Path integral approach to electrostatic problems

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A theory that is able to account for electrostatic effects in microscopic situations is formulated in terms of the path integral method. The theory relates the solution of the Poisson equation to the propagator of the diffusion equation. Applications are made to some typical problems of interest, such as the solvation energy of an ion in a solution and to the electrical properties of a diffuse surface.

I. INTRODUCTION

A number of problems of interest to chemical physicists and physical chemists involve the analysis of electrostatic interactions at the microscopic level. These include the evaluation of the image potential of an ion near a surface, the solvation energy of an ion in solution, the polarizability of a fragment of dielectric material, the local field induced by an externally imposed electric field, the lifetime of excited molecules near a solid, and the dynamics of energy transfer between molecules near a solid. Standard techniques exist for solving such problems, but they are usually applied only to very simple geometries. For example, the problem of determining the image potential of an ion near a surface of irregular shape is nontrivial. Similarly the calculation of the solvation energy of an ion in a cavity of irregular shape presents a formidable problem. The same would hold true for the other aforementioned problems. While these problems may be addressed by introducing finite elements or by discretizing the problem on some large lattice, these approaches are known to tax the capabilities of even the largest computers.

In this paper we introduce a method applicable to the above class of problems, as well as others, which is based on path integral techniques. The method is independent of the number of dimensions and will work even if the boundaries presented by the surfaces, solvation cavities, or particle shapes are sharp or diffuse in nature. Our technique involves relating the solution of the Poisson equation to the propagator of a related diffusion equation with drift. The propagator is then evaluated by path integral techniques. The goal of this paper is basically to define the method and to apply it to some overidealized problems to test its applicability. In future work we plan to study some more realistic problems in detail. In Sec. II we present the theory for the solvation energy of an ion in a cavity. In Sec. III we study the propagator for the diffusion equation in detail and discuss the semiclassical approximation. Section IV presents an exactly solvable model for a diffuse cavity which will prove useful for calibrating numerically based problems. In Sec. V we numerically obtain the solvation energy for an ion, evaluating the path integral by a Monte Carlo approach using influence weighting to accelerate the convergence. This is followed in Sec. VI by a matrix method appropriate to one-dimensional problems. Section VII concerns itself with some other quantities of physical interest. The relationship between our path integral approach and the semiclassical approximation of Miller is discussed in the Appendix.

II. THEORY OF THE SOLVATION ENERGY OF AN ION

Consider an ion of charge Q located at position R in a dielectric medium of dielectric constant $\epsilon(\mathbf{r})$. The medium will be assumed to be isotropic so $\epsilon(\mathbf{r})$ will be taken to be a scalar function of position. Furthermore, since the presence of the ion at point $\mathbf{R}$ excludes the presence of the surrounding medium at that point, we may assume that $\epsilon(\mathbf{R}) = 1$. Our goal will be to derive a general formula for the solvation energy of this ion, U, irrespective of the inhomogeneities inherent in the function $\epsilon(\mathbf{r})$. Included in such an expression will be the case of an ion embedded in a cavity of arbitrary shape. Extensions of the present formulas to the case of a set of ions or a smeared charge distribution can be readily found.

We start with Gauss's law

$$\nabla\cdot\mathbf{D}(\mathbf{r}) = 4\pi Q\delta(\mathbf{r}-\mathbf{R}), \tag{2.1}$$

where the electric displacement vector $\mathbf{D}(\mathbf{r})$ is

$$\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}), \tag{2.2}$$

and the electric field $\mathbf{E}(\mathbf{r})$ is given in terms of the electrostatic potential $\Phi(\mathbf{r})$ by

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}). \tag{2.3}$$

Let us write the Poisson equation as

$$\nabla^2\Phi(\mathbf{r}) + \mathbf{F}(\mathbf{r})\cdot\nabla\Phi(\mathbf{r}) = -\frac{4\pi Q}{\epsilon(\mathbf{R})}\delta(\mathbf{r}-\mathbf{R}), \tag{2.4}$$

where we have introduced a vector field $\mathbf{F}(\mathbf{r})$ related to the dielectric function by

$$\mathbf{F}(\mathbf{r}) = \nabla \ln \epsilon(\mathbf{r}). \tag{2.5}$$

In order to solve Eq. (2.4) we introduce a propagator to a diffusion equation with drift

$$[\nabla^2 + \mathbf{F}(\mathbf{r})\cdot\nabla]K(\mathbf{r},\mathbf{r}';t) = \frac{\partial K(\mathbf{r},\mathbf{r}';t)}{\partial t}, \tag{2.6}$$

where t is a variable that we will term the "time", although in fact it is simply a variable with the dimensions of length squared which we introduce for the purpose of mathematical convenience. The propagator satisfies the "initial" condition

$$K(\mathbf{r},\mathbf{r}';0) = \delta(\mathbf{r}-\mathbf{r}'). \tag{2.7}$$

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In addition we introduce the Green function $G(\mathbf{r},\mathbf{r}')$ defined as

$$G(\mathbf{r},\mathbf{r}') = -\int_0^\infty K(\mathbf{r},\mathbf{r}';t)dt. \tag{2.8}$$

If we integrate Eq. (2.6) over t from $t=0$ to $t=\infty$ and assume that $K(\mathbf{r},\mathbf{r}';t)\to 0$ as $t\to\infty$ we see that $G(\mathbf{r},\mathbf{r}')$ satisfies the equation

$$[\nabla^2 + \mathbf{F}(\mathbf{r})\cdot\nabla]G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{2.9}$$

Thus $G(\mathbf{r},\mathbf{r}')$ is simply related to the potential $\Phi(\mathbf{r})$, as can be seen by comparing Eqs. (2.9) and (2.4):

$$\Phi(\mathbf{r}) = -\frac{4\pi Q}{\epsilon(\mathbf{R})}G(\mathbf{r},\mathbf{R}). \tag{2.10}$$

