The variational method and the stochastic–Liouville equation. III. Infinite elements for CIDN(E)P[a)]

Gary P. Zientara and Jack H. Freed

Department of Chemistry, Cornell University, Ithaca, New York 14853
(Received 29 March 1979; accepted 17 April 1979)

The variational finite-element method introduced by Zientara and Freed for the solution of the stochastic-Liouville equation is modified to utilize the advantages of an infinite outer element. Within this infinite element, the correct asymptotic forms of the solutions may be used, and they may be matched to those of the inner finite elements. Large reductions in the computational effort are realized by this scheme while maintaining high accuracy as illustrated in the example of high-field chemically induced dynamic spin polarization. Applicability of this method extends to solutions of partial differential equations in chemical physics characterized by a large spatial region with simple interactions and a restricted region in which more complex behavior occurs, such as is found in treatments of chemical reactions modulated by liquid state diffusive processes and in scattering theory in quantum mechanics.

I. INTRODUCTION

Previous theoretical studies such as chemically induced dynamic spin polarization [CIDN(E)P] have been performed utilizing either numerical[1] or analytic[2,3] mathematical methods. Both approaches proved useful, but were generally unrelated in their employment. Recently, Zientara and Freed[4] (hereafter referred to as I) have introduced the use of variational methods for the solution of problems requiring the stochastic-Liouville equation (SLE). These problems include CIDN(E)P[4] and the simulation of electron spin resonance spectra.[5] Variational methods unify the mathematical techniques, particularly in a finite element (FE) format, since different local interpolation functions can be chosen as suggested by the appropriate form of the SLE.[6] Below we will show how characteristic features of the solutions of the SLE can be included in a numerical–variational scheme employing both FE's and an infinite element[7] (IE). For the IE, an element of infinite "length," we will use trial solutions that are more closely related to the asymptotic solutions of the SLE. To emphasize the numerical simplifications resulting from the IE, we will reanalyze the FE treatment of the high field CIDN(E)P problem. The reader is therefore directed to I for the elementary discussion of the FE method and notation, and CIDN(E)P theory [cf. Refs. 1–3 also].

The advantage of introducing an IE in a numerical scheme can be appreciated by analyzing the spatial behavior of the solutions of the SLE (or other partial differential equations in chemical physics). When dealing with problems involving the relative diffusion of two radical species in solution, most quantum (e.g., spin exchange) and classical (e.g., shielded-Coulombic) interactions that are functions of interradical separation quickly damp to zero [e.g., as $\exp(-cr)$, c/r^n, or $\delta(r-d)$, where c is some constant and d the distance of closest radical approach]. Typical treatments therefore involve the division of radial space into inner and outer regions. The inner region is characterized by complicated interactions and additional couplings which become reflected in the complex functional forms of the spin density matrix elements. Even in the simplest cases of CIDN(E)P, a general solution [i.e., for values of κ, q, and j_0 (the dimensionless rate constant, hyperfine differences, and exchange, respectively), cf. I] of the SLE in this inner region is feasible only for the simplest models, which are not very realistic. The outer region most often only includes the spatially invariant portion of the spin Hamiltonian and the spatial dependence may be characterized by simple diffusion. Thus, the asymptotic forms of the spin density matrix elements as $r \to \infty$ may easily be found.

Monchick and Adrian[3] utilized this overview in their approximate analytic treatment of CIDEP which illustrated how the knowledge of asymptotic solutions of the SLE aids in an analysis. In their study, they used a spin basis set for which the density matrix elements decoupled in the limit as $r \to \infty$. They then solved the SLE in the limit $\sigma \to 0$ (where σ is the dimensionless Laplace transform variable) and $q^{1/2} \ll 1$ utilizing a global Green's function method. Clearly, finite difference[1] (FD) numerical methods cannot take advantage of any knowledge of such asymptotic functional behavior. Instead, in the FD studies, and the FE method in I, the artifact of a "collecting" region at a finite $r = r(N)$ was employed, where $r(N)$ was chosen sufficiently large to include enough radical reencounters to yield negligible error. However, this strategy eliminated the possibility of applying asymptotic solutions in these numerical studies.

The analysis of problems in scattering theory[8] and quantum mechanics (especially using WKB approximations[9]) has similarly benefited from studies based on multiregion spatial segmentation with local solutions matched at boundaries. Particularly, Gordon[10] and Alexander and Gordon[11] have proposed the use of a piecewise linear representation of the Coulomb interaction leading to exact local solutions of Schrödinger's equation. Askar[12] later introduced the FE method in the solution of this same problem but applied linear interpolation functions.

