited Release
Printed January 1997

UC-411

Single-and Double-Layer Coupling of Schrödinger and Poisson-Boltzmann Equations

W. D. Wilson
Materials and Process Research Department
Sandia National Laboratories/California

C. M. Schaldach
University of California
Berkeley, CA 94720

W. L. Bourcier
Lawrence Livermore National Laboratories
Livermore, CA 94550

ABSTRACT

We present a method for incorporating solvent effects, including ionic strength, into ab initio electronic structure determinations and apply the method to the calculation of the free energy of solvation of the carbonate ion, CO_3^{-2}. The Green's function-based method couples the Schrödinger and linearized Poisson-Boltzmann equations through both the single and double layer surface charge distributions induced at a molecular-solvent interface. Single and double layers of charge are obtained from solution of the Poisson-Boltzmann equation (and added iteratively to the Hamiltonian) using electronic structure results (MP2/6-31G**) directly, eliminating the uncertainty in employing fractional charges.

Single-and Double-Layer Coupling of Schrödinger and Poisson-Boltzmann Equations

I. Introduction

A great deal of recent interest in solvation and, in particular, ionic strength effects, has been spearheaded by the biological community, challenged by the study of proteins and nucleic acids in aqueous environments. An extensive review of molecular interactions in solution has been provided by Tomasi and Persico (1). Hawkins, Cramer and Truhlar (2) have coupled semi-empirical quantum calculations with solutions of the Poisson equation to include solvation effects in the determination of the free energy of large molecules. Miertus, Scrocco and Tomasi (3) and also Zauhar and Morgan (4) made use of the boundary element method to solve the Poisson equation, a method which reduces the three dimensional problem to two-dimensional integrals over surfaces bounding regions characterized by different dielectric constants. Atoms within a molecule are assigned fractional source charges and Gauss's Law is applied on a discretized molecular boundary. Juffer, et al (5) developed a Green's function approach to the solution of the linearized Poisson-Boltzmann equation enabling ionic strength effects to be included. Zhou (6) extended and applied such a method to multiple boundaries. Grant, Williams and Scheraga (7) coupled a Poisson description of the solvent region (zero ionic strength) through a boundary element calculation to a quantum mechanical description of a molecule. They obtained potentials and electric fields at surface elements directly from the wave functions, eliminating possible inaccuracies introduced by representing the molecular charge distribution by fractional charges.

The linearized Poisson-Boltzmann equation formally applies only in regions where the potential, $\phi < kT$, and breaks down elsewhere, e. g., in the neighborhood of a strongly polarizing charge (5). Finite difference methods avoid the linear approximation by solving the full three-dimension Poisson-Boltzmann equation; several authors have coupled such a

three-dimensional calculation to ab initio charge distributions (8-11). The accuracy of the method, which originated with the work of Warwicker and Watson (12), depends upon a rectangular grid over all space, making convergence as a function of volume element size difficult to demonstrate. The discontinuity in dielectric constants is at the molecular interface, more naturally treated with surface elements than with a cubic lattice. Furthermore, as Zhou has pointed out (6), resolution problems make it difficult to apply this method to two separated molecules. Tannor, et al (8) have recently applied such a three-dimensional method, coupled to an ab initio calculation, to the determination of the solvation free energy of a number of organic molecules in water. The coupling is achieved by first determining partial charges from the electronic structure calculation using electrostatic fitting procedures. These point charges are then incorporated as source terms in the 3D Poisson-Boltzmann solver. Chen, et al (9) have used a similar method involving point charges fitted to density functional calculations.

We present a Green's function-based boundary element method which couples an ab initio electronic structure calculation to a Poisson-Boltzmann solution including ionic strength effects. The coupling is accomplished through both the single and double layers of charge at the boundary and allows for relaxation of the quantum electronic charge distribution in response to these surrounding layers. The method eliminates the need for assigning fractional charges at atomic positions within the boundary. The method is applied to the solvation energy of the doubly-charged carbonate ion and also to neutral carbon dioxide for comparison. In Section II, we present the Poisson-Boltzmann method generalized to include an arbitrary number of boundaries as well as the single-and-double-layer method of coupling (SDLC) the Poisson-Boltzmann with electronic structure calculations. Section III contains the results, including a validation for a spherical model for which an analytic solution is available.