Hence we obtain

$$\Phi(\mathbf{r}) = \frac{4\pi Q}{\epsilon(\mathbf{R})}\int_0^\infty K(\mathbf{r},\mathbf{R};t)dt. \tag{2.11}$$

If there were no dielectric present, $\epsilon(\mathbf{r})$ would equal one everywhere and $\mathbf{F}(\mathbf{r})$ would vanish. The corresponding propagator satisfying Eqs. (2.6) and (2.7) will be denoted by $K_0(\mathbf{r},\mathbf{R};t)$ and the corresponding potential will be denoted by $\Phi_0(\mathbf{r})$. Thus

$$\Phi_0(\mathbf{r}) = 4\pi Q\int_0^\infty K_0(\mathbf{r},\mathbf{R};t)dt. \tag{2.12}$$

The free propagator, $K_0(\mathbf{r},\mathbf{R};t)$, may be found by using Fourier transforms and is

$$K_0(\mathbf{r},\mathbf{R};t) = (4\pi t)^{-3/2}\exp[-(\mathbf{r}-\mathbf{R})^2/(4t)]. \tag{2.13}$$

Combining Eqs. (2.12) and (2.13) leads to the obvious result

$$\Phi_0(\mathbf{r}) = \frac{Q}{|\mathbf{r}-\mathbf{R}|}. \tag{2.14}$$

In calculating the solvation energy it is important to distinguish the singular part of the electrostatic potential from the nonsingular part. The singular contribution stems from $\Phi_0(\mathbf{r})$ and is present even in the absence of the dielectric. The nonsingular part is due to the presence of the dielectric and will be denoted by $\Phi(\mathbf{r})$. The electrostatic contribution to the solvation energy is

$$U = \frac{Q}{2}\bar{\Phi}(\mathbf{R}), \tag{2.15}$$

where the factor 1/2 arises due to the fact that the value of $\bar{\Phi}(\mathbf{R})$ itself is proportional to Q, so that if we regard Q as gradually increased from zero to its final value, integration would produce a factor 1/2. Here

$$\bar{\Phi}(\mathbf{R}) = \Phi(\mathbf{R}) - \Phi_0(\mathbf{R}). \tag{2.16}$$

Combining Eqs. (2.11), (2.12), (2.15), and (2.16) yields

$$U = 2\pi Q^2\int_0^\infty\left[\frac{K(\mathbf{R},\mathbf{R};t)}{\epsilon(\mathbf{R})} - K_0(\mathbf{R},\mathbf{R};t)\right]dt. \tag{2.17}$$

The problem has thus been reduced to one of obtaining the propagator which starts initially at the ion and returns to the ion a time t later. The path may be of arbitrary shape.

III. PATH INTEGRAL FORMULATION FOR THE PROPAGATOR

Although the calculation of the propagator by the path integral formalism is a familiar problem we must remember that the path integral method is generally applied to problems involving Hermitian Hamiltonians. Equation (2.6) involves a non-Hermitian Hamiltonian so some care must be exercised in evaluating it.

A formal solution to Eqs. (2.6) and (2.7) may be written in bra–ket notation

$$K(\mathbf{r},\mathbf{r}';t) = \langle\mathbf{r}|\exp[t(\nabla^2 + \mathbf{F}\cdot\nabla)]|\mathbf{r}'\rangle. \tag{3.1}$$

We shall derive two expressions for the path integral, one suitable for numerical integration and one suitable for the semiclassical approximation. We start with the former derivation first. A path integral representation of K is obtained by following a standard procedure.[1,2] We divide t into N steps of time $\Delta t = t/N$ and rewrite Eq. (3.1) as

$$K(\mathbf{r},\mathbf{r}';t) = \int d\mathbf{r}_1\cdots d\mathbf{r}_{N-1}\langle\mathbf{r}|U(\Delta t)|\mathbf{r}_{N-1}\rangle \times\langle\mathbf{r}_{N-1}|U(\Delta t)|\mathbf{r}_{N-2}\rangle\cdots\langle\mathbf{r}_1|U(\Delta t)|\mathbf{r}'\rangle, \tag{3.2}$$

where we have inserted $N-1$ complete sets of states and let

$$U(\Delta t) = \exp[\Delta t(\nabla^2 + \mathbf{F}\cdot\nabla)]. \tag{3.3}$$

A Fourier decomposition of $U(\Delta t)$ leads, to first order in Δt, to

$$\langle\mathbf{r}_n|U(\Delta t)|\mathbf{r}_{n-1}\rangle \doteq \int\frac{d\mathbf{p}_n}{(2\pi)^3}\exp\{i\mathbf{p}_n\cdot(\mathbf{r}_n-\mathbf{r}_{n-1}) + \Delta t[-\mathbf{p}_n^2 + i\mathbf{p}_n\cdot\mathbf{F}(\mathbf{r}_n)]\}. \tag{3.4}$$

Evaluating the $\mathbf{p}_n$ integral and reinserting back into Eq. (3.2) yields

$$K(\mathbf{r},\mathbf{r}';t) = (4\pi\Delta t)^{-3N/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_{N-1} \times\exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[\mathbf{F}(\mathbf{r}_n) + \frac{\mathbf{r}_n-\mathbf{r}_{n+1}}{\Delta t}\right]^2\right\}. \tag{3.5}$$

This expression is useful for numerical integration purposes and will, in fact, be utilized in Secs. V and VI as the basis for the development of a Monte Carlo method and a matrix multiplication method. However, we would like to also be able to go to a continuum limit and this requires some care, as has been amply pointed out in the literature.[3,4] In order for the usual rules of calculus to apply we must start with a Weyl-ordered operator[4] in Eq. (3.1). Thus we rewrite the propagator as

$$K(\mathbf{r},\mathbf{r}';t) = \langle\mathbf{r}|\exp(tQ)|\mathbf{r}'\rangle, \tag{3.6}$$

where the operator Q acting on a function $g(\mathbf{r})$ has the following form:

$$Qg = \nabla^2 g + \tfrac{1}{2}[\mathbf{F}\cdot\nabla g + \nabla\cdot(\mathbf{F}g)] - \tfrac{1}{2}(\nabla\cdot\mathbf{F})g. \tag{3.7}$$