II. INFINITE ELEMENT METHOD

As mentioned in I, a variational FE approach allows the flexibility of choosing different trial solutions to a

[a)]Supported by NSF Grant #CHE 77-26996 as well as the NRCC under a grant from NSF and U.S. DOE Contract #W-7405-ENG-48.

 0021-9606/79/020744-06$01.00

differential equation in each separate element or region of space. This ability implies that the asymptotic ($r \to \infty$) solutions to the SLE may be employed within this formalism. First, we must dispose of the previously used collecting element [near $r(N)$] and extend the spatial region we are considering to $r \to \infty$. This is accomplished by defining an Nth element,[13] the IE, which comprises the region hitherto omitted, where $r(N) < r < \infty$. As before, in the inner region of FE's (i.e., elements 1 through $N-1$), we will continue to apply the linear interpolation functions. This permits us to incorporate the two region strategy of analytic mathematical treatments. Here, though, our inner region (where the forms of the interactions, and hence the solution, is in general very complex) is still handled in a piecewise manner following the discussion of I. In the outer region, we shall make full use of the asymptotic behavior of the solutions to the SLE.

If $h^{(i)}$ denotes the dimensionless radial "length" of the ith element [cf. I, Eq. (2.35)], then we can characterize an IE by

$$h^{(N)} = \infty \ , \tag{1}$$

while, as in I, we still have the finite nodal distance [cf. I, Eq. (2.38b)]:

$$y(N) = r(N)/d = 1 + \sum_{m=1}^{N-1} h^{(m)} \ . \tag{2}$$

In the IE, we must define a slightly different[14] local spatial variable

$$z = y - y(N) \ , \tag{3}$$

where the dimensionless distance is $y = r/d$ and, in Eq. (3), $0 \le z \le \infty$. The matching conditions on any trial solutions $\bar{\rho}_\alpha^{(N)}$ to the αth spin density matrix element in the IE are

$$\bar{\rho}_\alpha^{(N)} = \bar{\rho}_\alpha(N) \ , \quad \text{at } y = y(N) \ , \tag{4}$$

where $\bar{\rho}_\alpha(N)$ is the value at the Nth node (i.e., that between the IE and the outermost FE), and the outer boundary condition

$$\lim_{y \to \infty} \bar{\rho}_\alpha^{(N)} = 0 \ . \tag{5}$$

(Superscripts refer to functions or properties within an element while nodal values are indicated by indices following in parentheses.) Equation (5) requires that we utilize asymptotically decaying forms but this often naturally appears in CIDN(E)P and quantum mechanical cases. A practical condition on any $\bar{\rho}_\alpha^{(N)}$ is that it must permit the evaluation of the variation in the functional integral [Eq. (2.44) of I]. This means that we must be able to describe the contribution of the IE, the Nth element, to the variation of the variational integral I [i.e., the $\partial I/\partial \bar{\rho}_\alpha(N)$] through the second term of

$$\frac{\partial I}{\partial \bar{\rho}_\alpha(N)} = \frac{\partial I^{(N-1)}}{\partial \bar{\rho}_\alpha(N)} + \frac{\partial I^{(N)}}{\partial \bar{\rho}_\alpha(N)} = 0 \ , \quad \text{for all } \alpha \tag{6}$$

[compare with Eqs. (2.49) of I]. We shall refer to the two RHS terms of Eq. (6) as its FE and IE components, respectively. Since the FE component of Eq. (6) produces several rows of the final supermatrix [cf. I, Eqs. (2.49) and (2.50)], the use of an IE will never require added computational effort. Below, we will discuss how the choice of particular trial solution in the IE determines the degree to which we can significantly reduce the dimension of the resulting numerical problem, and show that sometimes it may be reduced to a trival size.

The appropriate changes in the matrix elements derived in I to solve the CIDN(E)P problem are minimal, and they reflect the absence of a collecting element. The χ matrix [which is composed solely of geometric factors and is defined in I, Eq. (3.7)] remains the same but we must now use new terms in the final rows of the transition matrix $\mathbf{W}$ [which now replace Eqs. (3) and (6e) of I]:

$$W_{N-1,N} = X^{(N-1)}/h^{(N-1)^2} \ , \tag{7a}$$

$$W_{N,N} = -W_{N-1,N} \ , \tag{7b}$$

with $X_n^{(m)} \equiv h^{(m)^3} \int_0^1 z^n (\mathcal{Q}^{(m)} + z)^2 dz$ and $\mathcal{Q}^{(m)} \equiv y(m)/h^{(m)}$. These are due to the FE component of Eq. (6). The IE component is more easily expressed as the value of the term entering Eq. (6), so it can then be simply added to the appropriate supermatrix elements (already containing the other $\sigma\chi' + \Omega - \mathbf{W}'$ terms). The nodal values of the spin density matrix elements are then calculated as in I.

