The variational method and the stochastic–Liouville equation. I. A finite element solution to the CIDN(E)P problem[a)]

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A variational formulation is developed for the stochastic–Liouville equation (SLE). It is shown how this formulation may be used as a general basis for the study of numerical and approximate methods of solution of the SLE. The finite element method is developed for the approximate solution of the spin–density matrix elements using the variational formulation. The method is illustrated by employing it to obtain a compact computer-oriented solution to the (high-field) chemically-induced spin polarization problem. This solution is both more efficient as well as more accurate than the previous treatment by Pedersen and Freed using finite difference methods. Various features of finite element and finite difference methods are compared from the viewpoint of this solution. The great flexibility of finite element methods for solution of the SLE is discussed.

I. INTRODUCTION

In this work, we wish to show that the calculus of variations is an important tool in the numerical solution of the stochastic–Liouville equation (SLE) when analytic solutions are not readily obtainable. Variational methods have been extensively utilized in approximate treatments of quantum mechanical eigenvalue problems. Here we develop the variational method solution of the SLE and then illustrate its applicability by treating in detail the chemically induced dynamic nuclear (and electronic) polarization [CIDN(E)P] problem by the variational finite element[1] (FE) method.

Past numerical solutions of the SLE have employed either the eigenfunction-expansion[2] or finite difference (FD)[3] methods. In this study, the calculus of variations, through the Ritz (or Galerkin) method and the minimization of weighted residuals, is shown to lead to an approximate solution of the SLE equivalent to the eigenfunction-expansion approach. Also, the FE method is shown to yield an approximate formulation somewhat related to that which results from a FD treatment, but with significant and useful differences. Thus, the variational method helps to unify the subject of approximate solutions to the SLE. But, more importantly, it suggests entirely new approaches for potentially more effective numerical solutions.

Problems which arise in the field of CIDN(E)P[3] and magnetic-field modulated radical ion-pair recombination[4] may be analyzed by means of the numerical solution of the SLE. In each case, the numerical analysis of the diffusion part of the SLE has been performed using well-known FD techniques,[5] and the quantum mechanical terms of the SLE are then inserted to form an overall supermatrix construction. Numerical procedures have been of considerable value, since one can easily employ physically realistic models and boundary conditions. The new approach discussed below employs a FE approach to the SLE for the spatial variable, while the time derivative can be treated as before by FD methods[4] or else by Laplace transforms.[3]

Although this work introduces the FE method to problems involving the SLE, this method has had extensive applications in many fields of engineering.[1] Thus, there are extensive applications and techniques which could be usefully adaptable to problems in chemical physics as exemplified by this study on the SLE.

We first develop in Sec. II a variational principle for the SLE and then develop the FE method utilizing a very simple, but useful, variational function. In Sec. III, the CIDN(E)P problem appropriate for high fields is formulated using this FE method, and the computational details and results are given. Conclusions appear in Sec. IV.

II. THEORETICAL APPROACH

A. SLE and the calculus of variations

We start with a fairly general form for the stochastic–Liouville equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = -i\mathcal{H}^{\times}(\mathbf{r})\rho(\mathbf{r},t) + \nabla_{\mathbf{r}}\cdot\mathbf{D}\cdot\nabla_{\mathbf{r}}\rho(\mathbf{r},t) + \frac{1}{kT}\nabla_{\mathbf{r}}\cdot\mathbf{D}\cdot\{\rho(\mathbf{r},t)[\nabla_{\mathbf{r}}U(\mathbf{r},t)]\} + \mathcal{K}(\mathbf{r})\rho(\mathbf{r},t) + \Re\rho(\mathbf{r},t), \tag{2.1}$$

where $\rho(\mathbf{r},t)$ is the spin-density matrix, and $\mathcal{H}^{\times}(\mathbf{r})$ is the Liouville operator associated with the spin Hamiltonian $\mathcal{H}(\mathbf{r})$ (i.e., for any two operators A and B, $A^{\times}B \equiv [A,B]$). The term

$$\Gamma_{\mathbf{r}} = \nabla_{\mathbf{r}}\cdot\mathbf{D}\cdot\left\{\nabla_{\mathbf{r}} + \frac{1}{kT}[\nabla_{\mathbf{r}}U(\mathbf{r})]\right\} \tag{2.2}$$

represents the diffusion operator in the presence of a potential $U(\mathbf{r})$ and the tensorial properties of the diffusion tensor $\mathbf{D}$ are explicitly displayed. The operator $\mathcal{K}(\mathbf{r})$ is introduced phenomenologically, when needed, to represent reactivities, and may or may not be spin de-

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pendent. The $\mathcal{R}$ operator includes all relaxation contributions to the relaxation times T_1 and T_2 which are independent of $\mathbf{r}$. We now take the matrix elements of the operator (1), and adopt the notation that the $\rho_{ij} \to \rho_\alpha$ and $\mathcal{H}^x(\mathbf{r})_{ij,kl} \to \mathcal{H}^x(\mathbf{r})_{\alpha,\beta}$, such that ρ defines a column vector whose elements ρ_α are all the matrix elements of $\rho(\mathbf{r}, t)$ needed in the problem, while $\mathcal{H}^x(\mathbf{r})_{\alpha,\beta}$ defines the elements of a square matrix.

It is known that, since $\mathcal{H}$ is Hermitian, then $\mathcal{H}^x$ is Hermitian in this basis.[3] Furthermore, we will always choose that basis of spin states that renders $\mathcal{H}^x$ real so that it becomes a real symmetric matrix.[3] Also, $\mathcal{K}(\mathbf{r})$ can generally be written as a real symmetric matrix by appropriate choice of spin states. The relaxation operator $\mathcal{R}$ will have a real part that is symmetric and leads to the T_1 and T_2 effects, while it will also have a complex part which leads to dynamic frequency shifts. In all examples of interest, $\mathcal{R}$ generates a complex-symmetric matrix in spin space.

Now we will find it useful for variational applications to render $\Gamma_{\mathbf{r}}$ as a Hermitian matrix (in $\mathbf{r}$ space) by the similarity transformation defined by[3]

$$\tilde{\Gamma}_{\mathbf{r}} \equiv [P_0(\mathbf{r})]^{-1/2} \Gamma_{\mathbf{r}} [P_0(\mathbf{r})]^{1/2} \tag{2.3a}$$

and

$$\tilde{\rho}(\mathbf{r}, t) \equiv [P_0(\mathbf{r})]^{-1/2} \rho(\mathbf{r}, t), \tag{2.3b}$$

where $P_0(\mathbf{r})$ is the unique equilibrium distribution in $\mathbf{r}$ for which

$$\Gamma_{\mathbf{r}} P_0(\mathbf{r}) = 0. \tag{2.4}$$

Then, Eq. (2.4) becomes

$$\frac{\partial \tilde{\rho}_\alpha}{\partial t} = \sum_\beta [-i(\mathcal{H}^x)_{\alpha,\beta} + (\tilde{\Gamma}_{\mathbf{r}})\delta_{\alpha,\beta} + (\mathcal{K})_{\alpha,\beta} + (\mathcal{R})_{\alpha,\beta}]\tilde{\rho}_\beta, \tag{2.5}$$

where

$$\tilde{\Gamma}_{\mathbf{r}} = \nabla_{\mathbf{r}} \cdot \mathbf{D} \cdot \nabla_{\mathbf{r}} + \frac{\{\nabla_{\mathbf{r}} \cdot D \cdot [\nabla_{\mathbf{r}} U(\mathbf{r})]\}}{2kT} + \frac{\mathbf{F}(\mathbf{r}) \cdot \mathbf{D} \cdot \mathbf{F}(\mathbf{r})}{(2kT)^2}, \tag{2.6a}$$

which may be simply written as

$$\tilde{\Gamma}_{\mathbf{r}} = \nabla_{\mathbf{r}} \cdot \mathbf{D} \cdot \nabla_{\mathbf{r}} + f(\mathbf{r}). \tag{2.6b}$$

Note that

$$\mathbf{F}(\mathbf{r}) \equiv -\nabla_{\mathbf{r}} U(\mathbf{r}), \tag{2.6c}$$

which is the force resulting from the potential $U(\mathbf{r})$, and $f(\mathbf{r})$ is given by the last two terms in Eq. (2.6a). The form of Eq. (2.5) results when we recognize that $\mathcal{H}^x_{\alpha,\beta}$ and $\mathcal{K}_{\alpha,\beta}$ are simple functions of $\mathbf{r}$ and $\mathcal{R}_{\alpha,\beta}$ is independent of $\mathbf{r}$. Thus, we may rewrite Eq. (2.5) as

$$\frac{\partial \tilde{\rho}_\alpha}{\partial t} = \nabla_{\mathbf{r}} \cdot \mathbf{D} \cdot \nabla_{\mathbf{r}} \tilde{\rho}_\alpha + \sum_\beta a(\mathbf{r})_{\alpha,\beta} \tilde{\rho}_\beta, \quad \text{for all } \alpha, \tag{2.7}$$

where $\mathbf{a}(\mathbf{r})$ is a complex-symmetric matrix and where the $a(\mathbf{r})_{\alpha,\alpha}$ term also contains $f(\mathbf{r})$ from Eq. (2.6b). Often one is interested in the Laplace transform of Eq. (2.7) with respect to the time variable. One then has

$$\sum_\beta [(s1 - \nabla_{\mathbf{r}} \cdot \mathbf{D} \cdot \nabla_{\mathbf{r}})\delta_{\alpha,\beta} - a(\mathbf{r})_{\alpha,\beta}]\bar{\rho}_\beta(\mathbf{r}, s) = \tilde{\rho}_\alpha(\mathbf{r}, 0), \tag{2.8}$$

where

$$\bar{\rho}_\beta(\mathbf{r}, s) \equiv \int_0^\infty e^{-st} \tilde{\rho}_\beta(\mathbf{r}, t)\, dt \tag{2.9}$$

and where $\tilde{\rho}_\alpha(\mathbf{r}, 0)$ is the initial value of $\tilde{\rho}_\alpha(\mathbf{r}, t)$. For example, one is often interested in the limit

$$\lim_{t\to\infty} \tilde{\rho}_\alpha(\mathbf{r}, t) = \lim_{s\to 0} s\bar{\rho}_\alpha(\mathbf{r}, s) \tag{2.10}$$

in the analysis of CIDN(E)P. Also, the Fourier–Laplace transform, which is obtained from Eqs. (2.9) and (2.10) by letting $s \to -i\omega$, is often of interest. This is the form which appears in line shape problems such as the ESR slow-tumbling problem [although here the first term on the right in Eq. (2.7) is replaced by the appropriate rotational diffusion operator[2]].