These equations are mathematically identical to the previous equations but the term containing the square bracket is now

in Weyl-ordered form. In place of Eq. (3.4) we now have

$$\langle \mathbf{r}_n | U(\Delta t) | \mathbf{r}_{n-1} \rangle = \int \frac{d\mathbf{p}_n}{(2\pi)^3} \exp\left\{ -\Delta t \left[p_n^2 - i\mathbf{p}_n \cdot \left(\frac{\mathbf{F}(\mathbf{r}_n) + \mathbf{F}(\mathbf{r}_{n-1})}{2} + \frac{\mathbf{r}_n - \mathbf{r}_{n-1}}{\Delta t} \right) + \frac{1}{2} \nabla \cdot \mathbf{F}(\mathbf{r}_{n-1}) \right] \right\}, \tag{3.8}$$

and Eq. (3.5) becomes

$$K(\mathbf{r},\mathbf{r}';t) = (4\pi\Delta t)^{-3N/2} \int d\mathbf{r}_1 \cdots d\mathbf{r}_{N-1} \times \exp\left\{ -\frac{\Delta t}{4} \sum_{n=1}^{N} \left[\frac{\mathbf{F}(\mathbf{r}_n) + \mathbf{F}(\mathbf{r}_{n-1})}{2} + \frac{\mathbf{r}_n - \mathbf{r}_{n-1}}{\Delta t} \right]^2 - \frac{\Delta t}{2} \sum_{n=1}^{N} \nabla \cdot \mathbf{F}(\mathbf{r}_{n-1}) \right\}. \tag{3.9}$$

We may now pass to the continuum limit by using the rules of the standard calculus.

One usually writes this symbolically as a path integral

$$K(\mathbf{r},\mathbf{r}';t) = \int D[\mathbf{r}(t)] \exp(-s), \tag{3.10}$$

subject to the "initial" condition $\mathbf{r}(0) = \mathbf{r}'$ and the "final" condition $\mathbf{r}(t) = \mathbf{r}$.

If $\epsilon(\mathbf{r})$ is slowly varying in space we might expect a classical description to be a first approximation to the path integral. The classical "action" may be written as

$$S = \int_0^t L\left(\mathbf{r}, \frac{d\mathbf{r}}{dt}\right) dt, \tag{3.11}$$

where the "Lagrangian", is

$$L = \frac{1}{4}\left[\mathbf{F}(\mathbf{r}) + \frac{d\mathbf{r}}{dt}\right]^2 + \frac{1}{2} \nabla \cdot \mathbf{F}. \tag{3.12}$$

The Lagrange equation is

$$\frac{d^2\mathbf{r}}{dt^2} = \nabla\left[\frac{F^2}{2} + \nabla \cdot \mathbf{F}\right], \tag{3.13}$$

so we may regard this as Newton's equation of motion for a particle moving in the potential

$$V(\mathbf{r}) = -\tfrac{1}{2}F^2(\mathbf{r}) - \nabla \cdot \mathbf{F}, \tag{3.14}$$

and subject to the end-point conditions $\mathbf{r}(0) = \mathbf{r}'$ and $\mathbf{r}(t) = \mathbf{r}$. For this motion "energy" is constant, i.e.,

$$E = \frac{1}{2}\left[\left(\frac{d\mathbf{r}}{dt}\right)^2 - \mathbf{F}^2(\mathbf{r})\right] - \nabla \cdot \mathbf{F}. \tag{3.15}$$

The "canonical momentum" is

$$\mathbf{p} = \frac{1}{2}\left[\frac{d\mathbf{r}}{dt} + \mathbf{F}(\mathbf{r})\right], \tag{3.16}$$

and the classical action is

$$S_c = \int_0^t \{p^2(t') + \tfrac{1}{2}\nabla \cdot \mathbf{F}[\mathbf{r}(t')]\} dt'. \tag{3.17}$$

The semiclassical approximation consists of writing the propagator as

$$K(\mathbf{r},\mathbf{r}';t) \doteq F(\mathbf{r},\mathbf{r}';t) \exp[-S_c(\mathbf{r},\mathbf{r}';t)], \tag{3.18}$$

where $F(\mathbf{r},\mathbf{r}';t)$ is an appropriate normalization constant. In most cases it will be a function of both endpoint coordinates as well as t, but we will soon study a case where it depends only on t. The evaluation of $F(\mathbf{r},\mathbf{r}';t)$ is, in general, nontrivial. The form of F, however, is constrained by the following theorem:

$$\int K(\mathbf{r},\mathbf{r}';t)\epsilon(\mathbf{r}) d\mathbf{r} = \epsilon(\mathbf{r}'). \tag{3.19}$$

The proof of this theorem follows from Eq. (2.6) by rewriting it as

$$\nabla \cdot [\epsilon \nabla K] = \frac{\partial}{\partial t}[\epsilon K], \tag{3.20}$$

and integrating it over all space. Assuming that $K(\mathbf{r},\mathbf{r}';t)$ falls off for large r faster than $1/r$, the application of Green's theorem to the resulting integral will give zero for the left-hand side so

$$\int K(\mathbf{r},\mathbf{r}';t)\epsilon(\mathbf{r}) d\mathbf{r} = f(\mathbf{r}'). \tag{3.21}$$

The time-independent function $f(\mathbf{r})$ may be evaluated at time $t = 0$ using Eq. (2.7), so Eq. (3.19) results. Note that if Eq. (2.6) had been symmetrized so as to make the left-hand side a Hermitian operator the above theorem would not necessarily be true.

Equation (3.19) implies that the dielectric function is an eigenfunction of the transpose of the propagator. The corresponding eigenvalue is unity. Furthermore as time changes neither the eigenvalue nor the eigenfunction change.