To implement this scheme, we will choose a $\bar{\rho}_\alpha(N)$ that satisfies the conditions of Eqs. (4) and (5), and calculate the IE component of Eq. (6) for all spin density matrix elements. Therefore, for all α, we must solve

$$\frac{\partial I^{(N)}}{\partial \bar{\rho}_\alpha(N)} = \int_{y(N)}^{\infty} \left\{ \left(\frac{\partial \bar{\rho}_\alpha^{(N)}}{\partial y} \right) \frac{\partial (\partial \bar{\rho}^{(N)}/\partial y)}{\partial \bar{\rho}_\alpha(N)} - \sum_\beta \hat{a}_{\alpha,\beta} \bar{\rho}_\beta^{(N)} \left[\frac{\partial \bar{\rho}_\alpha^{(N)}}{\partial \bar{\rho}_\alpha(N)} \right] \right\} y^2 \, dy \ , \tag{8}$$

where we have simplified the general expression by assuming $\bar{\rho}_\alpha^{(N)} = 0$, i.e., the radicals were not initially in the IE.

A. Simple asymptotic forms: solution

For the first example of the use of an FE–IE scheme in treating CIDN(E)P, we have employed the solution to the Laplace transformed radial diffusion equation in spherical polar coordinates as our IE approximation. This corresponds to the $\kappa = q = j_0 = 0$ form of the SLE:

$$(\sigma - \nabla_y^2) \bar{\rho}_\alpha(y, \sigma) = \tilde{\rho}_\alpha(y, \tau = 0) \ , \tag{9a}$$

which yields our IE approximation

$$\bar{\rho}_\alpha^{(N)} = \bar{\rho}_\alpha(N) \frac{\exp(-\sqrt{\sigma} z)}{(y/y(N))} \ , \tag{9b}$$

using $\bar{\rho}_\alpha$ to denote $\bar{\rho}_{SS}$, $\bar{\rho}_{T_0T_0}$, $\mathrm{Re}\bar{\rho}_{ST_0}$, and $\mathrm{Im}\bar{\rho}_{ST_0}$. Equation (9b) satisfies the requirements of Eqs. (4) and (5). Although early studies have illustrated[1–3] that certain $\bar{\rho}_\alpha^{(N)}$ are oscillatory, Eq. (9b) does not violate any conditions on IE interpolation functions and, indeed, produces CIDNP results identical to those tabulated in I.

These results were obtained by creating the overall SLE supermatrix as described in I and Eq. (7), and calculating the IE component of Eq. (6). This latter task is accomplished by inserting the interpolation function (9b) in Eq. (8), yielding

$$\frac{\partial I^{(N)}}{\partial \bar{\rho}_\alpha(N)} = y(N)\left[1+y(N)\sqrt{\sigma}\right]\bar{\rho}_\alpha(N) + \frac{y(N)^2}{2\sqrt{\sigma}}\sum_\beta \hat{a}_{\alpha,\beta}\bar{\rho}_\beta(N) ,$$

$$\text{for all } \alpha , \tag{10}$$

which only affects the values of the elements within the bottom rightmost 4×4 submatrix of the supermatrix [given by Eq. (2.50) of I]. CIDN(E)P parameters are then found using the now IE-modified relations [cf. Eqs. (3.12) of I]:

$$\begin{aligned}\mathcal{P}(\sigma) = \sum_{m=1}^{N-1} &\{(X_0^{(m)} - X_1^{(m)})\left[\bar{\rho}_{SS}(m) + \bar{\rho}_{T_0T_0}(m)\right] \\ &+ X_1^{(m)}\left[\bar{\rho}_{SS}(m+1) + \bar{\rho}_{T_0T_0}(m+1)\right]\} \\ &+ (y(N)/\sigma)\left[1+y(N)\sqrt{\sigma}\right]\left[\bar{\rho}_{SS}(N) + \bar{\rho}_{T_0T_0}(N)\right]\end{aligned} \tag{11a}$$