II. Method of Calculation

A. Poisson-Boltzmann

We wish to find the electrostatic potential anywhere in space and the associated surface charge distribution associated with multiple boundaries separated by an intervening (solvent) medium characterized by a dielectric constant, ε_s, and a Debye length, κ^{-1}. Inside the boundaries, Poisson's Equation is satisfied while in the medium the linearized Poisson-Boltzmann Equation applies. The potential, $\phi_i(\mathbf{x})$, at a general point inside boundary i can be represented as

$$\phi_i(\mathbf{x}) = \int_{V_i} \frac{G\rho_i}{\varepsilon_i} dV_i + \frac{1}{4\pi} \oint_{S_i} \left[G \frac{\partial \phi_i}{\partial n_i} - \phi_i^{S_i} \frac{\partial G}{\partial n_i} \right] dS_i \tag{1}$$

and in the solvent region by,

$$\phi_s(\mathbf{x}) = \frac{1}{4\pi} \sum_{k=1}^{N_b} \oint_{S_k} \left[-P \frac{\partial \phi_s}{\partial n_k} + \phi_s^{S_k} \frac{\partial P}{\partial n_k} \right] dS_k \tag{2}$$

In the above, G is the Green's function for the Poisson Equation, $P = G\exp(-\kappa r)$, N_b is the number of boundaries; ε_i is the dielectric constant of region i; $\phi_s^{S_k}$ is the surface potential ($\phi_i^{S_i} = \phi_s^{S_k}$ for k=i); ρ_i is the real charge distribution within i (often approximated with fractional point charges in the absence of a more accurate charge distribution). The directions of the normals, n_i, are outward from the boundaries which are discretized into nodes (or "dots") on a molecular surface (13). The nodes form the vertices of triangular elements. Taking appropriate limits (5,14) as a boundary is approached from inside and out, one can express the potential at an element p on its inside, ψ_i^p, as,

$$\psi_i^p = \int_{V_i} \frac{G\rho_i}{\varepsilon_i} dV_i + \frac{1}{4\pi} \sum_q G_{ii}^{pq} \frac{\partial \phi_i^q}{\partial n_i} \Delta S_i^q - \frac{1}{4\pi} \sum_q A_{ii}^{pq} \phi_i^q \Delta S_i^q \tag{3}$$

and on its solvent side as,

$$\psi_{s_i}^p = -\frac{1}{4\pi} \sum_{k=1}^{N_b} \sum_{q=1}^{M_i} P_{ik}^{pq} \frac{\partial \phi_{S_i}^q}{\partial n_i} \Delta S_i^q + \frac{1}{4\pi} \sum_{k=1}^{N_b} \sum_{q=1}^{M_i} B_{ik}^{pq} \phi_{S_i}^q \Delta S_i^q \tag{4}$$

where M_i is the number of elements comprising boundary i; ΔS_i^q the elemental surface area associated with the qth element of the ith boundary. G_{ii}^{pq}, A_{ii}^{pq}, P_{ik}^{pq} and B_{ik}^{pq} are defined below.

Taking the directional derivative with respect to the outward normal gives

$$\frac{\partial \psi_i^p}{\partial n_i} = -\mathbf{n}_i^p \bullet \mathbf{E}_i^p + \frac{1}{4\pi}\sum_{q=1}^{M_i} A_{ii}^{pq} \frac{\partial \phi_i^q}{\partial n_i} \Delta S_i^q - \frac{1}{4\pi}\sum_{q=1}^{M_i} C_{ii}^{pq} \phi_i^q \Delta S_i^q \tag{5}$$

$$\frac{\partial \psi_{S_i}^p}{\partial n_i} = -\frac{1}{4\pi}\sum_{k=1}^{N_b}\sum_{q=1}^{M_k} B_{ik}^{pq} \frac{\partial \phi_{S_k}}{\partial n_k} \Delta S_k^q + \frac{1}{4\pi}\sum_{k=1}^{N_b}\sum_{q=1}^{M_i} D_{ik}^{pq} \phi_{S_k}^q \Delta S_k^q \tag{6}$$

In the above, $\mathbf{n}_i^p \bullet \mathbf{E}_i^p$ is the normal component of the electric field at the pth element of the ith boundary due to real charges within the boundary (preferably obtained from the actual electronic structure rather than from a point charge approximation to that distribution), and,

$$G_{ik}^{pq} = \frac{1}{\left|\mathbf{R}_{ik}^{pq}\right|}; \qquad P_{ik}^{pq} = G_{ik}^{pq} \exp\left(-\kappa\left|R_{ik}^{pq}\right|\right);$$

$$A_{ik}^{pq} = -\frac{\mathbf{n}_i^p \bullet \mathbf{R}_{ik}^{pq}}{\left|\mathbf{R}_{ik}^{pq}\right|^3}; \qquad B_{ik}^{pq} = \left(1+\kappa\left|\mathbf{R}_{ik}^{pq}\right|\right) A_{ik}^{pq} \exp\left(-\kappa\left|\mathbf{R}_{ik}^{pq}\right|\right);$$

$$C_{ik}^{pq} = \frac{\mathbf{n}_i^p \bullet \mathbf{n}_k^q}{\left|\mathbf{R}_{ik}^{pq}\right|^3} - \frac{3\left(\mathbf{n}_k^q \bullet \mathbf{R}_{ik}^{pq}\right)\left(\mathbf{n}_i^p \bullet \mathbf{R}_{ik}^{pq}\right)}{\left|\mathbf{R}_{ik}^{pq}\right|^5}$$