IV. A SOLVABLE MODEL

In order to make our discussion more explicit let us consider a solvable model. We introduce the dielectric function

$$\epsilon(\mathbf{r}) = \exp(\alpha|\mathbf{r} - \mathbf{R}|^2), \tag{4.1}$$

which is characterized by the parameter α. It represents, of course, an idealization because ϵ grows to be very large for large $|\mathbf{r} - \mathbf{R}|$ but it does satisfy the condition $\epsilon(\mathbf{R}) = 1$. We will see later, however, how this model can help us solve more realistic problems. It will be convenient to select point $\mathbf{R}$ as our reference point and to set $\mathbf{R} = 0$ henceforth.

From Eq. (2.5) the characteristic vector field is given by

$$\mathbf{F}(\mathbf{r}) = 2\alpha\mathbf{r}, \tag{4.2}$$

and the "potential" is

$$V(\mathbf{r}) = -2\alpha^2 r^2 - 6\alpha. \tag{4.3}$$

The general solution to Eq. (3.9) for time $t' < t$ is

$$\mathbf{r}(t') = \mathbf{A}\exp(2\alpha t') + \mathbf{B}\exp(-2\alpha t'), \tag{4.4}$$

where $\mathbf{A}$ and $\mathbf{B}$ are constants. Since $\mathbf{r}(0) = \mathbf{r}'$ we obtain

$$\mathbf{r}' = \mathbf{A} + \mathbf{B}. \tag{4.5}$$

At the terminal time t we have $\mathbf{r}(t) = \mathbf{r}$ so

$$\mathbf{r} = \mathbf{A}\exp(2\alpha t) + \mathbf{B}\exp(-2\alpha t). \tag{4.6}$$

The canonical momentum of Eq. (3.12) is

$$\mathbf{p}(t') = 2\alpha \mathbf{A} \exp(2\alpha t'). \tag{4.7}$$

The classical action of Eq. (3.13) is

$$S_c = \alpha A^2[\exp(4\alpha t) - 1] + 3\alpha t. \tag{4.8}$$

Solving Eqs. (4.5) and (4.6) for A and inserting this into Eq. (4.8) yields the classical action

$$S_c = \alpha \frac{[\mathbf{r}' - \mathbf{r}\exp(2\alpha t)]^2}{\exp(4\alpha t) - 1} + 3\alpha t. \tag{4.9}$$

Let us now proceed to derive the exact formula for the propagator. We begin by writing Eq. (3.5) in a factored form applicable to the vector field of Eq. (4.2):

$$K(\mathbf{r},\mathbf{r}';t) = K_1(x,x';t)K_1(y,y';t)K_1(z,z';t), \tag{4.10}$$

where

$$K_1(x,x';t) = (4\pi\Delta t)^{-N/2}\int dx_1 \cdots \int dx_{N-1} \times \exp\left\{ -\frac{1}{4\Delta t}\sum_{n=0}^{N-1}[X_n(1+2\alpha\Delta t) - X_{n+1}]^2\right\}. \tag{4.11}$$

Let

$$y_n = \beta x_{n-1} - x_n, \tag{4.12}$$

where $x_0 = x, x_N = x'$, and $\beta = 1 + 2\alpha\Delta t$. Since Eq. (4.12) implies the constraint

$$\sum_{j=0}^{N-1} \beta^j y_{N-j} = x_N - \beta^N x_0, \tag{4.13}$$

we may rewrite Eq. (4.11) as

$$K_1(x,x';t) = \int dy_1 \cdots dy_N \delta(x_N - \beta^N x_0 - \sum_{j=1}^{N} y_j \beta^{N-j})(4\pi\Delta t)^{-N/2} \times \exp\left[-\frac{1}{4\Delta t}\sum_{j=1}^{N} y_j^2\right], \tag{4.14}$$

where we have used the fact that the Jacobian of the transformation is unity. By Fourier decomposing the Dirac delta function and carrying out the dy_n integrations this reduces to

$$K_1(x,x';t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \exp\left[-\omega^2\Delta t \sum_{j=1}^{N} \beta^{2N-2j} + i\omega(x_N - \beta^N x_0)\right]. \tag{4.15}$$

The summation appearing in the exponent is simply evaluated and the ω integration may be completed, resulting in

$$K_1(x,x';t) = \left[\frac{1-\beta^2}{4\pi\Delta t(1-\beta^{2N})}\right]^{1/2} \times \exp\left[-\frac{1}{4\Delta t}\left(\frac{1-\beta^2}{1-\beta^{2N}}\right)(x_N - \beta^N x_0)^2\right]. \tag{4.16}$$

In the limit of large N we have

$$\frac{1-\beta^2}{1-\beta^{2N}} \to \frac{1}{N}\frac{4\alpha t}{\exp(4\alpha t) - 1}. \tag{4.17}$$

Since $\beta = 1 + 2\alpha t/N$. Combining Eqs. (4.10), (4.16), and (4.17) results in

$$K(\mathbf{r},\mathbf{r}';t) = \left\{\frac{\alpha}{\pi[\exp(4\alpha t) - 1]}\right\}^{3/2} e^{3\alpha t} \times \exp\left\{ -\frac{\alpha[\mathbf{r}' - \mathbf{r}\exp(2\alpha t)]^2}{\exp(4\alpha t) - 1} - 3\alpha t\right\}. \tag{4.18}$$

Comparison of this exact expression with Eqs. (3.18) and (4.9) shows that the semiclassical approximation for this $\epsilon(\mathbf{r})$ is exact and that the normalization constant F depends only on t:

$$F(\mathbf{r},\mathbf{r}';t) = \left[\frac{\alpha}{2\pi \sinh 2\alpha t}\right]^{3/2}. \tag{4.19}$$

Note that had we known *a priori* that F depends only on t, Eq. (4.19) could have been obtained directly from Eq. (3.19). Alternatively, we could have utilized the following identity:

$$\frac{\partial}{\partial t}\int K(\mathbf{r},\mathbf{r}';t)d\mathbf{r} = -\int K(\mathbf{r},\mathbf{r}';t)\nabla\cdot\mathbf{F}(\mathbf{r})d\mathbf{r}. \tag{4.20}$$

[This identity also follows from Eq. (2.6) by integrating over all space, making use of Green's theorem, and assuming that K vanishes sufficiently rapidly as $\mathbf{r} \to \infty$ so that surface contributions may be dropped.] Combining Eqs. (4.2) and (4.20) and integrating the resulting equation gives

$$\int K(\mathbf{r},\mathbf{r}';t)d\mathbf{r} = \exp(-6\alpha t). \tag{4.21}$$

Again, had we known *a priori* that $F(\mathbf{r},\mathbf{r}';t)$ depends only on t, Eq. (4.21) combined with Eqs. (3.18) and (4.9) are sufficient to yield Eq. (4.19). In the absence of such prior knowledge, however, Eqs. (3.19) and (4.21) act only as self-consistency checks.