with

$$\mathcal{P} \equiv \lim_{\sigma\to 0}\sigma\mathcal{P}(\sigma) \tag{11b}$$

and

$$\begin{aligned}P_a(\sigma) = -2\sum_{m=1}^{N-1}&\left[(X_0^{(m)} - X_1^{(m)})\,\mathrm{Re}\bar{\rho}_{ST_0}(m) + X_1^{(m)}\,\mathrm{Re}\bar{\rho}_{ST_0}(m+1)\right] \\ &- 2\left[y(N)/\sigma\right]\left[1+y(N)\sqrt{\sigma}\right]\mathrm{Re}\bar{\rho}_{ST_0}(N) ,\end{aligned} \tag{12a}$$

with

$$P_a^\infty \equiv \lim_{\sigma\to 0}\sigma P_a(\sigma) . \tag{12b}$$

In Eqs. (11) and (12), only the last term contributes significantly for small values of σ (we observed this using $\sigma < 10^{-15}$ in all recent studies[4]). This term originates from the value of the respective IE integral

$$\int_{y(N)}^\infty \bar{\rho}_\alpha^{(N)} y^2\, dy$$

$$= \bar{\rho}_\alpha(N)\, y(N) \exp\left[+\sqrt{\sigma}\, y(N)\right] \int_{y(N)}^\infty y \exp(-\sqrt{\sigma}\, y)\, dy , \tag{13}$$

which enters because the quantities $\mathcal{P}$ and P_a^∞ represent observables calculated from integrals over all space.

Our results showed that a minimum of 40 elements (i.e., FE's plus the IE) were needed to rigorously describe the CIDNP quantity $\mathfrak{F}^*$. As expected, this is not more efficient than the FE scheme in I, since the finite q causes an oscillating behavior in $(\bar{\rho}_{T_0T_0}^{(N)} - \bar{\rho}_{SS}^{(N)})$ and $\mathrm{Im}\bar{\rho}_{ST_0}^{(N)}$ that is not included in the form of Eq. (9b). However, even this naive approach illustrates that an IE formalism is successful in eliminating the previously used artificial collecting region. It also follows that only the calculation of the Nth nodal value of the spin density matrix elements is sufficient to represent an outward diffusive wave (i.e., $\bar{\rho}_\alpha^{(N)}$ extending to infinity, for $\sigma \to 0$, $\sigma \ll |q|$).

Nevertheless, no more than three elements (two FE's[15] and the IE) were needed to reproduce the analytic results for the reactivity parameter Λ to less than 0.5% error. Equation (9), as noted, is the exact solution (neglecting the inner excluded volume) to the $\kappa = q = 0$ (i.e., no spin state mixing) problem, so it is not surprising that it is suitable for this $q = 0$ case. Since $\kappa > 0$ in calculating Λ, we see that an FE–IE variational treatment is capable of representing interactions of possibly large magnitude within a small inner region.[16] The significant reduction in size of this diffusion-controlled kinetics problem should be advantageous in future calculations where additional degrees of freedom and/or interradical forces are included. These more complex cases, unlike this illustrative example, would require numerical methods.

B. Asymptotic forms for spin-dependent problems

In treating CIDN(E)P adequately, it is clear that one wishes IE interpolation functions that include, in some way, the effects of the coupling among the spin-density matrix elements due to the spatially independent part of the spin Hamiltonian. One would expect such interpolation functions to decrease the size requirements of the resulting numerical problems even when q and j_0 are nonzero. Thus, in our second example, we will use the solution of the $\kappa = j_0 = 0$, $q \neq 0$ case of the SLE in creating our IE trial functions. These approximations to the solution of the SLE may be obtained by analyzing the SLE in the uncoupled doublet spin representation,[1] where the q interaction is diagonal so analytic solutions are easily obtained. By transforming back to a coupled (i.e., singlet–triplet) basis, one finds that the singlet and triplet spin state populations are now mixed through the term $\mathrm{Im}\bar{\rho}_{ST_0}$. For $j_0 = 0$, $\mathrm{Re}\bar{\rho}_{ST_0}$ is decoupled from all others.