and finally,

$$D_{ik}^{pq} = \left(1+\kappa\left|\mathbf{R}_{ik}^{pq}\right|\right) C_{ik}^{pq} \exp\left(-\kappa\left|\mathbf{R}_{ik}^{pq}\right|\right) + \frac{\kappa^2\left(\mathbf{n}_k^q \bullet \mathbf{R}_{ik}^{pq}\right)\left(\mathbf{n}_i^p \bullet \mathbf{R}_{ik}^{pq}\right)}{\left|\mathbf{R}_{ik}^{pq}\right|^3} \exp\left(-\kappa\left|\mathbf{R}_{ik}^{pq}\right|\right) \tag{7}$$

Gauss's Law requires the discontinuity in the normal component of the displacement vector across a boundary to be equal to the real charge on the boundary:

$$\varepsilon_i \frac{\partial \psi_i}{\partial n_i} - \varepsilon_s \frac{\partial \psi_s}{\partial n_i} = 2\pi\sigma_i^{real} \tag{8}$$

Using this boundary condition and following Juffer, et al (5), a system of coupled linear equations is found for the surface potential and surface charge density on each element of a boundary. Solution of this system by the usual methods of linear algebra allows us to then use Eqs. (1) and (2) to obtain the potential everywhere.

B. Coupling to ab initio Charge Distribution

The Poisson-Boltzmann method described above can be applied to any molecule for which point charges have been assigned to the atoms. Any number of fixed point charges may be included; hence multipole distributions may be approximated by including multiple charges. Of course, it must be recognized that the actual electronic charge distribution of the molecule is being approximated by these point charges. The Scheraga group has eliminated this approximation by including the single layer surface charges determined by a Poisson solver directly in the Hamiltonian (7). The ab initio calculation then determines a new set of electric fields (normal components) at the boundary elements which provide the source charges for the Poisson solver. The calculation is iterated to convergence. Importantly, in this method, the quantum mechanically derived charge density relaxes in response to the electric field due the surrounding surface charges. In the solvent region, the Poisson equation is satisfied, i. e., $\kappa=0$ and ionic strength effects are neglected.

In the method presented here, the coupling of the electronic structure calculation in the presence of the solvent, i. e., with the Poisson-Boltzmann region, is implemented through the boundary elements which represent both single and double layers of charge. The potentials and electric fields due to point charges representing the molecular charge distribution are replaced by potentials and electric fields at surface elements derived from accurate electronic structure calculations. Consideration of Eq. (1) above for the potential within a molecular region serves to clarify the method.

The first (second) term in the surface integral of Eq. (1) represents the contribution from the single (double) layer of charge. An application of Green's theorem for a source within a boundary, integrating over the region external to the boundary, yields,

$$\oint_{S_i} \phi_i^{S_i} \frac{\partial P}{\partial n_i} dS_i = \oint_{S_i} P \frac{\partial \phi_s^{S_i}}{\partial n_i} dS_i \tag{9}$$

Continuity of the normal component of the displacement vector (in the absence of real charge at that boundary) requires that $\frac{\partial \phi_s^{S_i}}{\partial n_i} = \frac{\varepsilon_i}{\varepsilon_s} \frac{\partial \phi_i}{\partial n_i}$. For an infinite Debye length (κ=0), P=G and the familiar expression (1) for the potential within a single boundary is obtained (with an appropriate factor multiplying the surface charge density for the Green's function method),

$$\phi_i(\mathbf{x}) = \int_{V_i} \frac{G\rho_i}{\varepsilon_i} dV_i + \frac{(\varepsilon_s - \varepsilon_i)}{\varepsilon_s} \oint_{S_i} G\sigma dS_i \tag{10}$$

Gauss's Law provides a means of checking the accuracy of the numerically determined surface charge density and can be used to normalize the surface charges for comparison purposes. Tails of the electronic charge density may extend beyond the boundary, an effect which has been investigated in depth by Miertus, et al (3). Scaling or normalizing to the known charge enclosed provides a means of estimating the influence of this effect.

For finite Debye lengths, the double layer term in Eq. (1), the directional derivative of the Green's function (times the potential at the surface), can be recognized numerically as a double layer of (equal and opposite) charge of magnitude $\phi_i^{S_i} / 4\pi d$, where d is the separation between the layers. We find for a small separation, d, of ~0.01 Bohr that such a numerical description of the double layer contribution to the potential inside the boundary agrees quite well with the potential calculated using Eq. 3. This double layer of surface charge (as well as the single layer) is then added to the Hamiltonian in the subsequent

electronic structure calculation (GAMESS,15). The potential and electric field determined by the ab initio calculation in the presence of both single and double layers of charge are then both employed as source terms in the next iteration of the Poisson-Boltzmann solver, and the procedure is iterated to convergence. The electron distribution relaxes in response to the single and double layers of charge, a significantly different approach from classical methods in which the charge distribution is fixed.