At this point it is perhaps worthwhile noting that Miller's method[5] for calculating the normalization constant agrees with our previous derivation. This is discussed in the Appendix. The significance of this correspondence lies in the fact that semiclassical methods based on the Miller formalism may now be applied simply to electrostatics problems.

Before proceeding further let us use a direct approach to calculate the solvation energy for an ion at point $\mathbf{R}$ in a dielectric given by Eq. (4.1). This is very elementary since the electric displacement vector is

$$\mathbf{D}(\mathbf{r}) = \frac{Q\hat{r}}{r^2}. \tag{4.22}$$

So from Eqs. (2.2), (2.3), and (4.1) we obtain

$$\Phi(\mathbf{r}) = Q\int_r^{\infty} (\mathbf{r}')^{-2}\exp(-\alpha r'^2)dr'. \tag{4.23}$$

Since $\Phi_0(\mathbf{r}) = Q/r$, Eqs. (2.15) and (2.16) imply

$$U = \frac{Q^2}{2}\int_0^{\infty}\frac{dr}{r^2}[\exp(-\alpha r^2) - 1]. \tag{4.24}$$

Carrying out the integral proceeds by differentiation with respect to α, evaluating the resulting Gaussian integral over r and then integrating over α again. Thus

$$U = -\frac{Q^2}{2}(\pi\alpha)^{1/2}. \tag{4.25}$$

This same result is obtained from Eq. (2.17) by using the path integral formalism. Thus for $\mathbf{R}=0$ the propagator is

$$K(\mathbf{0},\mathbf{0};t)=\left\{\frac{1}{\pi}\frac{\alpha}{[\exp(4\alpha t)-1]}\right\}^{3/2}. \tag{4.26}$$

Thus

$$U=\frac{Q^2}{4}\left(\frac{\alpha}{\pi}\right)^{1/2}\int_0^\infty\left\{\left[\frac{4}{e^{4x}-1}\right]^{3/2}-x^{-3/2}\right\}dx, \tag{4.27}$$

where we have set $x=\alpha t$. A numerical evaluation of this integral confirms that this expression gives identical results to the formula given by Eq. (4.25).

From a statistical mechanical point of view a comparison of Eqs. (4.24) and (4.27) is most interesting. Equation (4.24) expresses the solvation energy as an integral over configuration space, whereas Eq. (4.27) expresses it as an integral over time. This is reminiscent of the ergodic hypothesis which relates averages over configuration space with averages over time. One may either determine the solvation energy by expressing it in terms of the electrostatic field, and thus by doing an appropriate spatial integration, as in Eq. (4.24), or by following the motion of fiduciary particles in time and performing the appropriate average. Both procedures give equivalent results. This again is reminiscent of particle-field duality.

V. MONTE CARLO EVALUATION OF SOLVATION ENERGY

The path integral formalism for the solvation energy yields the following prescription for its computation. Start at the position of an ion and draw a loop which, after time t, returns to the ion. By summing over all times Eq. (2.17) gives the desired result. The prescription is quite general and not restricted by any particular symmetry constraints. By summing over all loops the ion is able to sample the presence of all inhomogenieties and all asymmetries. It thus represents a general and elegant way of solving the Laplace equation.

We would like to treat problems which are more complex than the model dielectric of Eq. (4.1). To this end we now develop a Monte Carlo technique, similar to that used in the evaluation of path integrals associated with quantum mechanical problems.[6] In free space the propagator may be written, from Eq. (3.5) as

$$K_0(\mathbf{r},\mathbf{r}';t)=(4\pi\Delta t)^{-3N/2}\int d\mathbf{r}_1\cdots\int d\mathbf{r}_{N-1}\times\exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[\frac{\mathbf{r}_n-\mathbf{r}_{n+1}}{\Delta t}\right]^2\right\}. \tag{5.1}$$

Let us define a free probability function

$$P_0(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})=\frac{(4\pi\Delta t)^{-3N/2}}{K_0(\mathbf{r},\mathbf{r}';t)}\times\exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[\frac{\mathbf{r}_n-\mathbf{r}_{n+1}}{\Delta t}\right]^2\right\}, \tag{5.2}$$

which is normalized so that $P_0\geqslant 0$ and

$$\int P_0(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})d\mathbf{r}_1\cdots d\mathbf{r}_{N-1}=1. \tag{5.3}$$

Then Eq. (3.5) may be expressed as

$$K(\mathbf{r},\mathbf{r}';t)=K_0(\mathbf{r},\mathbf{r}';t)\left\langle\exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[F^2(\mathbf{r}_n)+\frac{2}{\Delta t}\mathbf{F}(\mathbf{r}_n)\cdot(\mathbf{r}_n-\mathbf{r}_{n+1})\right]\right\}\right\rangle_0, \tag{5.4}$$

where $\langle\cdots\rangle_0$ denotes an average with respect to the probability function $P_0(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})$. This average is now computed using a Monte Carlo procedure with importance sampling.

