Propagation Matrices from the Finite Element Method

Bjørn R. Jensen[†] and Jan Linderberg*[,‡]

Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 South 1400 East Rm Dock, Salt Lake City, Utah 84112-0850, and Department of Chemistry, Aarhus University, DK-8000 Aarhus, Denmark

Received: June 7, 1999; In Final Form: August 24, 1999

Optimization of action integrals is suggested as an alternative to initial value algorithms for the study of time-evolving quantum systems. The finite element method provides a convenient and rapidly convergent scheme for some simple cases where analytical solutions are available. Two level systems are given particular attention.

Introduction

Examination of the options offered by the finite element method, as a means of estimating the evolution of quantum mechanical systems, is the subject of this article. An action integral is defined and its optimization provides an alternative to time-stepping algorithms and provides a quadratic convergence toward the accurate result. Thus, inaccuracies in a state vector affect the propagator only in second order.

Molecular change, which is the essence of chemistry, derives from quantum mechanics in the time domain. Approximate solutions to Schrödinger's and Liouville's equations are desired, and a rich literature has evolved on different algorithms. Kosloff reviewed the field well in 1988[1] and later developments are represented in this issue, so no attempt is made here to create a survey of the methods favored at this time. An algorithm based on the time-integrated Lagrangian formulation[2] was suggested in 1992[3] as a means of effective application of the finite element method and is reconsidered here in further detail and with additional results on convergence properties and computational feasibility.

The action integral and the basics of the finite element method representation are presented in the next section. There follows a section with a few elementary results and a fourth section with application to a two-level problem as in a spin resonance situation. Conclusions are given in the last section.

Action Integral

Schrödinger's picture with a time-dependent state vector, $|\Psi(t)\rangle$, will be used and the symmetrized Lagrangian is formed as

$$L(t) = \frac{i\hbar}{2}\left\langle \Psi(t)\left|\frac{\partial\Psi(t)}{\partial t}\right.\right\rangle - \frac{i\hbar}{2}\left\langle \frac{\partial\Psi(t)}{\partial t}\right|\left.\Psi(t)\right\rangle - \langle\Psi(t)|H(t)|\Psi(t)\rangle \quad (1)$$

so that the action integral S, with the boundary terms will be

$$S(\Psi,\Lambda) = \int_0^T \mathrm{d}t L(t) + \frac{i\hbar}{2}\{\langle\Psi(T)|\Lambda_T\rangle - \langle\Lambda_T|\Psi(T)\rangle - \langle\Psi(0)|\Lambda_0\rangle + \langle\Lambda_0|\Psi(0)\rangle + \langle\Lambda_T|U|\Lambda_0\rangle - \langle\Lambda_0|U^\dagger|\Lambda_T\rangle\} \quad (2)$$

Auxiliary vectors $|\Lambda\rangle$ serve to define the evolution operator U. The variations of the action S and conditions of stationarity imply the equations

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle - H|\Psi(t)\rangle = 0$$
$$|\Psi(0)\rangle = |\Lambda_0\rangle \quad |\Psi(T)\rangle = |\Lambda_T\rangle$$
$$|\Psi(T)\rangle = U|\Lambda_0\rangle \quad |\Psi(0)\rangle = U^\dagger|\Lambda_T\rangle \quad (3)$$

that are the standard ones.

It will be assumed that an approximate state vector is defined in terms of parameters, which are functions of time. A common form is the linear one where a fixed basis in the relevant Hilbert space is used

$$|\Psi(t)\rangle = \sum_j |j\rangle a_j(t) \quad (4)$$

More involved are the forms where the state vector depends on general parameters

$$|\Psi[t;\alpha_1(t),\alpha_2(t),...]\rangle \quad (5)$$

such as the coherent state representations used by Öhrn and collaborators.[4]