We now may formally include the $(-s)$ term in the $a(\mathbf{r})_{\alpha,\alpha}$ matrix element without affecting the symmetry of $\mathbf{a}(\mathbf{r})$. Then, in Cartesian coordinates, the expanded form of Eq. (2.8) can be written

$$-\sum_{i,j} \frac{\partial}{\partial x_i}\left[D_{ij} \frac{\partial \bar{\rho}_\alpha(\mathbf{r}, s)}{\partial x_j}\right] - \sum_\beta a(\mathbf{r})_{\alpha,\beta}\bar{\rho}_\beta(\mathbf{r}, s) = \tilde{\rho}_\alpha(\mathbf{r}, 0), \quad \text{for all } \alpha, \tag{2.11}$$

with $x_i = x$, y, or z [since $\mathbf{r} = \mathbf{r}(x, y, z)$]. For practical purposes, other coordinate systems may be more advantageous for solution since they may simplify the diffusive or quantum effects involved in Eq. (2.8). Transforming $(\mathbf{r} \to \mathbf{q})$ yields the analogous form of Eq. (2.11) for any orthogonal coordinate system

$$-\frac{1}{\sqrt{g}} \sum_{i,j,k} \frac{\partial}{\partial q_i}\left[\sqrt{g}\, \frac{D_{ij}}{g_{jj}} \frac{\partial \bar{\rho}_\alpha(\mathbf{q}, s)}{\partial q_j}\right] - \sum_\beta a(\mathbf{q})_{\alpha,\beta}\bar{\rho}_\beta(\mathbf{q}, s) = \tilde{\rho}_\alpha(\mathbf{q}, 0), \quad \text{for all } \alpha, \tag{2.12}$$

where we have used the conventional metric coefficients[6,7] g_{ij} and the Jacobian of the transformation $\sqrt{g} \equiv \sqrt{g_{11} g_{22} g_{33}}$.

The basis of the variational method[8] is to employ a functional

$$F\left[\mathbf{q}, \bar{\rho}_\alpha(\mathbf{q}, s), \bar{\rho}_\beta(\mathbf{q}, s) \cdots \frac{\partial \bar{\rho}_\alpha}{\partial q_i}, \frac{\partial \bar{\rho}_\beta}{\partial q_i} \cdots \frac{\partial \bar{\rho}_\alpha}{\partial q_j}, \frac{\partial \bar{\rho}_\beta}{\partial q_j} \cdots\right] \tag{2.13a}$$

such that the associated integral (also a functional):

$$I = \int_{\mathbf{q}_a}^{\mathbf{q}_b} F\left[\mathbf{q}, \bar{\rho}_\alpha(\mathbf{q}, s) \cdots \frac{\partial \bar{\rho}_\alpha}{\partial \mathbf{q}_i} \cdots\right] d\mathbf{q} \tag{2.13b}$$

(with $d\mathbf{q} = dq_1 dq_2 dq_3$) is stationary with respect to variations in $\bar{\rho}_\alpha(\mathbf{q}, s)$ and $\partial\bar{\rho}_\alpha(\mathbf{q}, s)/\partial q_i$, for all α and i. We have implied in Eq. (2.13) that the functional F is specifically defined for each instant of time. This leaves the q_i as the only independent variables in F and I. The implications of ignoring the functional variations with respect to t (or s) are discussed further below. Once the form of F is known, one could try tentative forms for all the $\bar{\rho}_\alpha(\mathbf{q}, s)$ which then determine a trial functional.

The functional transforms as a scalar density[9] {and thus, by convention, contains the Jacobian of transformation [i.e., $F(\mathbf{q} \cdots)$ of Eq. (2.13) may be written also as $\sqrt{g}F(\mathbf{q} \cdots)$[8]]}. The value of the integral I is a scalar and invariant with respect to any transformation. It will, however, be a function of any variational param-

eters that one includes in the trial F via the $\bar{\rho}_\alpha(\mathbf{q}, s)$. By infinitesimal variations of the $\bar{\rho}_\alpha(\mathbf{q}, s)$, ... (represented by $\delta\bar{\rho}_\alpha$, ...), one may obtain the first variation in I, signified as δI:

$$\delta I = \int_{q_a}^{q_b} \left[\sum_{j=\alpha,\beta,\ldots} \frac{\partial F}{\partial \bar{\rho}_j} \delta\bar{\rho}_j + \sum_{i,j} \frac{\partial F}{\partial \bar{\rho}_j^i} \frac{\partial}{\partial q_i} (\delta\bar{\rho}_j) \right] d\mathbf{q} , \quad (2.14)$$

where we have used $\bar{\rho}_j^i \equiv \partial\bar{\rho}_j/\partial q_i$ and the fact that $\delta\bar{\rho}_j^i = (\partial/\partial q_i)(\delta\bar{\rho}_j)$. The stationary condition can be restated as

$$\delta I = \int_{q_a}^{q_b} \delta F \, d\mathbf{q} = 0 . \quad (2.15)$$

When this stationary condition is satisfied, the variational method then leads to the partial differential equations

$$\frac{1}{\sqrt{g}} \left[\frac{\partial F}{\partial \bar{\rho}_\alpha} - \sum_i \frac{\partial}{\partial q_i} \left(\frac{\partial F}{\partial \bar{\rho}_\alpha^i} \right) \right] = 0 , \quad \text{for all } \alpha , \quad (2.16)$$

and

$$\frac{\partial F}{\partial \bar{\rho}_\alpha^i} \delta\bar{\rho}_\alpha \Big]_{q_a}^{q_b} = 0 , \quad \text{for all } \alpha \text{ and } i , \quad (2.17)$$

which, if F is suitably chosen, will yield Eq. (2.8). Equation (2.16), the governing differential equation, is invariant under coordinate transformation[8,9] and is known as the Euler–Lagrange equation for the problem. Equation (2.17) gives either "natural" boundary conditions $\partial F/\partial\bar{\rho}_\alpha^i \big]_{q_a,\alpha}^{q_b,b} = 0$ or the "geometric" boundary conditions $\delta\bar{\rho}_\alpha(\mathbf{q}_a) = \delta\bar{\rho}_\alpha(\mathbf{q}_b) = 0$.

We now require a suitable F which through Eq. (2.16) leads to Eq. (2.8), the SLE. This will be given here for several cases. In Cartesian coordinates,

$$F = \frac{1}{2} \sum_\alpha \left[\sum_{i,j} D_{ij} \bar{\rho}_\alpha^i \bar{\rho}_\alpha^j - \sum_\beta a_{\alpha,\beta}(\mathbf{r}) \bar{\rho}_\alpha \bar{\rho}_\beta - 2\tilde{\rho}_\alpha(\mathbf{r}, 0)\bar{\rho}_\alpha \right] , \quad (2.18)$$

where the symmetric-tensor property of $\mathbf{D}$ has been used. In an orthogonal coordinate system where $\mathbf{D}$ is diagonal, we have

$$F = \frac{\sqrt{g}}{2} \sum_\alpha \left[\sum_i \frac{D_{ii}(\bar{\rho}_\alpha^i)^2}{g_{ii}} - \sum_\beta a_{\alpha,\beta}(\mathbf{q}) \bar{\rho}_\alpha \bar{\rho}_\beta - 2\tilde{\rho}_\alpha(\mathbf{q}, 0)\bar{\rho}_\alpha \right] . \quad (2.19)$$

One can easily show that the functionals given by Eqs. (2.18) or (2.19) inserted into the Euler–Lagrange equations (2.16) will produce the correct form of the SLE if one uses the symmetry of $\mathbf{a}(\mathbf{q})$. For example, from Eq. (2.18),

$$\frac{\partial F}{\partial \bar{\rho}_\eta} = -\frac{1}{2} \left[\sum_\beta a_{\eta\beta}(\mathbf{r}) \bar{\rho}_\beta + \sum_\alpha a_{\alpha\eta}(\mathbf{r}) \bar{\rho}_\alpha + 2\tilde{\rho}_\eta(\mathbf{r}, 0) \right]$$

$$= -\sum_\beta a_{\eta\beta}(\mathbf{r}) \bar{\rho}_\beta - \tilde{\rho}_\eta(\mathbf{r}, 0) \quad (2.20)$$

for any η.

It is also necessary to show that the functional F [cf. Eqs. (2.18)–(2.19)] is invariant to the particular choice of spin basis functions u_i used to calculate the density matrix elements $\rho_\alpha = \rho_{ij}$. This is easily done by recognizing that, for an M-dimensional spin space ($i, j = 1, 2, \ldots, M$), there are M^2 dimensional matrix elements ρ_α, each of which can be thought of as a component of the vector ρ in an M^2-dimensional vector space or Hilbert space of which the eigenstate products $u_i u_j^*$ constitute one set of base vectors. (This is also called the Liouville representation in which the M^2 unit base vectors are themselves operators; if the base operators are Hermitian, then the coefficients ρ_α become real.[10(a)]) Now, a unitary transformation $\mathbf{U}$ which transforms the spin basis functions u_i into the new set u_j' may be represented in this M^2-dimensional Liouville space by a Liouville type of unitary operator whose matrix elements $\tilde{U}_{\alpha,\beta} = \tilde{U}_{ij,kl} = U_{ij} U_{kl}^*$.[10(b)]