We find the iterative method to converge in only a few (~2-4) "complete" iterations; the determination of SCF wave functions for a given set of background charges involves, perhaps, tens of "micro" HF iterations. These HF wave functions are then employed to obtain an MP2 energy and also as the source charge distribution for the next Poisson-Boltzmann solution. MP2 wave functions are not determined, consistent with the conclusions of Angyan (16) who has shown that the second-order energy can be evaluated directly from the HF orbitals.

In this way, ionic strength effects are included and the need for a point charge description of the molecular charge distribution is obviated. A numerical check is provided in the limit of the dielectric constant of the solvent region being identical to the molecular region (which is most often unity), and the ionic strength zero (κ=0). There should be no effect of the boundary; the vacuum-state quantum result should be, and is, obtained.

III Results

A. Model Calculations

A sphere of radius 3.0 Å was discretized using 645 nodes (17). Within the sphere, which forms a boundary separating two media, the dielectric constant was chosen to be ε_1=1.0; outside the sphere, the dielectric constant of the medium (extending to infinity) was chosen to be either ε_s=20.0 or ε_s=81.0 (~water). In Fig. 1, we present the results of our

calculations of the charging free energy for a point charge of magnitude 2e enclosed within this sphere as a function of its relative distance from the origin. The calculations were performed numerically as described in Section II above and compared to the results obtained using the analytic expressions of Gilson, et al (18). The ionic strength of the outer medium was chosen to correspond to inverse debye lengths, κ, of 0.0, 0.1 and 1.0 $Bohrs^{-1}$. For these comparison calculations, the total surface charge density was normalized to the total charge enclosed using Gauss's law as described above.

The Born energy (E_A in Fig. 1) for zero salt (κ=0) was found to be ~8 kcal/mole lower for ε_s=81 than for the comparison ε_s=20 solution. The curves in Fig. 1 were obtained by subtracting these κ=0 energies from each. We see from Fig. 1, for ε_s=81 (water) the numerical and analytical methods are found to agree within a small fraction of a kcal/mole for relative off-center distances of the point charge <~ 0.7 from the sphere center.
For ε_s=20, the largest variation is found for the κ=0 (zero ionic strength) results, a variation of ~2 kcal/mole at r/a=0.6 and ~3 kcal/mole at r/a=0.7. Consistent with the findings of Juffer, et al (5), we do not have confidence in continuum calculations as the charge approaches ~1 Å from the sphere boundary (r/a >~0.65).

B. The Carbonate Ion

The discretized CO_3^{-2} molecule employing 590 nodes is shown in Fig. 2. In Fig. 3, we have plotted the calculated electrostatic component of the free energy of solution of a CO_3^{-2} ion emersed in a dielectric having ε_s=10 or ε_s=81 at the MP2 level of theory. The calculations are presented as a function of inverse debye length, κ. Normalized curves in Fig. 3 are obtained for comparison purposes by scaling the surface charge to the total charge enclosed (-2e) by the boundary in accordance with Gauss's Law, an ~1% effect on the charge (see above, Section II). It is first of all to be noted that the energy transferred in placing an ion into a solution characterized by a dielectric constant of ε_s=81 (relative to the

ion in a medium of dielectric constant ε_1) is ~15 kcal/mole greater than for a medium characterized by ε_s=10. The ionic strength dependence is greater for the ε_s=10 medium than for ε_s=81: at κ=10 Bohrs^{-1} we find the free energy of solution to be only ~2 kcal/mole different between the two solvent media. The dielectric constant and κ dependences are consistent with the approximate analytic expression for a sphere (19),

$$W = \frac{Q^2}{2\varepsilon_s}\left[\frac{(\varepsilon_1 - \varepsilon_s)}{r_0\varepsilon_1} - \frac{\kappa}{(1+\kappa a)}\right] \tag{11}$$

where Q is real charge enclosed, r_0 the radius of the sphere and "a" the exclusion radius of the dimensions of a salt ion. We find values of r_0 =6.18 Bohrs and a=10.0 Bohrs in Eq. 11 well-represent the first-principles calculations (see Fig. 3). Such a validation for a near-spherical ion is encouraging for future more complex molecules.

The comparison between the calculations and experiment is displayed in Fig. 4 where the abscissa is ionic strength and the scale is expanded for ε_s=81 (water) only. The normalization of the surface charge is seen to have little (<0.5 kcal/mole) effect. The experimental points in Fig. 4 are from a recent formulation of Pitzer's regression (20) for CO_3^{-2} in water relative to zero salt and translated to the zero ionic strength calculated value. Cavitation and dispersion contributions to the solvation free energy are assumed to be constant as a function of ionic strength alone and are hence not included in the comparison. The results indicate that the single-and-double-layer method of coupling (SDLC) the linearized Poisson-Boltzmann equation to an MP2-level quantum calculation gives reasonable results over a wide range of ionic strengths.