We consider first the linear case and introduce a finite element representation for the time dependence of the amplitudes $a_j(t)$ in terms of their values at a discrete set of times:

$$a_j(t) = \sum_k a_j(t_k) f_k(t) \quad f_k(t_{k'}) = \delta_{kk'} \quad 0 = t_0 < t_1 < ... < t_n = T \quad (6)$$

where the form functions[5] are localized on a few intervals which may have varying lengths. The set of amplitudes $\{a_j(t_k)\}$ are the variational parameters of the problem together with amplitudes of the auxiliary states at the beginning and end of the time interval

$$|\Lambda_\tau\rangle = \sum_j |j\rangle b_{j\tau} \quad \tau = 0,T \quad (7)$$

The action S becomes a sesquilinear form

[†] E-mail: bjorn@kemi.aau.dk
[‡] E-mail: jan@kemi.aau.dk

10.1021/jp991838f CCC: $18.00
Published on Web 10/21/1999

$$S = \sum_{jkj'k'} a_j^*(t_k) A_{jk,j'k'} a_{j'}(t_{k'}) + \frac{i\hbar}{2}\sum_j [a_j^*(T) b_{jT} - b_{jT}^* a_j(T) - a_j^*(0) b_{j0} + b_{j0}^* a_j(0)] + \frac{i\hbar}{2}\sum_{jj'} [b_{jT}^* U_{jj'} b_{j'0} - b_{j0}^* U_{jj'}^\dagger b_{j'T}] \quad (8)$$

and optimization results in a matrix problem. The detailed equations are

$$\sum_{j'k'} A_{jk,j'k'} a_{j'}(t_{k'}) = \begin{cases} \frac{i\hbar}{2} b_{j0}, & t_k = 0, \\ 0, & 0 < t_k < T, \\ -\frac{i\hbar}{2} b_{jT}, & t_k = T \end{cases} \quad (9)$$

$$a_j(0) = \sum_{j'} U_{jj'}^\dagger b_{j'T}$$

$$a_j(T) = \sum_{j'} U_{jj'} b_{j'0}$$

Matrix elements $A_{jk,j'k'}$ and $U_{jj'}$ are complex and the matrices **A** and **U** are hermitian and unitary, respectively. It has been implicit that the basis is orthonormal.

Elimination of the amplitudes at intermediate times from eq 9 reduces the system to a form that, in matrix notation, reads as

$$\tilde{\mathbf{A}}_{00}\mathbf{a}_0 + \tilde{\mathbf{A}}_{0n}\mathbf{a}_n = \frac{i\hbar}{2}\mathbf{b}_0; \quad \tilde{\mathbf{A}}_{n0}\mathbf{a}_0 + \tilde{\mathbf{A}}_{nn}\mathbf{a}_n = -\frac{i\hbar}{2}\mathbf{b}_n; \quad \mathbf{a}_0 = \mathbf{U}^\dagger \mathbf{b}_n; \quad \mathbf{a}_n = \mathbf{U}\mathbf{b}_0; \quad (10)$$

where the reduced matrices refer only to the initial and final times. A satisfactory, partial solution to this problem is obtained by looking for eigenvectors of the unitary transformation

$$\mathbf{U}\mathbf{b}_0 = \mathbf{b}_0 z \quad \mathbf{U}^\dagger \mathbf{b}_n = b_n z^* = \mathbf{b}_n\left(\frac{1}{z}\right) \quad (11)$$

so that

$$\tilde{\mathbf{A}}_{00}\mathbf{a}_0 + \tilde{\mathbf{A}}_{0n}\mathbf{b}_0 z = \frac{i\hbar}{2}\mathbf{b}_0 \quad \tilde{\mathbf{A}}_{n0}\mathbf{a}_0 + \tilde{\mathbf{A}}_{nn}\mathbf{b}_0 z = -\frac{i\hbar}{2}\mathbf{a}_0 z \quad (12)$$

which implies the eigenvalue equation

$$\begin{bmatrix} \frac{2i}{\hbar}\tilde{\mathbf{A}}_{n0} & 0 \\ \frac{2i}{\hbar}\tilde{\mathbf{A}}_{00} & 1 \end{bmatrix}\begin{bmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \end{bmatrix} = \begin{bmatrix} 1 & -\frac{2i}{\hbar}\tilde{\mathbf{A}}_{nn} \\ 0 & -\frac{2i}{\hbar}\tilde{\mathbf{A}}_{0n} \end{bmatrix}\begin{bmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \end{bmatrix} z \quad (13)$$

The reduced matrix $\tilde{\mathbf{A}}$ is hermitian and its off-diagonal block $\tilde{\mathbf{A}}_{0n}$ is assumed to have an inverse; a singularity would indicate a linear dependence in the basis.