Since for convenience we are considering only real values of ρ_α, then we can let $\mathbf{U}$ and $\tilde{\mathbf{U}}$ be orthogonal operators in their respective subspaces. Thus, we have

$$\rho_\beta' = \sum_\alpha \tilde{U}_{\beta\alpha} \rho_\alpha , \quad \rho_\alpha = \sum_\beta \tilde{U}_{\alpha\beta}^{-1} \rho_\beta' = \sum_\beta \tilde{U}_{\beta\alpha} \rho_\beta' , \quad (2.21a)$$

so that

$$\sum_{\alpha,\beta} a_{\alpha\beta} \rho_\alpha \rho_\beta = \sum_{\alpha,\beta,\gamma,\delta} a_{\alpha\beta} \tilde{U}_{\gamma\alpha} \tilde{U}_{\delta\beta} \rho_\gamma' \rho_\delta'$$

$$= \sum_{\gamma,\delta} a_{\gamma\delta}' \rho_\gamma' \rho_\delta' , \quad (2.21b)$$

where

$$a_{\gamma\delta}' \equiv \sum_{\alpha,\beta} \tilde{U}_{\gamma\alpha} a_{\alpha\beta} \tilde{U}_{\beta\delta}^{-1} \quad (2.21c)$$

is just the $\mathbf{a}$ matrix in the new representation. This demonstrates the invariance of the $\sum_{\alpha,\beta} a_{\alpha\beta} \rho_\alpha \rho_\beta$ term. Now,

$$\sum_\alpha \frac{\partial \rho_\alpha}{\partial q_i} \frac{\partial \rho_\alpha}{\partial q_j} = \sum_{\alpha,\gamma,\delta} \tilde{U}_{\gamma\alpha} \tilde{U}_{\delta\alpha} \frac{\partial \rho_\gamma'}{\partial q_i} \frac{\partial \rho_\delta'}{\partial q_j} = \sum_\gamma \frac{\partial \rho_\gamma'}{\partial q_i} \frac{\partial \rho_\delta'}{\partial q_j} \quad (2.22)$$

(since $\sum_\alpha \tilde{U}_{\gamma\alpha} \tilde{U}_{\delta\alpha} = \delta_{\gamma,\delta}$). Finally, by an identical argument to Eq. (2.22), we can show that

$$\sum_\alpha \tilde{\rho}_\alpha(\mathbf{r}, 0) \bar{\rho}_\alpha = \sum_\gamma \tilde{\rho}_\gamma'(\mathbf{r}, 0) \bar{\rho}_\gamma' , \quad (2.23)$$

so that Eqs. (2.18) and (2.19) remain invariant to transformation of the spin basis states.

All of the above discussion could be repeated dealing with the original form $\tilde{\rho}(\mathbf{q}, t)$, where the term $\partial\tilde{\rho}_\alpha(\mathbf{q}, t)/\partial t$ would be treated as a constant. Thus, in essence, we are applying the variational principle here to the "time-independent" form of the SLE. Such an approach has been referred to as a "quasivariational" method, and is introduced partly because it leads to more tractable numerical methods of solution and also because it eases the difficulty in obtaining the appropriate functional. Such a quasivariational method only allows us to optimize any trial functional forms for the $\tilde{\rho}_\alpha(\mathbf{q}, t)$ independently for each instant in time (or value of s) rather than over the complete time span of interest (or for s ranging from $0 \to \infty$).[11] One may then use standard methods (e.g., finite differences in time) to develop the time evolution of the problem.

It is of some interest to note that the functionals shown above may be properly included in a variational process where the Laplace transform variable s is treated as an independent variable and the functional is

allowed to vary with s. Then, the functionals given above are observed to satisfy the more general set of Euler–Lagrange equations [cf. Eq. (2.16)]

$$\frac{\partial F}{\partial \bar{\rho}_\alpha} - \sum_i \frac{\partial}{\partial q_i}\left(\frac{\partial F}{\partial \bar{\rho}^i_\alpha}\right) - \frac{\partial}{\partial s}\left(\frac{\partial F}{\partial \bar{\rho}^s_\alpha}\right) = 0, \tag{2.24}$$

where now $\bar{\rho}^s_\alpha \equiv \partial \bar{\rho}_\alpha(\mathbf{q}, s)/\partial s$, i.e., Eq. (2.24) with, for example, Eq. (2.18) yields a form of the SLE in Laplace space given by Eq. (2.11). We thus conclude that the functionals above are proper for the variation of $\bar{\rho}_\alpha(\mathbf{q}, s)$ with respect to independent variables $\mathbf{q}$ and s, and furthermore they automatically include the initial conditions $\tilde{\rho}_\alpha(\mathbf{q}, 0)$. This more general applicability of the functionals (2.18) and (2.19) is due to their chosen form, from which we note $\partial F/\partial \bar{\rho}^s_\alpha = 0$. {Since functionals are not unique, we may construct other equivalent forms, i.e., some $F'(\mathbf{q}, s, \bar{\rho}_\alpha, \ldots, \bar{\rho}^i_\alpha, \ldots, \bar{\rho}^s_\alpha, \ldots)$ where the term $(\partial/\partial s)(\partial F'/\partial \bar{\rho}^s_\alpha)$ is not zero, but yet where F' inserted in the Euler–Lagrange equation (for independent variables $\mathbf{q}$ and s) [Eq. (2.24)] still leads to the appropriate form of the SLE. However, functionals of more complex form, although easily constructed, usually complicate the resulting numerical solution.} Thus, we recognize that in Laplace space the analysis above is a useful and complete variational formulation of the SLE, while in t space it is only convenient to obtain a quasivariational formulation.

Once the functional is known, then it follows that we can attempt trial solutions $\tilde{\rho}_\alpha(\mathbf{q}, t, c^\alpha_i)$ or $\bar{\rho}_\alpha(\mathbf{q}, s, c^\alpha_i)$ by use of functional forms dependent on the set of variational parameters c^α_i (i.e., the ith variational parameter for ρ_α). This is known as a "direct" method of solution in which the integral of Eq. (2.15) becomes $I = I(c^1_1, c^1_2, \ldots, c^\alpha_i, \ldots)$. The condition that this integral be stationary then leads to the equations

$$\partial I/\partial c^\alpha_i = 0, \quad \text{for all } \alpha \text{ and } i. \tag{2.25}$$

Solutions of these equations yield the best possible values of the c^α_i and thus the best possible trial function, e.g., $\bar{\rho}_\alpha(\mathbf{q}, s, c^\alpha_i)$, of the assumed form. After the c^α_i have been calculated, the quality of the variational solution can be determined by computing the residual resulting from the trial function applied in the SLE, i.e., if we rewrite the SLE [Eq. (2.8)] in the form

$$\sum_\beta A_{\alpha,\beta}(\mathbf{q}, s)\bar{\rho}_\beta(\mathbf{q}, s) - \tilde{\rho}_\alpha(\mathbf{q}, 0) = 0, \quad \text{for all } \alpha, \tag{2.26}$$

then the residual (for the αth density matrix element) is defined as

$$R_\alpha \equiv \sum_\beta A_{\alpha\beta}(\mathbf{q}, s)\bar{\rho}_\beta(\mathbf{q}, s, c^\beta_i) - \tilde{\rho}_\alpha(\mathbf{q}, 0, c^\alpha_i), \tag{2.27}$$

where $R_\alpha = R_\alpha(\mathbf{q}, s, c^\beta_i)$ and clearly is a function of all the trial $\bar{\rho}(\mathbf{q}, s, c^\beta_i)$. Here, to be concise, we have used $\mathbf{A}$ as a matrix containing all terms on the LHS of Eq. (2.8). The magnitude of R_α may be used as a general indication of how close the trial function $\bar{\rho}_\alpha(\mathbf{q}, s, c^\alpha_i)$ is to the exact solution. This can be seen by writing the difference between Eqs. (2.26) and (2.27):

$$R_\alpha = \sum_\beta A_{\alpha\beta}(\mathbf{q}, s)[\bar{\rho}_\beta(\mathbf{q}, s) - \bar{\rho}_\beta(\mathbf{q}, s, c^\beta_i) - [\tilde{\rho}_\alpha(\mathbf{q}, 0) - \tilde{\rho}_\alpha(\mathbf{q}, 0, c^\alpha_i)], \tag{2.28}$$

where $\bar{\rho}_\beta(\mathbf{q}, s)$ is the exact solution for the βth density matrix element.[12] The criterion for an acceptable solution would then be related to the smallness of the size of its residual.

One can also employ another direct method[1,13] of solution called the Ritz method whereby we write the trial form of $\tilde{\rho}(\mathbf{q}, t)$ or $\bar{\rho}(q, s)$ as a linear combination of known functions with variable coefficients. In particular, let us use the complete orthonormal set of eigenfunctions of the diffusion operator, e.g., $D\nabla^2_{\mathbf{r}}$, for isotropic diffusion $G_{lm}(\mathbf{k}, \mathbf{r}) \equiv \sqrt{2/\pi} j_l(kr) Y^m_l(\Omega) Y^{m*}_l(\Omega')$, where $j_l(kr)$ is the spherical Bessel function of order l and $Y^m_l(\Omega)$ is the spherical harmonic of order l and rank m, while Ω and Ω' represent the polar angles defining the orientation of $\mathbf{r}$ and $\mathbf{k}$, respectively. Assuming a spherical outer boundary at $r = r_N$ such that the allowed wave vector $\mathbf{k}$ can take on the discrete values $|\mathbf{k}| = (2\pi n/r_N)$, $n = 1, 2, \ldots$, we may formulate our trial solution

$$\bar{\rho}_\alpha(\mathbf{r}, C^\alpha_{lmk}) = \sum_{l,m,k} C^\alpha_{lmk} G_{lm}(\mathbf{k}, \mathbf{r}), \quad \text{for all } \alpha. \tag{2.29}$$

This is a solution for a given value of s (i.e., invariant in s), which is a quasivariational treatment. To put our solution in the form applicable to line shape problems, let us assume a Fourier–Laplace transformation $s \to -i\omega$. A simple Ritz-method solution could then be obtained by inserting the trial $\bar{\rho}_\alpha(\mathbf{r}, C^\alpha_{lmk})$ in the proper functional [Eq. (2.18)] and minimizing the variation of the integral [Eq. (2.13b)] by use of Eq. (2.25). This leads to a set of linear simultaneous equations in the coefficients C^α_{lmk}.