These IE asymptotic functions[17] satisfying Eqs. (4) and (5) are (with some simplification of the notation):

$$(\bar{\rho}_{T_0T_0}^{(N)} + \bar{\rho}_{SS}^{(N)}) \equiv \bar{\rho}_I^{(N)} = \bar{\rho}_I(N)\,\frac{\exp(-\sqrt{\sigma}\, z)}{[y/y(N)]} , \tag{14a}$$

$$(\bar{\rho}_{T_0T_0}^{(N)} - \bar{\rho}_{SS}^{(N)}) \equiv \bar{\rho}_{II}^{(N)} = \bar{\rho}_{II}(N)\cos(vz)\,\frac{\exp(-uz)}{[y/y(N)]} , \tag{14b}$$

$$\mathrm{Re}\bar{\rho}_{ST_0}^{(N)} = \mathrm{Re}\bar{\rho}_{ST_0}(N)\,\frac{\exp(-\sqrt{\sigma}\, z)}{[y/y(N)]} , \tag{14c}$$

$$\mathrm{Im}\bar{\rho}_{ST_0}^{(N)} = C_{ST_0}\sin(vz)\,\frac{\exp(-uz)}{[y/y(N)]} , \tag{14d}$$

where we have used, for $q > 0$,[18]

$$u^2 \equiv (\omega + \sigma)/2 , \tag{15a}$$

$$v^2 \equiv (\omega - \sigma)/2 , \tag{15b}$$

with

$$\omega \equiv (4q^2 + \sigma^2)^{1/2} . \tag{15c}$$

The ease of producing the matching condition [Eq. (4)] at $y(N)$ in Eqs. (14) is obvious. Before applying these formulas, we must recognize the two constraints that enter our analysis due to the particular choice of Eqs. (14). These constraints are related to Eq. (14d), and are

$$\mathrm{Im}\bar{\rho}_{ST_0}(N) = 0 \tag{16a}$$

and

$$C_{ST_0} = -\bar{\rho}_{II}(N) . \tag{16b}$$

Equation (16a) is a consequence of the $\sin(vz)$ portion of Eq. (14d) which is zero at $y(N)$. In order to constrain the amplitude of this damped oscillatory function, we have introduced the variational parameter C_{ST_0}, which is not a nodal value but plays an important role. The constraint on C_{ST_0} [Eq. (16b)] follows from the solution of the original single element [i.e., $y(N) = 1$] problem with $\kappa = j_0 = 0$, where one notes that

$$\bar{\rho}_{II} + i\,\mathrm{Im}\bar{\rho}_{ST_0} \propto \exp[-(u+iv)z]\,. \tag{17}$$

The correct understanding of the forms of Eqs. (14) and the effects of the constraints (16) and (17) was important in the analysis.

Following our first example, we can insert Eqs. (14) in Eq. (8) to find the corresponding IE components of Eq. (6), written for all $\bar{\rho}_\alpha(N)$. However, by Eqs. (16), the variable $\mathrm{Im}\bar{\rho}_{ST_0}(N)$ is removed from the problem. (Note that we must properly constrain its value to zero in the other matrix equations.) Also, the newly introduced variational parameter, the amplitude factor C_{ST_0}, is removed from our set of unknowns by use of the constraint (16b). If more complicated constraints had been introduced, we could have utilized the method of Lagrange multipliers at this point in our analysis, but this technique was not necessary in the present example. Therefore, we are left with the set of equations for the IE ($q > 0$, $q \gg \sigma$ form shown here)

$$\begin{bmatrix} \frac{\partial I^{(N)}}{\partial \bar{\rho}_I(N)} \\ \frac{\partial I^{(N)}}{\partial \bar{\rho}_{II}(N)} \\ \frac{\partial I^{(N)}}{\partial\, \mathrm{Re}\bar{\rho}_{ST_0}(N)} \end{bmatrix} = \begin{bmatrix} y(N)[1+y(N)\sqrt{\sigma}] & 0 & 0 \\ 0 & y(N)[1+y(N)\sqrt{q}] & 0 \\ 0 & 0 & y(N)[1+y(N)\sqrt{\sigma}] \end{bmatrix} \times \begin{bmatrix} \bar{\rho}_I(N) \\ \bar{\rho}_{II}(N) \\ \mathrm{Re}\bar{\rho}_{ST_0}(N) \end{bmatrix}, \tag{18}$$

where the diagonal term multiplying $\bar{\rho}_{II}(N)$ results from the $\sigma \to 0$ limit of

$$\frac{\partial I^{(N)}}{\partial \bar{\rho}_{II}(N)} = y(N)\left[1 + \frac{y(N)u}{2}\left(1 + \frac{u^2}{\omega}\right)\right] \times \bar{\rho}_{II}(N) - \tfrac{1}{2} q\, C_{ST_0} y(N)^2 \left(\frac{v}{\omega}\right) \tag{19}$$

and the application of Eq. (16b) removes C_{ST_0} from our problem as mentioned. Note that, for $q = 0$, Eq. (19) produces the result of Eq. (10), and all spin density matrix elements have similar diffusion-type terms as expected. Equations (11) and (12) can then be employed to calculate CIDN(E)P properties after the nodal values of the spin density matrix elements are calculated.