Eigenvalues of the matrix[6]

$$\mathbf{T} = \begin{bmatrix} 1 & -\frac{2i}{\hbar}\tilde{\mathbf{A}}_{nn} \\ 0 & -\frac{2i}{\hbar}\tilde{\mathbf{A}}_{0n} \end{bmatrix}^{-1}\begin{bmatrix} \frac{2i}{\hbar}\tilde{\mathbf{A}}_{n0} & 0 \\ \frac{2i}{\hbar}\tilde{\mathbf{A}}_{00} & 1 \end{bmatrix} = \begin{bmatrix} 1 & \frac{2i}{\hbar}\tilde{\mathbf{A}}_{nn} \\ 0 & 1 \end{bmatrix}\begin{bmatrix} \frac{2i}{\hbar}\tilde{\mathbf{A}}_{n0} & 0 \\ 0 & \frac{i\hbar}{2}\tilde{\mathbf{A}}_{0n}^{-1} \end{bmatrix}\begin{bmatrix} 1 & 0 \\ \frac{2i}{\hbar}\tilde{\mathbf{A}}_{00} & 1 \end{bmatrix} \quad (14)$$

have unit modulus, $|z_j| = 1$, or come in pairs, $z_j^* = z_k^{-1}$, since the inverse of **T** is related to its adjoint through a similarity transformation

$$\mathbf{T}^\dagger = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{T}^{-1}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (15)$$

This implies that for a solution to eq 13

$$\mathbf{T}\begin{bmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \end{bmatrix} = \begin{bmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \end{bmatrix} z \quad (16)$$

it holds that

$$\mathbf{T}^\dagger\begin{bmatrix} \mathbf{b}_0 \\ \mathbf{a}_0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\mathbf{T}^{-1}\begin{bmatrix} \mathbf{a}_0 \\ \mathbf{b}_0 \end{bmatrix} = \begin{bmatrix} \mathbf{b}_0 \\ \mathbf{a}_0 \end{bmatrix}\frac{1}{z}$$

or, equivalently

$$[\mathbf{b}_0^\dagger \ \ \mathbf{a}_0^\dagger]\mathbf{T} = \frac{1}{z^*}[\mathbf{b}_0^\dagger \ \ \mathbf{a}_0^\dagger] \quad (18)$$

Two possibilities arise from this relation: (i) $z_j^* = z_j^{-1}$ where a "normalization" can be chosen so that

$$\mathbf{b}_{0j}^\dagger \mathbf{a}_{0j} + \mathbf{a}_{0j}^\dagger \mathbf{b}_{0j} = \pm 2 \quad (19)$$

and (ii) $z_j^* = z_{pj}^{-1}$ where *pj* indicates a permutation of the set of indices and where we choose the "normalization" such that

$$\mathbf{b}_{0j}^\dagger \mathbf{a}_{0pj} + \mathbf{a}_{0j}^\dagger \mathbf{b}_{0pj} = \mathbf{b}_{0pj}^\dagger \mathbf{a}_{0j} + \mathbf{a}_{0pj}^\dagger \mathbf{b}_{0j} = 2 \quad (20)$$

It is recognized that these eigenvalues are spurious in the sense that their magnitude differs from unity and cannot correspond to proper values of a unitary matrix. Their occurrence is related to large time steps in the finite element discretization. A form of orthogonality holds for eigenvalues that are unrelated

$$\mathbf{b}_{0j}^\dagger \mathbf{a}_{0k} + \mathbf{a}_{0j}^\dagger \mathbf{b}_{0k} = 0 \quad z_k^* \neq z_j^{-1} \quad (21)$$

The case of degenerate eigenvalues offers the possibility that there are two or more linearly independent vectors in the subspace, but there will be a linear transformation among them which brings them to the fulfill the conditions of eqs 19−21.