By another formulation, known as the minimization of weighted residuals (MWR),[14] we can obtain a similar result. First, the residuals R_α are calculated from Eq. (2.27). Then, let us weight these residuals by multiplication by the function $G_{l'm'}(\mathbf{k}', \mathbf{r})$, integrate, and set the result equal to zero. This procedure fixes the mean value of the residual at zero in the system volume, and is given by

$$\int_V G^*_{l'm'}(\mathbf{k}', \mathbf{r}) R_\alpha \, d\mathbf{r} = 0, \quad \text{for all } l', m', \alpha, \tag{2.30}$$

where the volume V has been previously specified. Equation (2.30) can be more explicitly written as

$$\sum_{l,m,k}\left[\sum_\beta C^\beta_{lmk}\int_V A_{\alpha,\beta}(\mathbf{r}, s) G^*_{l'm'}(\mathbf{k}', \mathbf{r}) G_{lm}(\mathbf{k}, \mathbf{r})\, d\mathbf{r} - C^\alpha_{lmk}(t=0) \times \int_V G^*_{l'm'}(\mathbf{k}', \mathbf{r}) G_{lm}(\mathbf{k}, \mathbf{r})\, d\mathbf{r}\right] = 0, \quad \text{for all } \alpha, \tag{2.31a}$$

where the known initial condition is

$$\tilde{\rho}_\alpha(\mathbf{r}, C^\alpha_{lmk})(t=0) = \sum_{l,m,k} C^\alpha_{lmk}(t=0) G_{lm}(\mathbf{k}, \mathbf{r}), \quad \text{for all } \alpha. \tag{2.31b}$$

The choice of the $G_{l'm'}(\mathbf{k}', \mathbf{r})$ as weighting functions formally constitutes the use of the Galerkin method,[1]

which is a special case of the MWR method. In the cases where the functional is not known, or cannot be developed, the MWR method may be used directly and is most valuable. When the functional is known, the Galerkin and Ritz methods yield equivalent results.

If one is able to expand the spin Hamiltonian matrix elements in terms of the $G_{lm}(\mathbf{k}, \mathbf{r})$ the above method yields a set of simultaneous linear equations in the unknown coefficients C^{α}_{lmk} for all α, l, m, and k. This preceding variational solution is equivalent to the well-known eigenfunction-expansion method[2,3,8] and presents an alternate formulation of this widely used approximation method.

Problems involving the solution of the SLE in nonorthogonal coordinate systems may also be handled by the methods mentioned above. For example, if we choose the case where $\mathbf{D} = D\mathbf{1}$ in Eq. (2.8), then the SLE becomes

$$-\frac{D}{\sqrt{g}}\sum_{i,j}\frac{\partial}{\partial q_i}\left[\sqrt{g}g^{ij}\frac{\partial\bar{\rho}_\alpha(\mathbf{q},s)}{\partial q_j}\right]-\sum_\beta a(\mathbf{q})_{\alpha\beta}\bar{\rho}_\beta(\mathbf{q},s) = \tilde{\rho}_\alpha(\mathbf{q},0), \quad \text{for all } \alpha, \tag{2.32a}$$

with the corresponding functional

$$F=\frac{D\sqrt{g}}{\alpha}\sum_\alpha\left[\sum_{i,j}g^{ij}\bar{\rho}^{\,i}_{\alpha}\bar{\rho}^{\,j}_{\beta}-\sum_\beta a_{\alpha,\beta}(\mathbf{q})\bar{\rho}_\alpha\bar{\rho}_\beta-2\tilde{\rho}_\alpha(\mathbf{q},0)\bar{\rho}_\alpha\right], \tag{2.32b}$$

where now $\sqrt{g}\equiv|\det(g_{ij})|^{1/2}$ and g_{ij} and g^{ij} are the covariant and contravariant components[6,7] of the metric tensor, respectively. (We note that the slow-tumbling problem[2] usually utilizes the Euler angles which constitute a nonorthogonal coordinate system.[6]) For cases where the functional is not available, the MWR techniques[12] (i.e., Galerkin method, method of moments, collocation method, least squares method) are readily applicable.

B. The finite element method

The FE method is a particular example of a variational method that emphasizes the subdivision of a region of, e.g., space, into small "elements" and allows one to choose trial solutions, including variational parameters, within each element. The FE method guarantees a numerical solution to the partial differential equation in question (i.e., the SLE) that may be a higher or lower bound to the exact solution. This is not, in general, true for the FD result. In our development, the FE method will be used only for variations in spatial variables, i.e., an approximate solution of Eq. (2.8) will be sought where s is fixed.

Guymon[15] first applied the variational FE method to the solution of the one and two dimensional diffusion-convection equations, and it is his FE analysis which serves as a basis for our study. However, additional attention must be given to a treatment of the SLE, since we must account for the more complicated spin-matrix properties in our solutions, the complex variables entering into the variational treatment, and new boundary conditions not encountered in the engineering applications. Also, we must consider the interpretation of the solutions, which are continuous in space (although this space has been segmented). This last point is the main difference between the FE and FD methods, as FD methods only yield a solution with known values at specific nodal points (however, the usual interpretation is that the FD nodal value represents a mean value of the solution throughout the small region of space). Many tests of the relative numerical accuracy of the FE versus FD methods exist [cf. Refs. 1(d), 13] for various engineering problems, but the usefulness of the FE method in dealing with problems in chemical physics has not previously been explored.

In our treatment of the case of three dimensional isotropic diffusion within a finite volume of space, we will segment the total ("global") region into $N-1$ volume elements connecting N nodes (by analogy to what was done in the FD solution[3]). An element consists of a well-defined region of space whose boundaries constitute nodes, which are usually chosen to be simply defined in the coordinate system used. For the case of isotropic diffusion, one solves the radial diffusion equation for which a node in r space is the spherical surface at a particular distance from the origin. Each volume element is, for this case, a spherical shell centered at the origin. [The relative diffusion of two particles may be treated as the diffusion of the second relative to the first fixed at the origin, but where the appropriate diffusion coefficient is the sum of those for both particles.[3]] Let us define the distance of closest approach of two spherical particles as d; then, the appropriate substitutions[6] into Eq. (2.12) yield

$$-\frac{1}{y^2}\frac{\partial}{\partial y}\left[y^2\frac{\partial\bar{\rho}_\alpha(y,\sigma)}{\partial y}\right]-\sum_\beta\hat{a}(y)_{\alpha\beta}\bar{\rho}_\beta(y,\sigma)=\tilde{\rho}_\alpha(y,\sigma), \quad \text{for all } \alpha, \tag{2.33}$$

where the dimensionless quantities $y=r/d$, $\sigma=sd^2/D$, and $\hat{a}(y)_{\alpha,\beta}=a(y)_{\alpha,\beta}d^2/D$ have been introduced. Also,

$$\bar{\rho}_\alpha(y,\sigma)=\frac{1}{4\pi}\int_0^{\pi}d\theta\sin\theta\int_0^{2\pi}d\varphi\bar{\rho}_\alpha(\mathbf{r},\sigma). \tag{2.34}$$

The "local" specifications, i.e., those within an element, depend directly on the two boundary nodes, i.e., the mth element is bounded by the mth and $(m+1)$th nodes with $1\le m\le N-1$. Following normal convention, nodal indices follow a quantity in parentheses, so the mth and $(m+1)$th nodes are found at a distance $y(m)$ and $y(m+1)$, respectively, from the origin. We can therefore define the (dimensionless) elemental length as

$$h^{(m)}=y(m+1)-y(m), \tag{2.35}$$

where the bracketed superscripts now refer to locally defined functions or quantities. The simplest trial variational function for each local problem is a linear function in y, and we employ this commonly used form in the succeeding discussion (although more complex trial functions may be employed[1] to better represent $\rho^{(m)}_\alpha$ at the expense of a more complex subsequent analysis). Thus, we may write

$$\bar{\rho}^{(m)}_\alpha=(1-z)\bar{\rho}_\alpha(m)+z\bar{\rho}_\alpha(m+1). \tag{2.36}$$

Here we have introduced the local distance variable

$$z=[y-y(m)]/h^{(m)}, \quad \text{for } y(m)\le y\le y(m+1), \tag{2.37}$$

so $0\le z\le 1$ in each element. Also, $\bar{\rho}_\alpha^{(m)}$ is the local trial function chosen to approximate $\bar{\rho}_\alpha(y,\sigma)$ in the region $y(m)\le y\le y(m+1)$, and $\bar{\rho}_\alpha(m)$ and $\bar{\rho}_\alpha(m+1)$ designate a nodal value of the trial function. Our global or overall solution to $\bar{\rho}_\alpha(y,\sigma)$ is then formed as

$$\bar{\rho}_\alpha(y,\sigma)\cong\sum_{m=1}^{N-1}\bar{\rho}_\alpha^{(m)}, \tag{2.38a}$$

while the total spatial extent of our problem is

$$y(N)=1+\sum_{m=1}^{N-1}h^{(m)}. \tag{2.38b}$$

Thus, $1\le y<y(N)$ since $y(1)=1$. The global solution to our problem [Eq. (2.38a)] is required to be continuous for all values of y, the important condition being continuity across the boundaries between the elements (i.e., at each node). We require the first derivative $\partial\bar{\rho}_\alpha(y,\sigma)/\partial y$ to be continuous only within each element in the present simple treatment, so it could be discontinuous at the nodes. These conditions are satisfied by our choice of $\bar{\rho}_\alpha^{(m)}$, given by Eq. (2.36).

The functional which is associated with the SLE [Eq. (2.33)] is given by the appropriate form of Eq. (2.19). In each element, though, we adopt a different trial solution given by Eq. (2.36), and this leads to a local functional $F^{(m)}$ such that

$$F=\sum_{m=1}^{N-1}F^{(m)}, \tag{2.39a}$$

where

$$F^{(m)}=\frac{y^2}{2}\sum_\alpha\left[\left(\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial y}\right)^2-\sum_\beta\hat{a}(y)_{\alpha,\beta}\bar{\rho}_\alpha^{(m)}\bar{\rho}_\beta^{(m)}-2\tilde{\rho}_\alpha^{(m)}\bar{\rho}_\alpha^{(m)}\right]$$

$$\text{for } y(m)\le y\le y(m+1). \tag{2.39b}$$

The variational method then requires the integral of Eq. (2.13) to be stationary with respect to changes in the variational parameters of our problem, which are taken as the nodal values $\bar{\rho}_\alpha(m)$ given in Eq. (2.36). The integral (2.13) may now be written explicitly for the present case as

$$I=\int_1^{y(N)}F(y,\bar{\rho}_\alpha^{(m)},\partial\bar{\rho}_\alpha^{(m)}/\partial y,\ldots)\,dy. \tag{2.40}$$