The free energy of solvation of a neutral carbon dioxide molecule was also determined using the single and double layer (SDLC) coupling method presented here. Using the same parameters for the solvent surface as for CO_3^{-2}, we employed 544 dots to describe the

surface. We find effectively zero free energies (to four places of accuracy) as a function of both dielectric constant and ionic strength, consistent with experiment (20).

In conclusion, we have developed a method to couple Schrödinger calculations of the properties of molecules with Poisson-Boltzmann calculations of the influence of an electrolyte on a molecule. The coupling is accomplished through both the single and double layers of charge induced on the boundary and represents the main focus of this communication. The results for the solvation energy of the carbonate ion as a function of ionic strength are found to be in excellent agreement with experiment.

References

1. J. Tomasi and M. Persico, Chem. Rev. **94**, 2027 (1994).
2. G. D. Hawkins, C. J. Cramer and D. G. Truhlar, Chem. Phys. Lett. **246** (1995) 122.
3. S. Miertus, E. Scrocco and J. Tomasi, J. Chem. Phys. **55** (1981) 117.
4. R. J. Zauhar and R. S. Morgan, J. Mol. Biol. **186** (1985) 815. (See also J. Comp. Chem. **9** (1988) 171; J. Comp. Chem. **11** (1990) 603; J. Comp. Chem. **12** (1991) 575).
5. A. H. Juffer, E. F. F. Botta, B. A. M. van Keulen, A. van der Ploeg and H. J. C. Berendsen, J. Comp. Phys. **97** (1991) 144.
6. H. X. Zhou, Biophys. J. **65** (1993) 955.
7. J. A. Grant, R. L. Williams and H. A. Scheraga, Biopolymers **30** (1990) 929.
8. D. J. Tannor, et al, J. Am. Chem. Soc. **116** (1994) 11875.
9. J. L. Chen, L. Noodleman, D. A. Case and D. Bashford, J. Phys. Chem. **98** (1994) 11059.
10. K. Baldridge, R. Fine and A. Hagler, J. Comp. Chem. **15** (1994) 1217.
11. M. W. Wong, M. J. Frisch and K. B. Wiberg, J. Am. Chem. Soc. **113** (1991) 4776. (See also M. W. Wong, K. B. Wiberg and M. J. Frisch, J. Chem. Phys. **95** (1991) 8991).
12. J. Warwicker and H. C. Watson, J. Mol. Biol. **157** (1982) 671.
13. B. Lee and F. M. Richards, J. Mol. Biol. **55** (1971) 379.
14. I. Stackgold, Boundary Value Problems of Mathematical Physics, Vol. 2 (MacMillan and Co., New York, 1968).
15. GAMESS:, J. Comp. Chem. **14** (1993) 1347.
16. J. G. Angyan, Int. J. Quantum Chem. **47** (1993) 469.
17. No significant difference was found for several larger (983-dot) calculations.

18. M. K. Gilson, et al, J. Mol. Biol. **183** (1985) 503. (See also T. L. Hill, J. Phys. Chem. **60** (1956) 253).

19. C. Tanford and J. G. Kirkwood, J. Amer. Chem. Soc. **79** (1957) 5333; J. G. Kirkwood, J. Chem. Phys. **2** (1934) 351.