The use of the IE functions (14) significantly reduces the size of the resulting numerical problems for the calculation of CIDN(E)P when $\kappa, q, j_0 \neq 0$. CIDNP calculations of the spin-dependent recombination probability $\mathcal{F}$ (for $j_0 = 0$) can be performed over the entire range of q with results exhibiting no more than about 25% error using as few as three elements,[15] where, for comparison, 400 finite difference nodes were required in the accurate Pedersen–Freed studies,[1] and 50 nodes in I.[19] If more exact results are required, the number of inner region FE's may be increased. We have, using Eqs. (14) with an IE, reproduced the analytic results for $\mathcal{F}^*$ (valid for $j_0 = 0$) given by Pedersen[2] with $< 0.1\%$ error, using at most about 30 elements and on the average about 15 FE's for the entire range of q values (i.e., $10^{-6} < q$). The interior elements employed had a geometrically increasing "length" $h^{(i)}$ (cf. discussion in I) which further aided in the optimization leading to the above results. This large reduction in computational effort makes feasible the consideration of more complex problems, e.g., that of low-field CIDN(E)P, where large basis sets made calculations previously intractable. Of course, this efficiency will be related to proper choices of IE asymptotic functions (see Appendix). An added feature is that the exact σ dependence can be retained, if necessary, in Eqs. (18) and (19). Thus, the FE–IE method still allows calculation of all σ dependent properties for $\sigma > 0$. The time dependence of these observables therefore can be found through, for example, a numerical Laplace transformation.[20]

The calculation of CIDEP using Eqs. (14) and an IE has led to computing benefits similar to those evidenced in the case of CIDNP. There was no alteration in the effectiveness of the IE $j_0 = 0$ approximation when a finite $j(y)$ (i.e., with $j_0 \neq 0$) was included within the interior region of FE's. This was demonstrated by numerical results obtained using an exponential $j(y)$ form[1,4] and finite exchange distance $y_{ex} = r_{ex}/d$. A maximum of about 30 elements was needed to reproduce with negligible error the FE CIDEP results of I, where 50 to 70 FE's were employed. This emphasizes that the IE interpolation functions satisfactorily represent the q-induced oscillations of the spin-density matrix in the outer region regardless of the mixing of states in the inner (FE) region.

III. CONCLUSION

In the above discussion, we have introduced the concept and use of an infinite element in a variational solution of the SLE applied to the CIDN(E)P problem. Within this IE, we employed successively more sophisticated trial solutions derived from the exact solution of some simpler problems. This simplifying feature has previously been only available in the context of (approximate) analytic methods. It was well demonstrated that the FE–IE method can lead to reductions in the dimension of resulting matrix equations, i.e., results as accurate as in I and more accurate than in Ref. 1 are obtained with far less labor. In future studies, when multiregion segmentation schemes can be invoked in the theoretical solution of complex problems,[21] the variational FE–IE format will be advantageous since it includes the ease

of numerical methods in its application, yet it retains the mathematical insight of an analytical analysis.

APPENDIX

We can generalize the prescription for obtaining IE asymptotic solutions to spin basis sets of arbitrary size. This is needed, for example, in the case of low field[19] CIDN(E)P. We start by writing the Laplace transformed SLE in its form used for CIDN(E)P (with only simple radial diffusion, see I for more complex forms for the diffusion) as

$$[s+i\mathcal{H}^x(r)-D\nabla_r^2]\,\bar{\rho}(r,s)=\tilde{\rho}(r,t=0)\ . \tag{A1}$$

For the IE, we use the asymptotic form of $\mathcal{H}^x(r)$:

$$\lim_{r\to\infty}\mathcal{H}^x(r)=\mathcal{H}_0^x\ , \tag{A2}$$

where $\mathcal{H}_0^x$ is independent of r. Either analytically or using a numerical diagonalization,[22] we can obtain the orthogonal transformation $\mathbf{T}$ and eigenvalues in Λ (diagonal) such that

$$\mathbf{T}\mathcal{H}_0\mathbf{T}^{-1}=\Lambda\ , \tag{A3}$$

where $\mathcal{H}_0$ is the Hamiltonian matrix operator and $\mathbf{T}^{-1}=\mathbf{T}^{tr}$. Then we may construct the Hamiltonian supermatrix transformation[23]