To compute the average in Eq. (5.4) we begin a computation cycle by randomly selecting a point in the $3(N-1)$ dimensional configuration space $q=(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})$. We compute $P_0(q)$ as well as $Q(q)$ where

$$Q(q)=\exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[F^2(\mathbf{r}_n)+\frac{2}{\Delta t}\mathbf{F}(\mathbf{r}_n)\cdot(\mathbf{r}_n-\mathbf{r}_{n+1})\right]\right\}. \tag{5.5}$$

We then select an index j randomly in the range $1\leqslant j\leqslant N-1$. A point $\mathbf{r}_j^*$ is selected randomly in space (within some specified range of the point $\mathbf{r}_j$). Let us denote the new point in configuration space by $q^*=(\mathbf{r}_1,\ldots,\mathbf{r}_{j-1},\mathbf{r}_j^*,\mathbf{r}_{j+1},\ldots,\mathbf{r}_{N-1})$. The free probability at point q^* is computed:

$$P_0^*=P_0(q^*). \tag{5.6}$$

We define the probability for changing the configuration space point as G:

$$G=\frac{P_0^*}{P_0+P_0^*}. \tag{5.7}$$

The corresponding probability for not changing the point is $1-G$. Let us call the configuration space point for the next cycle q'. Thus

$$q'=\begin{cases}q^* & \text{with probability } G\\ q & \text{with probability } 1-G\end{cases}. \tag{5.8}$$

After running through M cycles we evaluate Eq. (5.4) as

$$K(\mathbf{r},\mathbf{r}';t)\doteq K_0(\mathbf{r},\mathbf{r}';t)\frac{1}{M}\sum_{m=1}^{M}Q(q_m). \tag{5.9}$$

In practice we allow the configuration point to incubate for some number of cycles M_i before actually starting the averaging procedure. This allows the originally selected point in configuration space to relax to a more probable region of space. When computing the average we also allow a few cycles to evolve between successive augmentations to the sum in Eq. (5.9). This makes for a more uniform sampling of the important parts of configuration space. Since $K_0(\mathbf{r},\mathbf{r}';t)$ is known analytically from Eq. (2.13), Eq. (5.9) gives a useful representation for the propagator.

In our discussion of the Monte Carlo procedure we based our average on the use of the free propagator $K_0(\mathbf{r},\mathbf{r}';t)$. This, however, is not necessary. Any propagator which is known analytically may be used as a base upon which to build the Monte Carlo averaging scheme. In particular we can replace $K_0(\mathbf{r},\mathbf{r}';t)$ by the $K(\mathbf{r},\mathbf{r}';t)$ given by Eq. (4.18). Let us call this the quadratic case and indicate this by

using a subscript α. Thus

$$K_\alpha(\mathbf{r},\mathbf{r}';t) = \left\{\frac{\alpha}{\pi[\exp(4\alpha t)-1]}\right\}^{3/2} \times\exp\left\{-\alpha\frac{[\mathbf{r}'-\mathbf{r}\exp(2\alpha t)]^2}{\exp(4\alpha t)-1}\right\}. \quad (5.10)$$

Then the associated probability distribution is

$$P_\alpha(q) = \frac{(4\pi\Delta t)^{-3N/2}}{K_\alpha(\mathbf{r},\mathbf{r}';t)} \times\exp\left\{-\frac{1}{4\Delta t}\sum_{n=0}^{N-1}[(1+2\alpha\Delta t)\mathbf{r}_n-\mathbf{r}_{n+1}]^2\right\}. \quad (5.11)$$

The quantity $Q(q)$ to be evaluated is now

$$Q(q) = \exp\left\{-\frac{\Delta t}{4}\sum_{n=0}^{N-1}\left[\left(\mathbf{F}(\mathbf{r}_n)+\frac{\mathbf{r}_n-\mathbf{r}_{n+1}}{\Delta t}\right)^2 - \left(2\alpha\mathbf{r}_n+\frac{\mathbf{r}_n-\mathbf{r}_{n+1}}{\Delta t}\right)^2\right]\right\}. \quad (5.12)$$

Now α is a parameter to be suitable defined. The rest of the Monte Carlo calculation proceeds as before except that averages are taken with respect to P_α.

A big advantage of employing these particular Monte Carlo procedures is that at each cycle only one three-dimensional subsector of the $3(N-1)$ dimensional configuration space is changed. Thus, for $2\leqslant j\leqslant N-2$:

$$P_\alpha(q^*) = P_\alpha(q)\exp\left(-\frac{1}{4\Delta t}(\mathbf{r}_j^*-\mathbf{r}_j) \cdot\{[1+(1+2\alpha\Delta t)^2](\mathbf{r}_j+\mathbf{r}_j^*) - 2(1+2\alpha\Delta t)(\mathbf{r}_{j-1}+\mathbf{r}_{j+1})\}\right). \quad (5.13)$$

For $j=1$ the formula is valid but the term $\mathbf{r}_{j-1}$ is omitted. For $j=N-1$ the term $\mathbf{r}_{j+1}$ is omitted instead. A similar simple formula applies to $Q(q^*)$. Thus one need only change one sector of configuration space at a time and modify the functions P and Q in the immediate vicinity of that sector.

As a simple test of the Monte Carlo method we have evaluated the one-dimensional propagator $K_x(0,0;t)$ both exactly and by using the Monte Carlo approach. For the model dielectric of Eq. (4.1) we have from Eq. (4.18) (applied to one dimension)

$$K_x(0,0;t) = \left\{\frac{\alpha}{\pi[\exp(4\alpha t)-1]}\right\}^{1/2}. \quad (5.14)$$

The results are tabulated in Table I in which we compute the ratio of K_x evaluated by the Monte Carlo procedure to K_x given by Eq. (5.14). The value of α was taken to be 1. In these calculations we took 15 intervals (N) and allowed the initial configuration space point to lie in the range $-1\leqslant x_n\leqslant 1$. A total incubation period of 10 000 steps was chosen during which we allowed these points to relax towards a high probability distribution. For each new random excursion of a given point x_n to x_n^* we allowed the distance to move randomly up to 0.2 units. When computing the Monte Carlo average we allowed five steps to evolve between samplings. The results show that for short times the agreement between the exact and approximate results are excellent. As t grows, however, fluctuations become more important. To maintain accuracy an increased number of samplings, M, are required.