20. J. C. Peiper and K. S. Pitzer, J. Chem. Thermodynanics **14** (1982) 613.

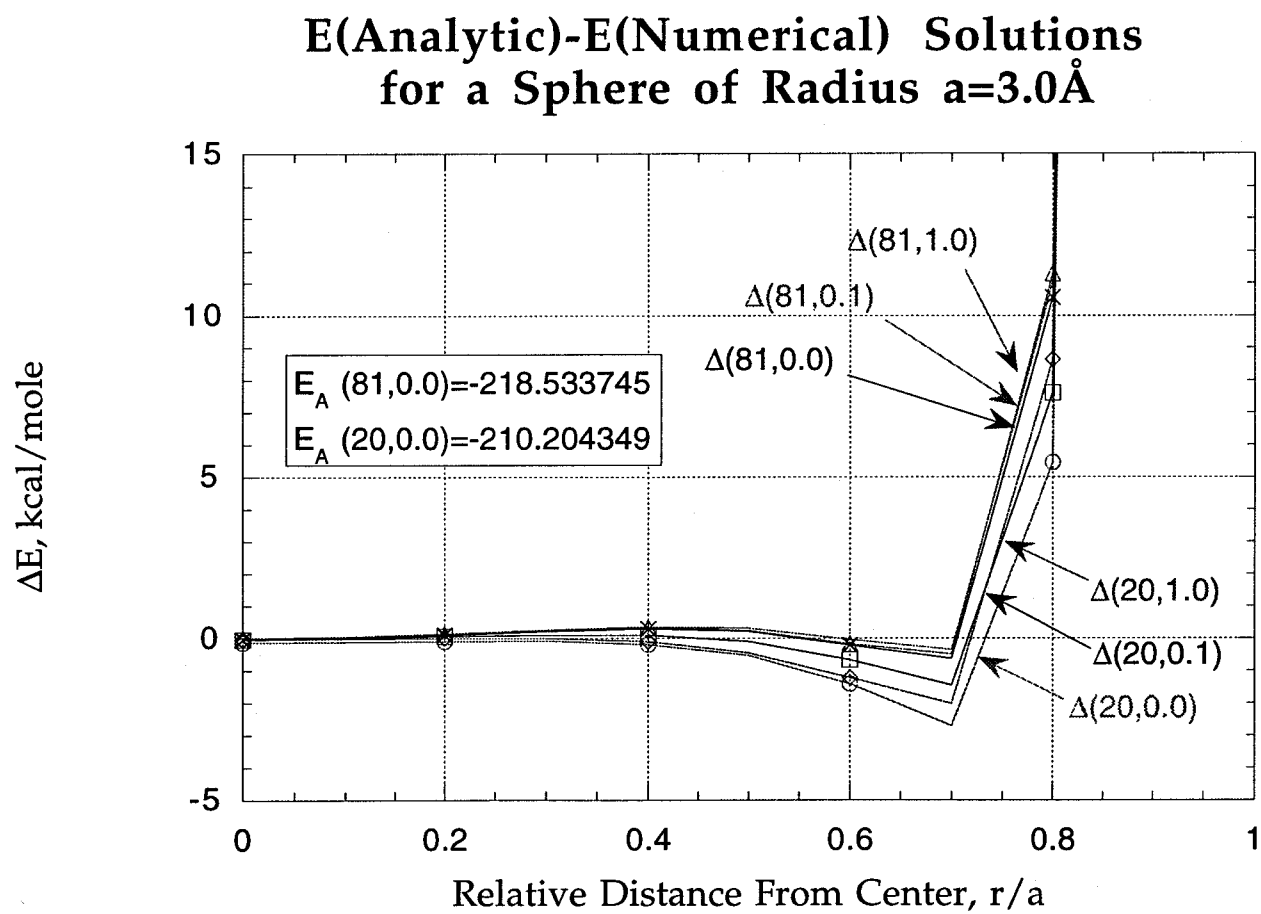

Figure 1. Difference in free energy between numerical and analytic solutions for a point charge within a sphere of radius 3.0 Å characterized by a dielectric constant of ε_1=1.0. The numerical results employed a discretized boundary of 645 nodes and were performed for outer region dielectric constants of ε_s=20 and ε_s=81 which had ionic strengths characterized by inverse debye lengths of 0.0, 0.1 and 1.0. The agreement for water (ε_s=81) is better than ~1 kcal (~0.5%) as far off center as r/a=0.70; that for ε_s=20 is of order 2.5%. At r/a=0.70, the point charge is less than ~1 Å from the sphere boundary where continuum methods break down.