This integral may now be separated, as were the trial function and functional, as

$$I=\sum_{m=1}^{N-1}I^{(m)}, \tag{2.41}$$

where, using Eq. (2.39b), we find in terms of local variables

$$I^{(m)}=\frac{h^{(m)3}}{2}\sum_\alpha\int_0^1\left[\frac{1}{h^{(m)2}}\left(\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial z}\right)^2-\sum_\beta\hat{a}_{\alpha,\beta}\bar{\rho}_\alpha^{(m)}\bar{\rho}_\beta^{(m)}-2\tilde{\rho}_\alpha^{(m)}\bar{\rho}_\alpha^{(m)}\right](\mathfrak{a}^{(m)}+z)^2\,dz, \tag{2.42}$$

in which the substitution $y=(\mathfrak{a}^{(m)}+z)h^{(m)}$ has been used, where $\mathfrak{a}^{(m)}\equiv y(m)/h^{(m)}$, and where $\hat{a}_{\alpha,\beta}=\hat{a}(y)_{\alpha,\beta}=\hat{a}(\mathfrak{a}^{(m)}+z)_{\alpha,\beta}$. To complete the variational process, we now may insert our trial solution, for $\bar{\rho}_\alpha(y,s)$, into I and then minimize I with respect to the variational parameters. This has been simplified by the FE method to merely require the insertion of Eq. (2.36) into (2.42), at which point all integrations may be done analytically [for well-behaved $\hat{a}(y)_{\alpha,\beta}$] and a set of coupled simultaneous equations in the unknown nodal values $\bar{\rho}_\alpha(m)$ result. Boundary conditions follow from Eq. (2.17) and will be discussed in the context of our example calculation. One may analytically minimize the variation of the global integral with respect to a particular nodal value (which serves as a variational parameter) to obtain from Eq. (2.41):

$$\frac{\partial I}{\partial\bar{\rho}_\alpha(i)}=\sum_{m=1}^{N-1}\frac{\partial I^{(m)}}{\partial\bar{\rho}_\alpha(i)}=0, \quad \text{for all } \alpha \text{ and } i, \tag{2.43}$$

where Eq. (2.43) refers to the ith nodal value of the αth spin-density matrix element. One typical term [e.g., $\partial I^{(m)}/\partial\bar{\rho}_\alpha(i)$] of Eq. (2.43) may be shown to be

$$\frac{\partial I^{(m)}}{\partial\bar{\rho}_\alpha(i)}=h^{(m)3}\int_0^1\left\{\frac{1}{h^{(m)2}}\left(\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial z}\right)\frac{\partial(\partial\bar{\rho}_\alpha^{(m)}/\partial z)}{\partial\bar{\rho}_\alpha(i)}-\sum_\beta\hat{a}_{\alpha,\beta}\bar{\rho}_\beta^{(m)}\left[\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial\bar{\rho}_\alpha(i)}\right]-\tilde{\rho}_\alpha^{(m)}\left[\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial\rho_\alpha(i)}\right]\right\}(\mathfrak{a}^{(m)}+z)^2\,dz, \tag{2.44}$$

for all α and i,

where we have made use of Eq. (2.23), and the fact that

$$\frac{\partial\hat{a}_{\alpha,\beta}}{\partial\bar{\rho}_\alpha(i)}=\frac{\partial\tilde{\rho}_\alpha^{(m)}}{\partial\bar{\rho}_\alpha(i)}=0, \quad \text{for all } \alpha,\ \beta,\ i, \text{ and } m. \tag{2.45}$$

Now we can write Eq. (2.44) in terms of nodal values by using

$$\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial z}=\bar{\rho}_\alpha(m+1)-\bar{\rho}_\alpha(m), \tag{2.46a}$$

which follows from Eq. (2.36). Then,

$$\frac{\partial}{\partial\bar{\rho}_\alpha(i)}\left(\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial z}\right)=\begin{cases}+1, & \text{for } i=m+1,\\ -1, & \text{for } i=m,\\ 0, & \text{for } i\ne m \text{ or } m+1,\end{cases} \tag{2.46b}$$

and

$$\frac{\partial\bar{\rho}_\alpha^{(m)}}{\partial\bar{\rho}_\alpha(i)}=\begin{cases}1-z, & \text{for } i=m,\\ z, & \text{for } i=m+1,\\ 0, & \text{for } i\ne m \text{ or } m+1.\end{cases} \tag{2.46c}$$

We may then rewrite Eq. (2.44) such that $\hat{a}_{\alpha,\beta}$ contains purely quantum terms entering from the SLE. [This means extracting a term from $\hat{a}_{\alpha\alpha}$ of $(-\sigma)$.] Then, choosing, for example, $i=m+1$, we find

$$\frac{\partial I^{(m)}}{\partial \bar{\rho}_\alpha(m+1)} = h^{(m)3}\int_0^1 \Bigg(\frac{1}{h^{(m)2}}\,[\bar{\rho}_\alpha(m+1)-\bar{\rho}_\alpha(m)](+1) + \{(1-z)[\sigma\bar{\rho}_\alpha(m)-\tilde{\rho}_\alpha(m)]$$

$$+ z[\sigma\bar{\rho}_\alpha(m+1)-\tilde{\rho}_\alpha(m+1)]\}(z) - \Bigg[(1-z)\sum_\beta \hat{a}_{\alpha,\beta}\bar{\rho}_\beta(m) + z\sum_\beta \hat{a}_{\alpha,\beta}\bar{\rho}_\beta(m+1)\Bigg](z)\Bigg)(\mathfrak{a}^{(m)}+z)^2\,dz\,. \tag{2.47}$$

Here, in Eq. (2.47), the factor of σ, the nodal quantities, and integrations appear explicitly. This equation may be converted to the similar equation for $\partial I^{(m)}/\partial\bar{\rho}_\alpha(m)$ by noting from Eqs. (2.46) that only two factors need be changed [i.e., $(+1)\to(-1)$ in the first term and $(z)\to(1-z)$ multiplying the last two bracketed terms]. We can now write the equations for the variation in the local integral for the mth element with respect to the αth spin density matrix element in matrix form

$$\begin{pmatrix} \dfrac{\partial I^{(m)}}{\partial\bar{\rho}_\alpha(m)} \\ \dfrac{\partial I^{(m)}}{\partial\bar{\rho}_\alpha(m+1)} \end{pmatrix} = \frac{X_0^{(m)}}{h^{(m)2}}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} \bar{\rho}_\alpha(m) \\ \bar{\rho}_\alpha(m+1) \end{pmatrix}$$

$$+ \begin{pmatrix} X_0^{(m)} - 2X_1^{(m)} + X_2^{(m)} & X_1^{(m)} - X_2^{(m)} \\ X_1^{(m)} - X_2^{(m)} & X_2^{(m)} \end{pmatrix}\left\{\sigma\begin{pmatrix} \bar{\rho}_\alpha(m) \\ \bar{\rho}_\alpha(m+1) \end{pmatrix} - \begin{pmatrix} \tilde{\rho}_\alpha(m) \\ \tilde{\rho}_\alpha(m+1) \end{pmatrix}\right\}$$

$$- \sum_\beta \begin{bmatrix} \hat{X}_0^{(m)}(\alpha,\beta) - 2\hat{X}_1^{(m)}(\alpha,\beta) + \hat{X}_2^{(m)}(\alpha,\beta) & \hat{X}_1^{(m)}(\alpha,\beta) - \hat{X}_2^{(m)}(\alpha,\beta) \\ \hat{X}_1^{(m)}(\alpha,\beta) - \hat{X}_2^{(m)}(\alpha,\beta) & \hat{X}_2^{(m)}(\alpha,\beta) \end{bmatrix}\begin{pmatrix} \bar{\rho}_\beta(m) \\ \bar{\rho}_\beta(m+1) \end{pmatrix}, \quad \text{for all } m \text{ and } \alpha, \tag{2.48a}$$

where the integrals have been defined as

$$X_n^{(m)} \equiv h^{(m)3}\int_0^1 z^n(\mathfrak{a}^{(m)}+z)^2\,dz \tag{2.48b}$$

and

$$\hat{X}_n^{(m)}(\alpha,\beta) \equiv h^{(m)3}\int_0^1 \hat{a}_{\alpha,\beta}\,z^n(\mathfrak{a}^{(m)}+z)^2\,dz\,, \tag{2.48c}$$

noting again that the $\hat{a}_{\alpha,\beta}$ may be a function of distance inside each element. From Eq. (2.48b), we see that $X_0^{(m)}$ is the *exact* volume of the mth shell divided by 4π. This quantity enters the above discussion naturally while the analogous discrete volume factor[3] $V(i)$ arises in a FD discussion of the conservation of probability. Also, from Eq. (2.48c), we see that the continuous spatial variation of the quantum terms $\hat{a}_{\alpha,\beta}$ has been retained unlike an FD treatment. However, Eq. (2.48) shows that a specifically weighted mean value of the quantum terms enters into the present "simple" FE treatment. The inherent advantages of Eqs. (2.48) (written for all spin density matrix elements) come from their specific application to a single finite element. Only the physical properties of that element appear in Eq. (2.48), i.e., the element "length" $h^{(m)}$ and the diffusion properties of the element which comprise the scaling factor d^2/D. The flexibility of the FE method lies in the allowed variability of these factors from element to element, and this will be seen in the next section as a computational advantage in treating the CIDN(E)P problems.

After one creates the N-1 sets of Eqs. (2.48) for each spin density matrix element α, one may complete the variational procedure (the Rayleigh–Ritz method) by the minimization condition of Eq. (2.43), which simplifies, since only two elements have any one node in common. For example,

$$\frac{\partial I}{\partial\bar{\rho}_\alpha(m)} = \frac{\partial I^{(m-1)}}{\partial\bar{\rho}_\alpha(m)} + \frac{\partial I^{(m)}}{\partial\bar{\rho}_\alpha(m)} = 0\,, \quad \text{for all } \alpha\,, \tag{2.49a}$$

for $2 \le m \le N-1$, with the remaining boundaries giving

$$\frac{\partial I^{(1)}}{\partial\bar{\rho}_\alpha(1)} = \frac{\partial I^{(N-1)}}{\partial\bar{\rho}_\alpha(N)} = 0\,, \quad \text{for all } \alpha\,. \tag{2.49b}$$

Equations (2.49) imply that, for a typical node, two equations need be summed, one from Eq. (2.48) written for the mth element and one from Eq. (2.48) written as pertaining to the $(m-1)$th element. This summation, Eq. (2.49) completed for each node, creates a set of N coupled equations for each α (which bears an analogy to the FD method). When this minimization and summation is done for each spin density matrix element, a "supermatrix" equation results, similar in basic form (but not content) to those found in past FD solutions.[3] This matrix equation may be written as

$$(\sigma\chi' + \Omega - \mathbf{W}')\rho = \chi'\rho_0 \tag{2.50}$$

and it is assumed that the equations have been assembled in a coherent nodal-oriented fashion that leads to the matrix on the LHS of Eq. (2.50) being banded. Also, ρ_0 contains the nodal values for the initial condition, with $\rho(\sigma)$ the required solution. Typically, ρ_0 has only one (or at most a few) nonzero elements so that the product $\chi'\rho_0$ can be found trivially. χ', Ω, and $\mathbf{W}'$ are supermatrices resulting from Eqs. (2.43), (2.48), and (2.49). The χ' or $\mathbf{W}'$ are formed from the more basic χ and $\mathbf{W}$ matrices by multiplication of each element by a $L\times L$ unit matrix, where L is the total number of spin density matrix elements ($1 \le \alpha \le L$, $L = M^2$). The elements of these matrices are more clearly discussed in

terms of specific cases, so this will be deferred till the discussion of the CIDN(E)P example. The Ω matrix differs significantly in comparison with its FD counterpart, and is basically due to the integration in Eq. (2.48c). From Eqs. (2.48) and (2.49), we see that the matrix elements of Ω are complex-valued quantum mechanical "source and sink" terms added into a general diffusion framework. Thus, this application is considerably different from past FE works,[15] and demonstrates its usefulness for problems in chemical physics where the $\hat{a}_{\alpha\beta}$ need not be real valued such as is the case with a broad range of quantum-mechanically related problems.