There are twice as many eigenvalues of **T** as there are of the unitary transformation **U**. Vectors $\mathbf{a}_0$,$\mathbf{b}_0$ represent approximations to an initial state and should be close to parallel, thus we choose those solutions which have a positive "normalization" value in relation (eq 19) as being the ones giving the appropriate representation for **U**. Solutions of the type considered in eq 20 require a reconsideration of the procedure from the start. We will first establish the relation between the vectors $\{\mathbf{a}_{0j},\mathbf{b}_{0j} | j = 1,2...\}$ and conclude, from the set of eq 10 that

$$\tilde{\mathbf{A}}_{00}\mathbf{a}_{0j} + \tilde{\mathbf{A}}_{0n}\mathbf{b}_{0j} z_j = \frac{i\hbar}{2}\mathbf{b}_{0j} \quad \tilde{\mathbf{A}}_{n0}\mathbf{a}_{0j} + \tilde{\mathbf{A}}_{nn}\mathbf{b}_{0j} z_j = -\frac{i\hbar}{2}\mathbf{a}_{0j} z_j \quad (22)$$

and that

$$\mathbf{a}_{0k}^\dagger \tilde{\mathbf{A}}_{00} + z_k^* \mathbf{b}_{0k}^\dagger \tilde{\mathbf{A}}_{n0} = -\frac{i\hbar}{2}\mathbf{b}_{0k}^\dagger \quad \mathbf{a}_{0k}^\dagger \tilde{\mathbf{A}}_{0n} + z_k^* \mathbf{b}_{0k}^\dagger \tilde{\mathbf{A}}_{nn} = \frac{i\hbar}{2} z_k^* \mathbf{a}_{0k}^\dagger \quad (23)$$

which provides the relations

$$\mathbf{a}_{0k}^\dagger \tilde{\mathbf{A}}_{00}\mathbf{a}_{0j} + z_k^* \mathbf{b}_{0k}^\dagger \tilde{\mathbf{A}}_{n0}\mathbf{a}_{0j} + \mathbf{a}_{0k}^\dagger \tilde{\mathbf{A}}_{0n}\mathbf{b}_{0j} z_j + z_k^* \mathbf{b}_{0k}^\dagger \tilde{\mathbf{A}}_{nn}\mathbf{b}_{0j} z_j = i\hbar\delta_{kj} - \frac{i\hbar}{2}\mathbf{b}_{0k}^\dagger \mathbf{a}_{0j}(1 + z_k^* z_j) \quad (24)$$

and the conclusion

$$\mathbf{b}_{0k}^{\dagger}\mathbf{a}_{0j} = \delta_{kj} + iL_{kj}; \quad L_{kj} = L_{jk}^{*} \tag{25}$$

where the new, hermitian matrix **L** is a transformation of the hermitian matrix **A**. Neither set of vectors, $\{\mathbf{a}_{0j}|j = 1,2...\}$ nor $\{\mathbf{b}_{0j}|j = 1,2...\}$, is an orthogonal basis set for the unitary transformation nor are they normalized.

A constrained optimization is required in order to arrive at an acceptable representation of the propagation matrix **U**. It is necessary to make the vectors $\mathbf{a}_0$ and $\mathbf{b}_0$ of eq 13 proportional to a common one

$$\mathbf{a}_0 = \mathbf{c}_0\kappa \quad \mathbf{b}_0 = \mathbf{c}_0\lambda \tag{26}$$

and use the consistency of the two components of the equation to determine the ratio of κ to λ. The constraints (eq 26) lead in the system (eq 10), with substitutions (eq 11), to the forms

$$(\tilde{\mathbf{A}}_{00}\kappa + \tilde{\mathbf{A}}_{0n}\lambda z)\mathbf{c}_0 = \frac{i\hbar}{2}\lambda\mathbf{c}_0 \quad (\tilde{\mathbf{A}}_{n0}\kappa + \tilde{\mathbf{A}}_{nn}\lambda z)\mathbf{c}_0 = -\frac{i\hbar}{2}\kappa z\mathbf{c}_0 \tag{27}$$