$$\mathbf{T}^x\mathcal{H}_0^x(\mathbf{T}^x)^{-1}=\Lambda^x\ , \tag{A4a}$$

where

$$T^x_{ijkl}=T_{ik}T^{-1}_{lj} \tag{A4b}$$

and

$$[(T^x)^{-1}]_{ijkl}=T_{ij}T^{-1}_{ik}\ . \tag{A4c}$$

Equation (A1) then becomes, for all α, in dimensionless form,

$$[\sigma+i\lambda_\alpha-\nabla_y^2]\rho_\alpha^\dagger(y,\sigma)=\rho_\alpha^{\dagger\dagger}(y,\tau=0)\ , \tag{A5}$$

where (letting $ij\to\alpha$ and $kl\to\beta$):

$$\rho_\alpha^\dagger(y,\sigma)=\sum_\beta T^x_{\alpha\beta}\,y\,\bar{\rho}_\beta(y,\sigma)\ , \tag{A6a}$$

$$\rho_\alpha^{\dagger\dagger}(y,\tau=0)\equiv\sum_\beta T^x_{\alpha\beta}\,y\,\tilde{\rho}_\beta(y,\tau=0)\ , \tag{A6b}$$

with $\nabla_y^2=\partial^2/\partial y^2$ and $\lambda_\alpha\equiv\Lambda^x_{\alpha\alpha}\,d^2/D$. Equation (A5) is diagonal, and if we consider the radicals as initially in contact, it has the solution

$$\rho_\alpha^\dagger(x,\sigma)=\rho_\alpha^0\exp[-(\sigma+i\lambda_\alpha)^{1/2}x] \tag{A7a}$$

where

$$x=y-1 \tag{A7b}$$

and the assumed initial condition is explicitly

$$\rho_\alpha^{\dagger\dagger}(y,\tau=0)=\rho_\alpha^0\,\delta(x)\ , \tag{A7c}$$

with the ρ_α^0 being constants. The expansion of Eq. (A7a) yields

$$\rho_\alpha^\dagger(x,\sigma)=\rho_\alpha^0\,[\cos(v_\alpha x)-i\sin(v_\alpha x)]e^{-u_\alpha x}\ , \tag{A8}$$

where

$$(u_\alpha+iv_\alpha)\equiv(\sigma+i\lambda_\alpha)^{1/2} \tag{A9}$$

is the analog of Eqs. (15). Thus, the solution to the original dimensionless SLE

$$[\sigma+i\mathcal{H}^x(d^2/D)-d^2\nabla_r^2]\,\bar{\rho}_\alpha(y,\sigma)=\tilde{\rho}(y,\tau=0) \tag{A10}$$

is given by

$$\bar{\rho}_\alpha(y,\sigma)=\frac{1}{y}\sum_\beta[(T^x)^{-1}]_{\alpha\beta}\rho_\beta^\dagger(y,\sigma)\ . \tag{A11}$$

The resulting IE interpolation functions then are

$$\bar{\rho}_\alpha^{(N)}=\frac{\bar{\rho}_\alpha(N)}{[y/y(N)]}\sum_\beta[(T^x)^{-1}]_{\alpha\beta}\times[\cos(v_\beta z)-i\sin(v_\beta z)]\rho_\beta^0 e^{-u_\beta z}\ ,\quad\text{for all }\alpha\ , \tag{A12}$$

where the ρ_β^0 in the IE (related to some "initial condition," albeit arbitrary) are retained to keep the various $\bar{\rho}_\alpha(N)$ in phase.

It is often advantageous in the calculation of CIDN(E)P to employ elements in $\bar{\rho}$ that are real valued (e.g., by the separation of $\bar{\rho}_I$, $\bar{\rho}_{III}$, $\mathrm{Re}\bar{\rho}_{ST_0}$, and $\mathrm{Im}\bar{\rho}_{ST_0}$ as used in Sec. II B). This enables the use of only real-valued arithmetic in any subsequent matrix inversions, although the symmetry of $\mathcal{H}^x(r)$ (and hence Ω) is destroyed. If this technique is utilized, then the relevant portions of Eq. (A12) become

$$\bar{\rho}_\alpha^{(N)}=\frac{\bar{\rho}_\alpha(N)}{[y/y(N)]}\sum_\beta[(T^x)^{-1}]_{\alpha\beta}\cos(v_\beta z)\,\rho_\beta^0 e^{-u_\beta z}\ , \tag{A13}$$