III. THE CIDN(E)P PROBLEM SOLVED BY THE METHOD OF FINITE ELEMENTS

A. Theory

In the previous section, the FE analysis for isotropic three dimensional diffusion was discussed. Equations (2.48) and (2.50) thus provide a viable framework for the numerical solution of CIDN(E)P type problems, and what remains is the specification of the quantum mechanical behavior (in the $\hat{a}_{\alpha,\beta}$) of the spin systems. The three dimensional high-field CIDN(E)P problem is a good test of the variational FE method. It has been treated theoretically and numerically[3] in the past by FD methods, and certain aspects of CIDNP have been formulated analytically,[16] allowing for comparison of results.

For two diffusing radicals, each of which contains an unpaired electron, we can write $\mathcal{H}^x$, the Hamiltonian superoperator from Eq. (2.1), as[3]

$$\mathcal{H}^x(y)= \begin{array}{c} \begin{matrix} SS & ST_0 & T_0S & T_0T_0 \end{matrix} \\ \begin{pmatrix} 0 & -Q & Q & 0 \\ -Q & 2J(y) & 0 & Q \\ Q & 0 & -2J(y) & -Q \\ 0 & Q & -Q & 0 \end{pmatrix} \end{array} , \tag{3.1}$$

where $2Q$ is the difference in the ESR frequencies of the two radicals, $J(y)$ is the spatially varying spin exchange operator, and the S and T_0 indices denote the singlet and ($m_s=0$) triplet electron spin states, respectively. Therefore, one has to consider matrix elements $\hat{a}_{\alpha,\beta}$ for α or $\beta = SS$, ST_0, T_0S, and T_0T_0. Also, the exchange operator is usually assumed to be of the form[3] $J(y) = (J_0 d^2/D)\exp[-\lambda(y-1)]$ with $\lambda \equiv 5\ln 10/y_{ex}$. y_{ex} represents a dimensionless exchange distance (usually $y_{ex} \approx d$).

Because of the form of Eqs. (2.7) and (2.33), we find, for all α and β,

$$\hat{a}_{\alpha,\beta} = -i(\mathcal{H}^x)_{\alpha,\beta} d^2/D \tag{3.2a}$$

except for

$$\hat{a}_{SS,SS} = -(kd^2/D)\delta(y-1) \tag{3.2b}$$

and we note from Eq. (3.1) that $\hat{a}_{\alpha,\beta} = \hat{a}_{\alpha,\beta}(y)$. Also, in Eq. (3.2b), the (pseudo)first order reaction rate constant k is introduced for a reaction of radicals in contact in the singlet state. Inserting Eqs. (3.2) into Eq. (2.48c), we find that a limited number of integrals need to be solved. For example,

$$\hat{X}_n^{(m)}(SS, T_0S) = -i(Qd^2/D)X_n^{(m)}, \tag{3.3a}$$

$$\hat{X}_n^{(m)}(SS, SS) = (kd^2/D)h^{(1)}\delta_{n,0}\delta_{m,1}, \tag{3.3b}$$

$$\hat{X}_n^{(m)}(ST_0, ST_0) = -i(2J_0 d^2/D)h^{(m)3}(\alpha^{(m)2}E_n^{(m)} + 2\alpha^{(m)}E_{n+1}^{(m)} + E_{n+2}^{(m)})\exp\{-\lambda[y(m)-1]\}, \tag{3.3c}$$

with

$$E_n^{(m)} \equiv \int_0^1 z^n \exp(-\lambda h^{(m)} z)\, dz . \tag{3.3d}$$

Thus, the only integrations needed are $X_n^{(m)}$ for $n=0$ to 2 and $E_n^{(m)}$ for $n=0$ to 4. These may easily be solved analytically giving polynomials in $\alpha^{(m)}$ which are trivially handled in the computation. Because the spatial dependence of the $\hat{X}_n^{(m)}$ and $X_n^{(m)}$ enters the calculation via simple powers of $\alpha^{(m)}[=y(m)/h^{(m)}]$, the FE method has retained its flexibility in the choice of element specifications even after accounting for the terms of $\hat{\mathbf{a}}(y)$.

The matrix Ω may then be constructed with knowledge of the $\hat{X}_n^{(m)}(\alpha,\beta)$ and Eq. (2.48a). It involves terms which couple all the spin density matrix elements at one node with those at the nearest neighbor nodes. This feature is unlike that of the quantum mechanical supermatrix of a FD treatment and, in comparison, only increases the bandwidth of Ω relative to the FD case.

Prior to the calculation of the individual matrix elements needed to solve the diffusive aspect of Eq. (2.50), we must set down the proper boundary conditions that will lead to physically realistic results. These have been discussed previously[3] and can be summarized by noting the need for a reflecting inner boundary and a *non*reflecting outer boundary that must have no effect on final results. At the inner boundary $y=1$, the *natural* boundary condition [cf. Eq. (2.17)] associated with the variational approach is

$$\left.\frac{\partial \bar{\rho}_\alpha^{(1)}}{\partial y}\right]_{y=1} = 0, \quad \text{for all } \alpha . \tag{3.4}$$

This mathematically models a pair of hard sphere nuclei. Since we wish a nonreflecting outer boundary (so as not to induce artificial re-encounters), we may create a "collecting" element[3a,17] [the $(N-1)$th element] where this FE relation exists:

$$\frac{\partial \bar{\rho}_\alpha^{(N-1)}}{\partial z} = -\bar{\rho}_\alpha(N-1) . \tag{3.5}$$

This condition does not enter naturally into the solution as does Eq. (3.4), and thus it must be explicitly applied when one writes Eq. (2.47) for the variations in $I^{(N-1)}$. Equation (3.5) is the local flux equation (2.46a) of the $(N-1)$th element where dependence on the final nodal value has been removed. This allows a flux into the element regardless of any concentration gradient so collection can occur.

With these boundary conditions we can now appropriately define the elements of the fundamental matrices. All elements of χ, $\mathbf{W}$, and Ω are formed by the procedure outlined in the last section, i.e., Eq. (2.49) requires the addition of two equations coming from two

specific cases of Eq. (2.48a). These are summed to form one row of the overall supermatrix equation [Eq. (2.50)]. This procedure is repeated for all L spin density matrix elements at each node and then repeated for all N nodes. $\mathbf{W}$ is defined in terms of the integrals $X_n^{(m)}$ and the element size $h^{(m)}$:

$$W_{1,1} = -W_{1,2} = -X_0^{(1)}/h^{(1)^2}, \tag{3.6a}$$

$$W_{i,i-1} = X_0^{(i-1)}/h^{(i-1)^2}, \tag{3.6b}$$

$$W_{i,i} = -(X_0^{(i-1)}/h^{(i-1)^2} + X_0^{(i)}/h^{(i)^2}), \tag{3.6c}$$

$$W_{i,i+1} = X_0^{(i)}/h^{(i)^2}, \tag{3.6d}$$

for $i = 2$ to N except for the elements

$$W_{N-1,N} = W_{N,N} = 0. \tag{3.6e}$$

The conservation of probability condition in our FE treatment

$$\sum_i W_{ij} = 0, \quad \text{for all } j, \tag{3.6f}$$

is then satisfied. These FE transition matrix elements for variable nodal separation are similar in form to their discrete FD analogs,[18] except we see in Eq. (3.6) the elemental volume factor appearing.

The χ' supermatrix is formed from the more basic χ in the same fashion as $\mathbf{W}'$ is created from $\mathbf{W}$. χ is defined by

$$\chi_{1,2} = X_0^{(1)} - 2X_1^{(1)} + X_2^{(1)}, \tag{3.7a}$$

$$\chi_{1,2} = X_1^{(1)} - X_2^{(1)}, \tag{3.7b}$$

$$\chi_{i,i-1} = X_1^{(i-1)} - X_2^{(i-1)}, \tag{3.7c}$$

$$\chi_{i,i} = X_1^{(i-1)} + X_0^{(i)} - 2X_1^{(i)} + X_2^{(i)}, \tag{3.7d}$$

$$\chi_{i,i+1} = X_1^{(i)} - X_2^{(i)}, \tag{3.7e}$$

for $N \geq i \geq 2$ except for

$$\chi_{N,N} = X_2^{(N-1)}. \tag{3.7f}$$

The initial condition is usually chosen to be unit probability that the radical pair is in contact and in some well defined spin state. This implies, for our FE analysis, that

$$1 = h^{(1)^3} \int_0^1 \tilde{\rho}_\alpha^{(1)} (\alpha^{(1)} + z)^2 dz \tag{3.8}$$

if the radicals start in the αth spin matrix state. (This expression may easily be generalized for any particle separation or mixture of initial spin matrix states.) It follows from Eq. (2.36) that

$$1 = h^{(1)^3} \int_0^1 [(1-z)\tilde{\rho}_\alpha(1) + z\tilde{\rho}_\alpha(2)](\alpha^{(1)} + z)^2 dz. \tag{3.9}$$

We can then choose $\tilde{\rho}_\alpha(2) = 0$ so as to initially constrain the probability to the first element, giving finally

$$\tilde{\rho}_\alpha(1) = [X_0^{(1)} - X_1^{(1)}]^{-1}, \tag{3.10a}$$

e.g., for random initial spin states, we set

$$\tilde{\rho}_{SS}(1) = \tilde{\rho}_{T_0T_0}(1) = 1/2[X_0^{(1)} - X_0^{(1)}]^{-1} \tag{3.10b}$$

and all other

$$\tilde{\rho}_\alpha(i) = 0. \tag{3.10c}$$

These $\tilde{\rho}_\alpha(i)$ can be assembled in increasing value of the nodal index, thus forming ρ_0, the RHS vector of Eq. (2.50).