In Fig. 1 we show a typical set of points $\{x_n\}$ at two times t. These represent the configurations attained right after the incubation period of 10 000 steps. We notice that as t increases the size of the fluctuations in the path increases. These fluctuations mean that the propagator tends to be less and less dominated by the semiclassical approximation. Fortunately, however, the actual size of $K_x(0,0;t)$ falls rapidly with increasing t, so that the solvation energy is rather unaffected.

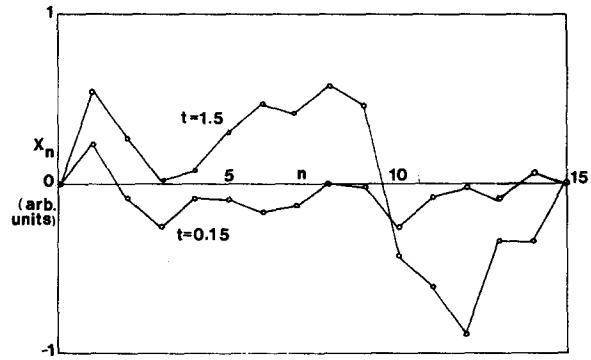

FIG. 1. A sampling of two paths at two different times t. Here n is the index labeling the intermediate values of the coordinates x_n. These paths appear in the evaluation of the one-dimensional propagator after the incubation period has elapsed.

TABLE I. Comparison of exact and Monte Carlo calculations of the one-dimensional propagator. In the Monte Carlo calculation (Sec. V) the time interval $0\cdots t$ was divided into $N=15$ intervals and, following an incubation period of 10 000 steps, $M(=10\,000)$ more steps were used to evaluate the average (5.9). The ratio between these Monte Carlo results and the exact ones (5.14) is given in column R_1. The ratio between the calculation based on matrix multiplication and the exact result appears in column R_2. In the matrix multiplication calculation the time and length intervals used were $\Delta t=0.015$, $\Delta x=0.125$. The x matrices were truncated at $L=40$.

t	$K_x(0,0;t)$ (exact)	R_1	R_2
0.015	2.269	1.0008	1.008
0.15	0.622	1.014	1.008
0.3	0.370	1.030	1.010
0.6	0.178	1.008	1.015
0.9	0.095	1.095	1.018
1.5	0.028	1.107	1.033
3.8	0.00028	···	1.062

VI. THE MATRIX MULTIPLICATION METHOD

While the Monte Carlo procedure is expected to be the most suitable approach to evaluate the propagator (3.5) in the general multidimensional case, a much simpler approach to one-dimensional problems is based on the matrix multiplication procedure of Thirumalai *et al.*[7] In this method the time discretized path integral, Eq. (3.5) is further discretized in space by introducing a grid on the one-dimensional

TABLE II. Diagonal matrix elements $M(I,I)$ at time $t = 3.8$. $x = 0.125$, $t = 0.15$, $L = 40$.

I	$K_x(I\Delta x, I\Delta x; t)$ (exact)	R_2
0	2.61×10^{-4}	1.062
10	5.47×10^{-5}	1.050
20	5.06×10^{-7}	1.014
25	1.51×10^{-8}	0.988
30	2.06×10^{-10}	0.957
35	1.29×10^{-12}	0.920
38	4.23×10^{-14}	0.861
40	3.70×10^{-15}	0.531

space axis

$$K(x,x';t) = (4\pi\Delta t)^{-N/2} \times \sum_{l_1=-\infty}^{\infty} \cdots \sum_{l_{N-1}=-\infty}^{\infty} M_{l_N l_{N-1}} M_{l_{N-1} l_{N-2}} \cdots M_{l_1 l_0}, \quad (6.1)$$

where M is the (non-Hermitian) matrix

$$M_{l_{n+1},l_n} = \exp\left\{ -\frac{\Delta t}{4}\left[F(\Delta x l_n) + \frac{\Delta x}{\Delta t}(l_n - l_{n+1}) \right]^2 \right\}, \quad (6.2)$$

and where Δx is the spatial discretization step. In the actual calculation the infinite l summations are truncated:

$$\sum_{l=-\infty}^{\infty} \rightarrow \sum_{l=-L}^{L}, \quad (6.3)$$

where the truncation number L is chosen large enough so that $L\Delta x$ is large relative to all physical distances in the problem. Equations (4.1) and (4.2) imply that $K(x,x',t)$ may be obtained as a function of t by iterative matrix multiplication

$$K(l\Delta x, l'\Delta x; t + \Delta t) = (4\pi\Delta t)^{-1/2} \sum_{l''=-L}^{L} M_{ll''} K(l''\Delta x, l'\Delta x; t). \quad (6.4)$$

Using Eq. (4.4) the time evolution of the propagator is easily evaluated in the one-dimensional case.

To demonstrate the use of this procedure we have evaluated the propagator $K(x,x';t)$ using the matrix multiplication method. R_2 in Table I denotes the ratio between the so evaluated $K_x(0,0;t)$ and the corresponding exact value calculated from Eq. (5.14). It should be noted that the calculation gives for each time all the elements $K(x,x';t)$. For all of them except those corresponding to the first few points near the edge of the truncated x axis the result is of accuracy similar to that shown in the table. The erosion of accuracy at the edges of the truncated zone is shown by the results of Table II where $K_x(I\Delta x, I\Delta x; t)$ is listed for different values of I. $I = 0$ is the center of the zone. The computer time required for these one dimensional calculations is considerably less than the corresponding Monte Carlo calculations. The latter becomes superior for problems of higher dimensionalities.