where here the $\bar{\rho}_\alpha(N)$ are equal to linear combinations of the $\bar{\rho}_{ii}^{(N)}$ for diagonal elements [cf. Eq. (A6a)] or equal to $\mathrm{Re}\bar{\rho}_{ij}^{(N)}$ with $i,j=S,T_0,T_+,\ldots$, and $i\neq j$. Also, the constraint (16a) is now

$$\bar{\rho}_\alpha(N)=0\ , \tag{A14}$$

where $\bar{\rho}_\alpha(N)=\mathrm{Im}\bar{\rho}_{ij}(N)$ for $i\neq j$. Other constraints follow from an analysis similar to that used to obtain Eq. (16b), in the context of the form of Eq. (A8). Since the elements of $(\mathbf{T}^x)^{-1}$ are known and constant, all that remains is the insertion of Eq. (A13) in Eq. (8). Once one obtains general expressions for $\partial I^{(N)}/\partial\rho_\alpha(N)$ [cf. Eq. (19)], then the above outline constitutes a procedure which may be performed entirely by the computer for any spin state basis set.

[1] J. H. Freed and J. B. Pedersen, Adv. Magn. Reson. **8**, 1 (1976) and references cited therein; 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, Dortrecht, 1977).

[2] J. B. Pedersen, J. Chem. Phys. **67**, 4097 (1977); Chem. Phys. Lett. **52**, 333 (1977).

[3] L. Monchick and F. J. Adrian, J. Chem. Phys. **68**, 4376 (1978).

[4] G. P. Zientara and J. H. Freed, J. Chem. Phys. **70**, 2587 (1979), part I of this series.

[5] A. E. Stillman, G. P. Zientara, and J. H. Freed, J. Chem. Phys. **71**, 113 (1979), part II of this series.

[6] Note the use of quadratic interpolation functions in Ref. 5 and their suitability for representing the SLE solution describing rotational diffusion.

[7] P. Bettess, Int. J. Numer. Methods Eng. **11**, 53 (1977).

[8] For example, see K. Smith, *The Calculation of Atomic Collision Processes* (Wiley, New York, 1971). The application of the FE method to a reactive quantum mechanical scattering problem is discussed by A. Askar, A. S. Cakmak, and H. A. Rabitz, Chem. Phys. **33**, 267 (1978).

[9] For example, See D. Bohm, *Quantum Theory* (Prentice-Hall,

Englewood Cliffs, 1951), Chap. 12.
[10]R. G. Gordon, J. Chem. Phys. **51**, 14 (1969); **52**, 6211 (1970).
[11]M. H. Alexander, R. G. Gordon, J. Chem. Phys. **55**, 4889 (1971).
[12]A. Askar, J. Chem. Phys. **62**, 732 (1975). Askar notes that asymptotic decaying forms could be applied if needed, although they were not used in this published study.
[13]We note that in I the entire spatial region was segmented into $N-1$ elements connecting N boundary nodes. The related element "lengths" were chosen to be geometrically increasing. In paper II (Ref. 5), internal nodes were employed, but they are a consequence of using higher order interpolation functions within *finite* elements.
[14]In the mth finite element (i.e., $h^{(m)}$ finite), the local spatial variable is defined as $z=(y-y(m)/h^{(m)}$, where $0\le z\le 1$, and $y(m)\le y\le y(m+1)$.
[15]The first FE is small, with $h^{(1)}=10^{-5}$, in order to simulate a delta function initial condition. The second FE is used as a bridging element.
[16]For example, with three elements, we can use Eq. (9), the exact solution for $\kappa=0$, in the IE, yet we can calculate Λ accurately for $\kappa\gg 1$ (e.g., 10^{10}).
[17]Also, see Ref. 3, Eqs. (25) and (27).
[18]CIDN(E)P polarizations in cases where $q<0$ differ only by a change of sign from those calculated for $q>0$. For a discussion of this point, see Refs. 1, 3, and 17.
[19]G. P. Zientara and J. H. Freed, J. Chem. Phys. **70**, 1359 (1979).
[20]H. Dubner and J. Abate, J. Assoc. Comp. Mach. **15**, 115 (1968).
[21]One such problem of importance in magnetic resonance relaxation is discussed by Hwang and Freed [J. Chem. Phys. **63**, 4017 (1975)] in the context of finite difference methods. The present FE–IE method can readily be applied to this case of spin relaxation induced by modulation of dipolar interactions by relative translational motion in the presence of interactions between the molecules.
[22]J. Wilkinson, *The Algebraic Eigenvalue Problem* (Oxford University, London, 1965).
[23]See, for example, G. K. Fraenkel, J. Chem. Phys. **42**, 4275 (1965).