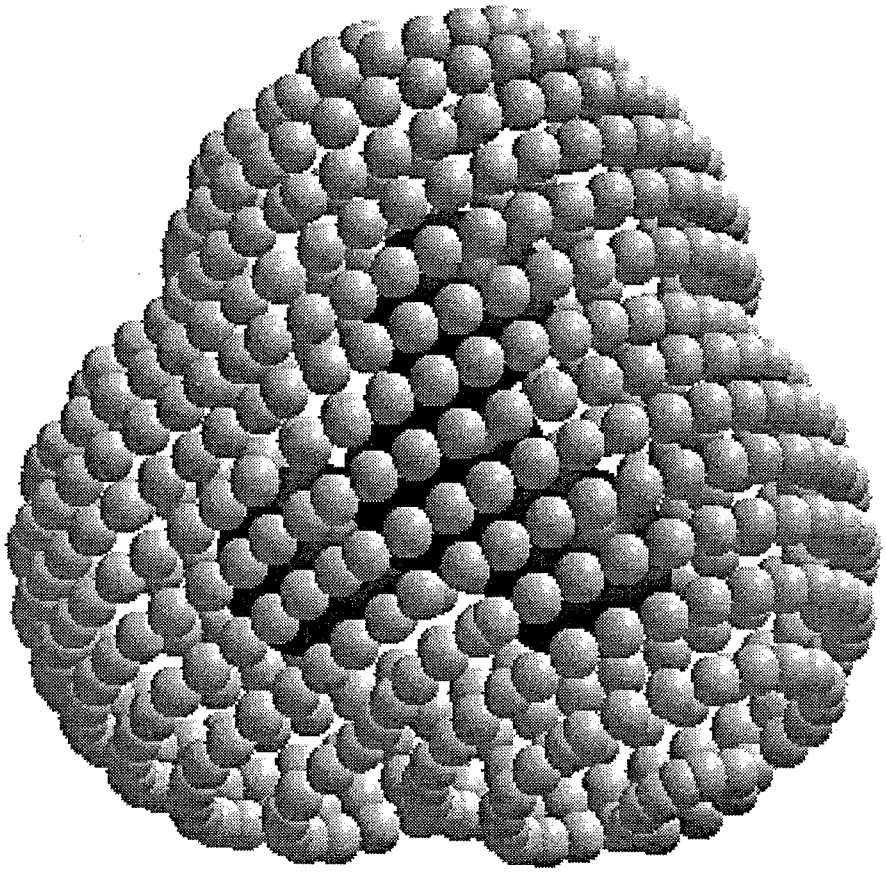

Figure 2. Discretized CO_3^{-2} molecule employing 590 nodes.

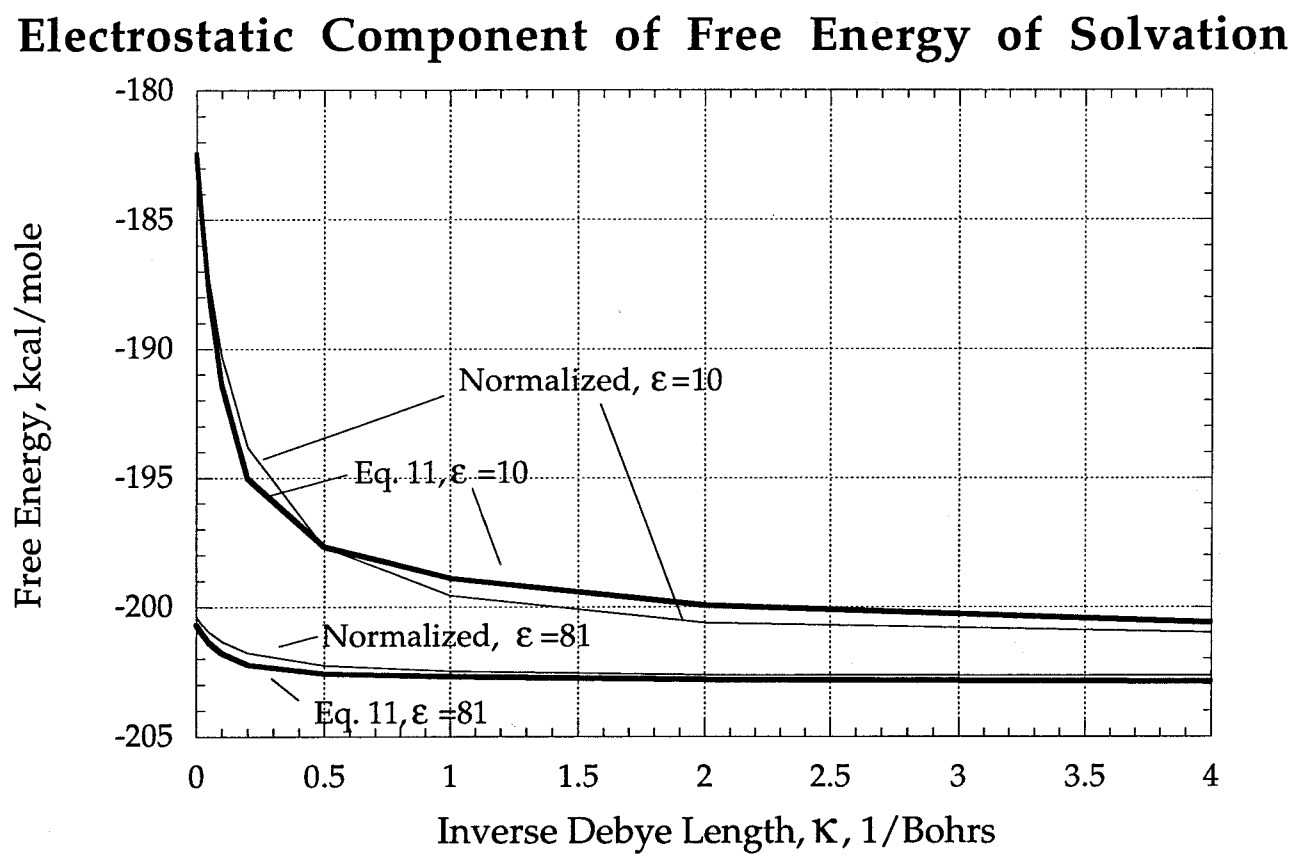

Figure 3. Electrostatic component of the solvation energy of a CO_3^{-2} molecule as a function of inverse Debye length, κ, for dielectric constants of ε_s=10 and ε_s=81 (water). The curves are calculated at the MP2 level of theory and the experimental data points are from Peiper and Pitzer (20).