which are combined to the hermitian eigenvalue relation

$$(\kappa^*\tilde{\mathbf{A}}_{00}\kappa + \kappa^*\tilde{\mathbf{A}}_{0n}\lambda z + z^*\lambda^*\tilde{\mathbf{A}}_{n0}\kappa + z^*\lambda^*\tilde{\mathbf{A}}_{nn}\lambda z)\mathbf{c}_0 = \frac{i\hbar}{2}(\kappa^*\lambda - z^*\lambda^*\kappa z)\mathbf{c}_0 \tag{28}$$

Only the ratio κ/λ is relevant, and we replace λ with μ according to

$$\lambda z = \mu \tag{29}$$

to obtain

$$(\kappa^*\tilde{\mathbf{A}}_{00}\kappa + \kappa^*\tilde{\mathbf{A}}_{0n}\mu + \mu^*\tilde{\mathbf{A}}_{n0}\kappa + \mu^*\tilde{\mathbf{A}}_{nn}\mu)\mathbf{c}_0 = \frac{i\hbar}{2}(\kappa^*\mu z^* - \mu^*\kappa z)\mathbf{c}_0 \tag{30}$$

which exhibits the relation between the phase of the unitary matrix eigenvalue and an eigenvalue of a suitably time-integrated Lagrangian. It is seen that only the phase of the product $\kappa^*\mu$ and one of the magnitudes $|\kappa|$ or $|\mu|$ are numerically relevant. Thus it is convenient to choose

$$|\kappa^*\mu| = |\kappa||\mu| = 1 \tag{31}$$

Eigenvalues of the matrix on the left-hand side in eq 30 will be functions of the two real parameters and are denoted as $s_j(\kappa,\mu)$ and it follows that

$$z_j = \frac{\kappa^*\mu}{\hbar}(\sqrt{\hbar^2 - s_j^2(\kappa,\mu)} + is_j(\kappa,\mu)) \tag{32}$$

and, with properly normalized eigenvectors, the propagation matrix is

$$\mathbf{U} = \sum_j \mathbf{c}_{0j} z_j \mathbf{c}_{0j}^{\dagger} \tag{33}$$

while there remains to resolve the appropriate values of the parameters κ and μ.

Optimal choices of the parameters will be studied further as more numerical experience is acquired.

Integrable Examples

Two cases are examined with the view of showing the numerical stability and accuracy of the variational formulation in the finite element implementation. The evolution of a single state under a constant or periodic Hamiltonian is governed by the energy function

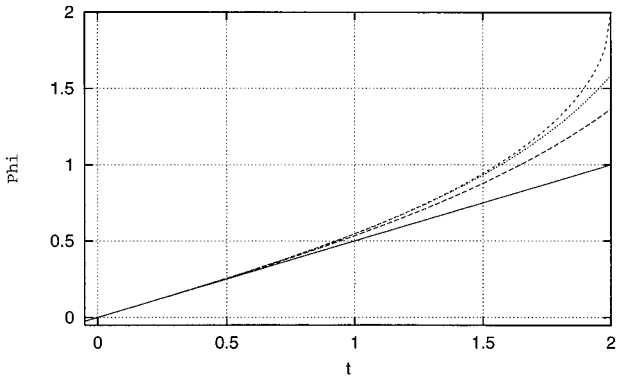

Figure 1. Approximations to the evolution operator phase from finite element method calculations for a constant energy case. The normal line represents the correct result where φ is proportional to the time elapsed. Variational results are, from the top, for two pieces of linear interpolation, parabolic interpolation, and the linear wave function choice on the interval.

$$E(t) = E(0)\cos(\omega t) \tag{34}$$

so that the evolution operator is

$$U(t) = U(0)\exp\left[-\frac{iE(0)}{\hbar\omega}\sin(\omega t)\right] \tag{35}$$

The static case is the limit at zero frequency ω. All integrals in the action integral are elementary, and the matrix problem for the wave function amplitudes is tridiagonal and readily solvable.