This completes the information needed to create Eq. (2.50), which may then be solved to find the $\bar{\rho}_\alpha(m)$ from

$$\rho = (\sigma\chi' + \Omega - \mathbf{W}')^{-1}\chi'\rho_0. \tag{3.11}$$

Then, since the density matrix elements vary linearly with distance through each element (in our present treatment), we may calculate the desired quantities $\mathcal{P}(\sigma)$ and $P_a(\sigma)$. Using the definitions of Freed and Pedersen,[3(a)] we have

$$\mathcal{P}(\sigma) \equiv \int_1^{y(N)} [\bar{\rho}_{SS}(y,\sigma) + \bar{\rho}_{T_0T_0}(y,\sigma)]\, y^2\, dy \tag{3.11a}$$

and

$$P_a(\sigma) \equiv -2\,\mathrm{Re} \int_1^{y(N)} \bar{\rho}_{ST_0}(y,\sigma)\, y^2\, dy, \tag{3.11b}$$

where $\mathcal{P}(\sigma)$ represents the total probability of (separated) radical pairs which remain for given value of σ, while $P_a(\sigma)$ is the electron spin polarization of the radical "a" chosen as the fixed origin of our coordinate system. Using Eq. (2.36), the FE forms can be written

$$\mathcal{P}(\sigma) = \sum_{m=1}^{N-1} h^{(m)3} \int_0^1 \{(1-z)[\bar{\rho}_{SS}(m) + \bar{\rho}_{T_0T_0}(m)] + z[\bar{\rho}_{SS}(m+1) + \bar{\rho}_{T_0T_0}(m+1)]\}(\alpha^{(m)} + z)^2\, dz \tag{3.12a}$$

and

$$P_a(\sigma) = -2\sum_{m=1}^{N-1} h^{(m)3} \int_0^1 [(1-z)\,\mathrm{Re}\bar{\rho}_{ST_0}(m) + z\,\mathrm{Re}\bar{\rho}_{ST_0}(m+1)](\alpha^{(m)} + z)^2\, dz, \tag{3.12b}$$

where all the nodal quantities $\bar{\rho}_\alpha(m)$ will enter from the solution ρ of Eq. (3.11). The important long-time limiting values of Eqs. (3.12) ($\mathcal{P}$ and P_a^∞) are found by noting that, in the Laplace transformed case, one uses $\sigma \approx 0$ and Eq. (2.10).

B. Computational details and results

In the CIDN(E)P problem, we often wish to use as an initial condition

$$\tilde{\rho}_\alpha(y,0) = \text{constant} \times \delta(y-1), \tag{3.13}$$

i.e., the particles are initially in contact. The results for other initial particle separations can then be made by previously discussed relations.[3(a),16(a)] Thus, because of the form of Eq. (3.10a), we shall require $X_0^{(1)} - X_1^{(1)} \ll 1$ to simulate Eq. (3.13) with a negligible error. Since

$$X_0^{(1)} - X_1^{(1)} = \tfrac{3}{2}h^{(1)} + \tfrac{5}{3}h^{(1)^2} + \tfrac{7}{12}h^{(1)^3}, \tag{3.14}$$

we shall select $h^{(1)} \cong 10^{-5}$ to satisfy Eq. (3.13) for practical purposes. This means that the probability that the two radicals will never encounter[16(a)] is $\approx 10^{-6}$, or that the probability that the two will at least encounter each other once is sufficiently close to unity (the value for two particles actually in contact).

As discussed above, the features of each individual element enter the matrix equations explicitly and rigor-

ously through the mathematical derivation. Thus, it is easy to make use of the varying element size entering the equations and administer special treatment (in the form of small size elements) in those regions of space where the CIDN(E)P effects are most sensitive to the diffusion, i.e., where $J(y) \gtrsim Q$. In the FD studies,[3] it was also found that $y(N)$ must be chosen large enough so as to allow all natural re-encounters. Unfortunately, in those FD studies,[3] the necessity of satisfying these requirements led to immense matrix inversions requiring the use of high-speed, large-core computers. Recent FD calculations[18] using more general transition matrices have allowed us to largely surmount these problems. We note however that such generality is inherent in the FE approach.

The independence of each $h^{(i)}$ in Eqs. (3.3), (3.6), and (3.7) allows us to easily choose, for example, a geometrically increasing element size as one strategy in reducing the number of finite elements needed. One then has a fine-grained inner region where important effects occur via $J(y)$ and Q, while the outer elements are large enough that only a small number are required to fulfill the conditions on the outer boundary. By choosing the ratio $h^{(m+1)}/h^{(m)}$ to always be less than 2, this scheme also leads to numerical stability which would not necessarily be guaranteed were this ratio to be larger.[19] [Since Eqs. (3.3), (3.6), (3.7), and (3.10) are general enough, one may easily employ a variety of schemes for the magnitudes of the $h^{(i)}$. However, our choice most simply satisfies the constraints placed on the numerical solution.] We shall then define the spatial properties of our system with fixed $h^{(1)} = 10^{-5}$, as discussed earlier and

$$h^{(2)} \equiv \Delta_I ; \tag{3.15a}$$

also,

$$h^{(m)} \equiv \Delta_O^{m-2} h^{(2)} \tag{3.15b}$$

for $N - 1 \geq m \geq 2$. The nodal distances then follow from Eq. (2.38b) as

$$y(1) = 1 , \tag{3.16a}$$

$$y(2) = 1 + h^{(1)} , \tag{3.16b}$$

and

$$y(i) = 1 + (h^{(1)} + \Delta_I)(\Delta_O^{i-2} - 1)/(\Delta_O - 1) \tag{3.16c}$$

for $N \geq i \geq 3$.

This choice of successively increasing element size leads to significant reduction in the number of elements needed as compared to the FD calculations,[3] while allowing the spatial extent of the problem to increase by more than one order of magnitude. (In general, about 50 elements are needed by this scheme compared to the 400 required in past studies.[3]) Hence, the CIDN(E)P problem may be handled by employing relatively small matrices which are ideal for inversion on a small-core minicomputer. Our results were obtained on a PDP 11/34 minicomputer with a 64 Kbyte core. A Gaussian elimination algorithm utilizing partial pivoting was used for the matrix inversion, with run times averaging about 1 min for one result.

The effect of the outer boundary may be studied by observing the CIDNP quantity $\mathfrak{F}^*$ (the probability of conversion of triplets to singlets per total collision) for small values of Qd^2/D, which is a case very sensitive to reencounters after long diffusive "walks." It is required to select the outer boundary $y(N)$ such that any calculated results are independent of N. [Also, it must act as a collector for radicals that have diffused so far apart that the re-encounter probability is virtually zero; compare Eq. (3.5).] Added insight is found by comparison to the analytic result[16(a)] (for $J_0 = 0$) of Pedersen for $\mathfrak{F}^*$. One sees from Table I that a $y(N) \gtrsim 1.5 \times 10^4$ in a FE calculation reproduces the analytic result to within 1%. Tests performed by calculating both $\mathfrak{F}^*$ and Λ (i.e., the probability of reaction for two singlets in contact) reveal that a value of $\Delta_I \cong 0.1875$ (i.e., if $d = 4$ Å, then $\Delta_I d = 3/4$ Å) and at least 40 elements are necessary to reproduce analytic results to within 2%. Table II exhibits the FE calculated values of $\mathfrak{F}^*$ versus Qd^2/D in comparison with the analytic results. Excellent agreement is found not only here, but in the results of the calculations of the property Λ. Although these specific CIDNP comparisons give no new information, they confirm the accuracy of the numerical FE treatment and point out the computational advantages of our nodal spacing scheme [Eqs. (3.15) and (3.16)]. The major quality of numerical methods is that they allow solutions of CIDEP problems where no rigorous analytic solutions exist.

CIDEP effects are given by the P_a^∞, which are directly affected by the exchange interaction. Since the exchange interaction varies dramatically in magnitude through a relatively small region of space (i.e., when $1 \leq y \leq y_{ex}$), particle diffusion must be simulated in a more precise manner in order to avoid unwanted artificial effects. This implies that different values of Δ_I and Δ_O must be tested till suitable sizes are found. The convergence of P_a^∞ with varying Δ_I and Δ_O [and thus $y(N)$] is shown in Table III for several values of Qd^2/D. One might note that the results by Pedersen and Freed[20] are most closely reproduced by ours where $y(N) = 47.7$ [as expected,

TABLE I. Convergence of $\mathfrak{F}^*$ calculations.

$y(N)$	Δ_0	$\mathfrak{F}^* \times 10^3$ [a,b]
1 223	1.10	1.589
3 472	1.12	1.862
9 918	1.14	1.959
16 764	1.15	1.980
47 776	1.17	2.000
80 488	1.18	2.004

[a] FE numerical results found using $Qd^2/D = 1.6 \times 10^{-5}$, $J_0 = 0$, $N = 70$, $\Delta_I = 0.1875$, $kd^2/D = 10^{20}$ ($\Lambda = 1$), $\sigma = 10^{-15}$, triplet initial.

[b] Exact analytic result of Pedersen [Ref. 16(a)] is $\mathfrak{F}^* \times 10^3 = 2.004$ for $p = 0.9999$ (the probability of at least one radical–radical encounter).

TABLE II. $\mathcal{F}^*$: Analytic, FE and FD results.