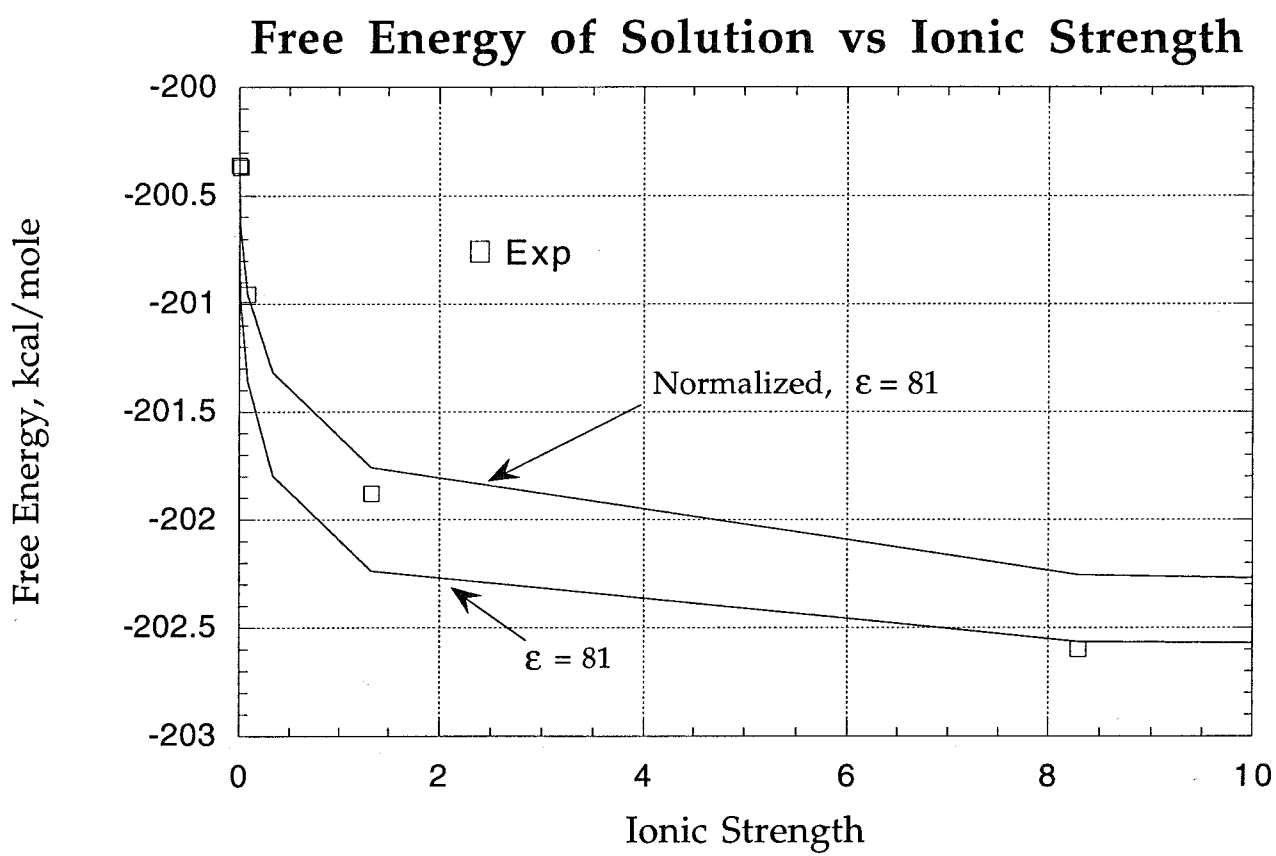

Figure 4. Electrostatic component of the solvation energy of a CO_3^{-2} molecule as a function of ionic strength in units of molality. The curves are calculated at the MP2 level of theory and the experimental data points are from Peiper and Pitzer (20).

UNLIMITED RELEASE

INITIAL DISTRIBUTION

MS 0188 LDRD

MS 9001 T. O Hunter, 8000
Attn: J. B. Wright, 2200
M. E. John, 8100
L. A. West 8200
W. J. McLean, 8300
R. C. Wayne, 8400
P. N. Smith, 8500
P. E. Brewer, 8800
D. L. Crawford, 8900 MS

MS 9401 M. T. Dyer, 8700
Attn: M. W. Perra, 8711
J. C. F. Wang, 8713
G. J. Thomas, 8715
K. L. Wilson, 8716
W. G. Wolfer, 8717
G. A. Benedetti, 8741
M. R. Birnbaum, 8742
P. E. Nielan, 8743
W. A. Kawahara, 8746

MS 9403 M. I. Baskes, 8712

MS 9904 W. D. Wilson, 8700 (20)

MS 9021 Technical Communications Department, 8815/Technical Library, MS0899, 4414

MS 0899 Technical Library, 4414 (4)

MS 9018 Central Technical Files, 8940-2 (3)