VII. POLARIZABILITY AND LOCAL FIELD

Having found an expression for the Green function in terms of path integrals allows us to obtain other quantities of physical interest. Two such quantities are the polarizability of an inhomogeneous dielectric "cloud" and the local field at any point in the cloud when it is subjected to a uniform electric field. Both calculations are similar, so we present them together. To calculate the polarizability let us place a point charge Q at position R far from the cloud. The field produced by this charge will be approximately uniform if $\mathbf{R}$ is large enough and this field will induce an electric dipole

$$\boldsymbol{\mu} = -Q\frac{\boldsymbol{\alpha}\cdot\mathbf{R}}{R^3}, \quad (7.1)$$

where α is the polarizability tensor of the dielectric cloud. The dipole can also be expressed in terms of the volume integral of the polarization vector $\mathbf{P}$ which in turn is related to the electric field by $\mathbf{P} = [\epsilon(r) - 1]\mathbf{E}/(4\pi)$. Thus

$$\boldsymbol{\mu} = \frac{1}{4\pi}\int \Phi(\mathbf{r})\nabla\epsilon(\mathbf{r})d\mathbf{r}, \quad (7.2)$$

where we have integrated by parts. From Eq. (2.10), assuming that $\epsilon(\mathbf{R}) = 1$ (i.e., that the charge is in free space) we have

$$\Phi(\mathbf{r}) = -4\pi Q G(\mathbf{r},\mathbf{R}). \quad (7.3)$$

Combining this with Eq. (2.8) gives finally

$$\boldsymbol{\alpha}\cdot\hat{R} = -\lim_{R\to\infty} R^2 \int_0^\infty dt \int d\mathbf{r}\, K(\mathbf{r},\mathbf{R};t)\nabla\epsilon(\mathbf{r}). \quad (7.4)$$

Thus the various components of the α tensor may be determined by carrying out the space and time integration called for in the above equation.

In calculating the local field we simply combine Eq. (7.3) with Eq. (2.3). Let us intoduce the "amplification" tensor A defined as

$$\mathbf{E}(\mathbf{r}) = \mathsf{A}(\mathbf{r})\cdot\mathbf{E}_0, \quad (7.5)$$

where $\mathbf{E}_0 = -Q\mathbf{R}/R^3$ is the external electric field. Then employing Eq. (2.8) yields

$$\mathsf{A}\cdot\hat{R} = \lim_{R\to\infty} 4\pi R^2 \int_0^\infty dt\, \nabla K(\mathbf{r},\mathbf{R};t). \quad (7.6)$$

Here the local field is simply related to the time integral of the propagator.

VIII. CONCLUSION

In this paper we have developed a method based on the path integral formalism, for the numerical solution of several electrostatic problems relevant to solid state physics and to ionic solutions. For one-dimensional problems iterative matrix multiplication provides an efficient computational method, while in more complicated situations a Monte Carlo technique can be used. Numerical evaluation of simple model cases that can also be solved exactly demonstrates the potential usefulness of this method.

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APPENDIX: THE MILLER SEMICLASSICAL APPROACH

Miller has presented a formalism which allows one to calculate the semiclassical approximation to the propagator. We will apply the formalism to the model $\epsilon(\mathbf{r})$ of Sec. IV.

According to Miller the semiclassical formula for the propagator would be

$$K(\mathbf{r},\mathbf{r}';t)=\left[(2\pi)^3\left|\left|\frac{\partial \mathbf{r}}{\partial \mathbf{p}'}\right|\right|_{\mathbf{r}'}\right]^{-1/2}\exp[-S_c(\mathbf{r},\mathbf{r}';t)], \tag{A1}$$

where $\|\cdots\|$ denotes the determinant of the matrix of partial derivatives. From Eq. (4.7) we have the "initial" momentum given by

$$\mathbf{p}'=2\alpha\mathbf{A}. \tag{A2}$$

Combining this with Eqs. (4.4)–(4.6) allows us to write

$$\mathbf{r}=\frac{\mathbf{P}'}{2\alpha}\exp(2\alpha t)+\left[\mathbf{r}'-\frac{\mathbf{p}'}{2\alpha}\right]\exp(-2\alpha t). \tag{A3}$$

Then

$$\left|\left|\frac{\partial \mathbf{r}}{\partial \mathbf{p}'}\right|\right|=\left[\frac{\sinh(2\alpha t)}{\alpha}\right]^3, \tag{A4}$$

so

$$K(\mathbf{r},\mathbf{r}';t)=\left[\frac{2\pi\sinh(2\alpha t)}{\alpha}\right]^{-3/2}\exp(-S_{cl}). \tag{A5}$$

This formula is in agreement with Eq. (4.18), as should be expected for this quadratic problem.

[1] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[2] L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, New York, 1981).

[3] K. Ito, Mem. Am. Math. Soc. **4**, 1 (1951); H. Haken, Z. Phys. B **24**, 321 (1976); K. Kitahara and H. Metiu, J. Stat. Phys. **15**, 141 (1976); K. C. Hunt and J. Ross, J. Chem. Phys. **75**, 976 (1981).

[4] A. Jevicki, Dissertation, City University of New York, 1976; B. Sakita, *Quantum Theory of Many Variable Systems and Fields* (World Scientific, Singapore, 1985). The Weyl-ordered product for two canonically conjugate operators P and Q is defined in terms of the binomial expansion:

$$[sP+tQ]^N=\sum_{k=0}^{N}\binom{N}{k}s^k t^{N-k}[P^kQ^{N-k}]_W.$$

The Weyl ordering is signified by a subscript W. For example,

$$[PQ]_W=\tfrac{1}{2}[PQ+QP],$$

$$[P^2Q]_W=\tfrac{1}{3}[P^2Q+PQP+QP^2],$$

$$[PQ^2]_W=\tfrac{1}{3}[PQ^2+QPQ+Q^2P],$$

etc.

[5] W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).

[6] J. A. Barker, J. Chem. Phys. **70**, 2914 (1979); D. Thirumalai and B. J. Berne, *ibid.* **79**, 5029 (1983), and references therein.

[7] D. Thirumalai, E. J. Bruskin, and B. J. Berne, J. Chem. Phys. **79**, 5063 (1983).