$(Qd^2/D)/1.6$	$\mathcal{F}^*$[a]	$\mathcal{F}^*$[b]	$\mathcal{F}^*$[c]
10^{-6}	6.33×10^{-4}	6.29×10^{-4}	•••
10^{-5}	0.00200	0.00199	•••
10^{-4}	0.00636	0.00633	•••
0.001	0.0203	0.0202	0.0199
0.004	0.0412	0.0410	•••
0.01	0.0657	0.0654	0.0680
0.04	0.132	0.131	•••
0.1	0.205	0.204	0.201
0.4	0.366	0.365	•••
1.0	0.497	0.495	0.496
4.0	0.685	0.684	•••
10.0	0.783	0.782	0.784
10^2	0.924	0.925	0.936
$\geq 10^6$	1.00	1.00	1.00

[a]Analytic results for continuous diffusion from Pedersen [Ref. 16(a)] using $p=0.9999$, $J_0=0$.
[b]FE numerical results found using $\Delta_I=0.03125$, $\Delta_0=1.25$, $N=70$, $y(N)\cong 4\times10^6$, $J_0=0$, $kd^2/D=10^{20}$ $(\Lambda=1)$, $\sigma=10^{-15}$, triplet initial.
[c]FD results published elsewhere [Ref. 3(a)].

since, in Ref. 19, $y(N)\cong 53$ was used]. However, since the FE approach readily allows the use of much larger $y(N)$ values, we have found that small variations in the results for P_a^∞ persist till $y(N)\approx 10^3$. This shows that the FE method readily enables one to obtain more accurate values of P_a^∞.

As observed from Table III, a value of the inner nodal spacing parameter Δ_I of 0.03125 (i.e., for $d=4$ Å, $\Delta_I d=1/4$ Å) is sufficient for numerical convergence to within 1% of the asymptotic polarization. Our studies show that the minimum number of elements needed is about 40 elements in order to obtain results satisfying this error criterion. Thus, the combined tests for CIDNP and CIDEP are consistent with the use of $\Delta_I=0.03125$, $\Delta_0\cong 1.295$, and $N\cong 50$ [so $y(N)\cong 3\times10^4$] in order to yield accurate results. These choices yield matrices of a small enough size to permit calculations with minicomputer (small-core) devices.

IV. CONCLUSION

In this work, we have developed and discussed a variational formulation of the SLE. We have then shown how the finite element method may be employed to develop useful trial variational functions in which local properties of the density matrix elements in each region of space can be represented in as fine detail as required for highly accurate solutions. The FE method as applied to the high-field CIDN(E)P problem is found to yield very accurate numerical results, while its flexibility permits compact matrix solutions which can easily be handled by minicomputers. Some flexible features include variability in size (and shape) of the elements as well as continuous representations of the density-matrix elements, features which do not naturally appear in the corresponding FD analysis. However, we believe that another feature, viz., the great freedom of choice available for trial functions to represent the density-matrix elements in each spatial element, will prove to be of great significance in developing the applications of this approach. Our analysis in this work was characterized by only the simplest choice of trial function (i.e., linear interpolation functions). We have also seen how the variational formulation allows for a general framework for the analysis of the different numerical solutions of the SLE, and this could prove useful, in the future, in the development of new numerical methods.

TABLE III. Convergence of P_a^∞ calculations.[a]

Qd^2/D	Δ_I	$y(N)=27.7$	47.7	100.7	340.3	1223
0.016	0.1875	16.0(1.02)	15.7(1.033)	15.5(1.05)	15.4(1.075)	15.4(1.1)
	0.125	15.5(1.03)	15.1(1.042)	14.9(1.058)	14.7(1.083)	14.7(1.108)
	0.0625	15.5(1.045)	15.2(1.057)	14.9(1.072)	14.8(1.096)	14.8(1.121)
	0.03125	15.5(1.06)	15.2(1.071)	14.9(1.086)	14.8(1.11)	14.8(1.134)
0.032	0.1875	21.3	20.9	20.6	20.5	20.5
	0.125	20.6	20.1	19.8	19.6	19.6
	0.0625	20.6	20.2	19.9	19.7	19.7
	0.03125	20.6	20.2	19.9	19.7	19.7
0.128	0.1875	35.7	35.0	34.5	34.3	34.3
	0.125	34.3	33.6	33.1	32.8	32.7
	0.0625	34.5	33.8	33.2	32.9	32.9
	0.03125	34.5	33.8	33.2	32.9	32.8

[a]Values of P_a^∞ $(\Lambda=0)$ are listed first with the value of Δ_0, needed to yield the $y(N)$, following in parentheses. (The Δ_0 values are independent of Qd^2/D.) All results were obtained using $N=70$, $J_0d^2/D=1.6\times10^3$, $kd^2/D=0$, $y_{ex}=1$, $\sigma=10^{-15}$.

[1](a) O. Zienkiewicz, *The Finite Element Method* (McGraw-Hill, New York, 1977), 3rd edition; (b) J. Bathe and E. Wilson, *Numerical Methods in Finite Element Analysis* (Prentice-Hall, Englewood Cliffs, 1976); (c) C. Desai and J. Abel, *Introduction to the Finite Element Method* (Van Nostrand-Reinhold, New York, 1972); (d) T. Chung, *Finite Element Analysis in Fluid Dynamics* (McGraw-Hill, New York, 1978).

[2](a) J. H. Freed, G. Bruno, and C. Polnaszek, J. Phys. Chem. **75**, 3385 (1971); (b) J. H. Freed, in *Spin Labeling: Theory and Applications*, edited by L. Berliner, (Academic, New York, 1976).

[3](a) J. H. Freed and J. B. Pedersen, Adv. Magn. Reson. **8**, 1 (1976) and references cited therein; (b) J. H. Freed, in NATO ASI, *Chemically-Induced Magnetic Polarization: Theory, Technique, and Applications*, edited by L. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen (Reidel, 1977). We use the symbols and notation of these references.

[4](a) Z. Schulten and K. Schulten, J. Chem. Phys. **66**, 4616 (1977); (b) H. Werner, Z. Schulten, and K. Schulten, J. Chem. Phys. **67**, 646 (1977).

[5](a) R. Richtmyer and K. Morton, *Difference Methods for Initial-Value Problems* (Wiley-Interscience, New York, 1967); (b) J. Crank, *Mathematics of Diffusion* (Oxford University, London, 1975), 2nd edition; (c) F. Hildebrand, *Finite Difference Equations and Simulations* (Prentice-Hall, Englewood Cliffs, 1968); (d) J. Crank and P. Nicolson, Proc. Cambridge Philos. Soc. **43**, 50 (1947); (e) W. Foster, Comp. Phys. C Commun. **4**, 173 (1972).

[6]H. Margenau and G. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, 1957).

[7]A. Wills, *Vector Analysis with an Introduction to Tensor Analysis* (Dover, New York, 1958).

[8](a) R. Courant, *Calculus of Variations* (Courant, New York, 1962); (b) R. Weinstock, *Calculus of Variations* (McGraw-Hill, New York, 1952); (c) V. Smirnov, *A Course on Higher Mathematics* (Pergamon, New York, 1964).

[9](a) D. Lovelock and H. Rund, *Tensors, Differential Forms and Variational Principles* (Wiley, New York, 1975); (b) J. Logan, *Invariant Variational Principles* (Academic, New York, 1977).

[10](a) U. Fano, Rev. Mod. Phys. **29**, 74 (1957); (b) Specific examples of such types of transformations are given by G. K. Fraenkel, J. Chem. Phys. **42**, 4275 (1965).

[11]If we wish to recognize the SLE as a dissipative initial value problem which requires the specification of $\tilde{\rho}_\alpha(\mathbf{q},\ t=0)$ for all α, then this boundary condition on the time variable must be included in the functional. Such a functional may be written with time as an independent variable $F[\mathbf{q}, t,\ \tilde{\rho}_\alpha(\mathbf{q},t),\ \cdots,\ \tilde{\rho}^i_\alpha(\mathbf{q},t),\ \cdots]$ or similarly for the Laplace transformed case $F[\mathbf{q}, s,\ \bar{\rho}_\alpha(\mathbf{q},s), \cdots,\ \bar{\rho}^i_\alpha(\mathbf{q},s),\ \cdots]$. Then, the integral I of Eq. (2.13b) becomes $I=\int_{s=0}^{\infty}\int_{q_a}^{q_b} F(\mathbf{q}, s, \cdots)d\mathbf{q}ds$ or the analogous integral in the time domain. The dissipative and initial-value aspects have been studied for diffusion equations [cf. P. P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953); *Finite Element Methods in Flow Problems*, edited by J. Oden (University of Alabama), and would require the introduction of adjoint functions of the $\tilde{\rho}_\alpha(\mathbf{q},t)$ corresponding to an unphysical reverse of diffusion as well as an added term in I shown above to take care of the initial value.

[12]The minimization of weighted residuals method consists of setting the weighted mean of the residual in a spatial region equal to zero, i.e.,

$$\int_{\mathbf{r}_a}^{\mathbf{r}_b} R(\mathbf{r})\,\varphi(\mathbf{r})\,d\mathbf{r}=0\ .$$

$R(\mathbf{r})$ is the residual similar to our Eq. (2.27) and $\varphi(\mathbf{r})$ is an arbitrary weighting function satisfying the boundary conditions at $\mathbf{r}_a$ and $\mathbf{r}_b$.

[13]See, for example; (a) *Variational Methods in Engineering*, edited by C. Brebbia and H. Tottenham (Southampton University, 1973, Surrey, U.K.), Vols. I and II; (b) *Mathematics of Finite Elements and Applications*, edited by J. Whiteman (Academic, New York, 1973); (c) *Finite Elements in Water Resources*, edited by W. Gray, O. Pindar, and C. Brebbia (Pentech, London, 1977).

[14]J. Villadsen and M. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation* (Prentice-Hall, Englewood Cliffs, 1978).

[15](a) G. Guymon, Water Resource Res. **6**, 204 (1970); (b) G. Guymon, V. Scott, and L. Hermann, Water Resource Res. **6**, 1611 (1970).

[16](a) J. B. Pedersen, J. Chem. Phys. **67**, 4097 (1977); (b) J. B. Pedersen, Chem. Phys. Lett. **52**, 333 (1977); (c) L. Monchick and F. Adrian, J. Chem. Phys. **68**, 4376 (1978).

[17]H. Carslaw and J. Jaeger, *Conduction of Heat in Solids* (Oxford University, London, 1959), 2nd edition.

[18]G. Zientara and J. H. Freed, J. Chem. Phys. **70**, 1359 (1979).

[19]In the FD studies of Pedersen and Freed (cf. Ref. 3), the ratio of neighboring nodal separations across the M^{th} node is about 100 or greater.

[20](a) J. B. Pedersen and J. H. Freed, J. Chem. Phys. **58**, 2746 (1973); (b) J. B. Pedersen and J. H. Freed, J. Chem. Phys. **59**, 2869 (1973).