We show in Figure 1 a comparison of three approximations to the phase of the evolution matrix for a constant energy state and the accurate result: a linear interpolant over the interval, two pieces of linear, and a parabolic interpolant. All are quite accurate as long as $\varphi \equiv |E(0)t|/\hbar < 0.5$ and there is no advantage to the more elaborate approximations for larger intervals even though an error analysis shows that for small φ errors occur in third, fifth, and seventh order, respectively. One pays for the accuracy at small intervals by decreasing the range of applicability of the formulation; the analytical solutions have branch points for smaller parameter values for the higher order forms.

Numerical calculations have been carried out for the oscillatory form (eq 34) and the results are given in Figure 2. Parameters and units are chosen so that $E(0) = \hbar\omega$ and integrations are for the interval where $0 \le \omega t \le 5$. Piecewise linear approximations are used on equidistant intervals. Rapid convergence is observed with the number of time steps. These findings hold for longer time lapses, and there is no propagation of errors as might be the case in finite difference stepping of an initial value; the variational formulation optimizes the propagator and not the wave function.

A Matrix Propagator

Additional complications arise in a system with several states as is evident from the formal development. An examination of a two-state system is facilitated by the use of the Pauli spin matrix basis and we express the Hamiltonian as

$$H(t) = \alpha(t)\sigma_0 + \beta_x(t)\sigma_x + \beta_y(t)\sigma_y + \beta_z(t)\sigma_z = \begin{bmatrix} \alpha(t) + \beta_z(t) & \beta_x(t) - i\beta_y(t) \\ \beta_x(t) + i\beta_y(t) & \alpha(t) - \beta_z(t) \end{bmatrix} \tag{36}$$

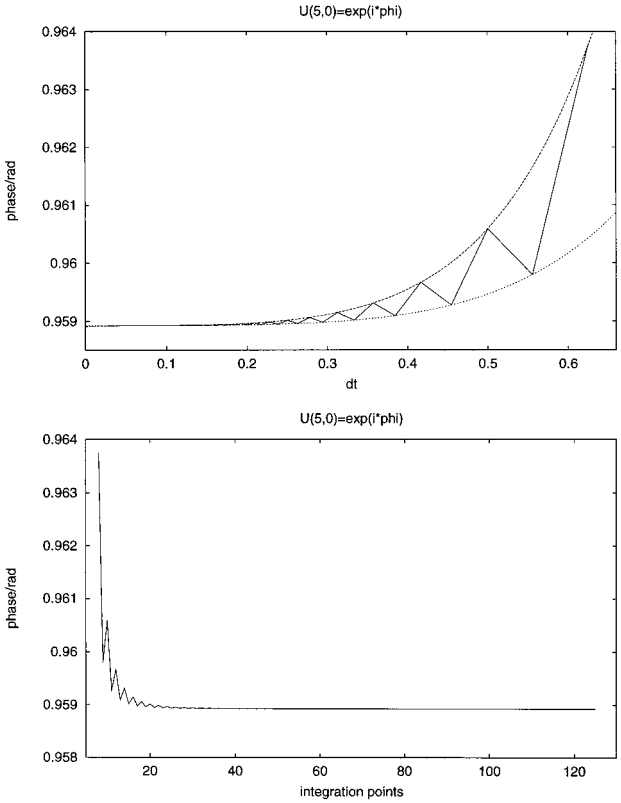

Figure 2. Display of approach to the accurate evolution operator phase value for the function (eq 35) with finite element method equidistant interval length, upper panel, and number of intervals, lower panel for total interval $0 \leq \omega t \leq 5$.

in terms of real functions of time. For simplicity we consider only one interval with linear interpolants for the state vector

$$\Psi(t) = \begin{bmatrix} a_{10}\left(1 - \frac{t}{T}\right) + a_{11}\frac{t}{T} \\ a_{20}\left(1 - \frac{t}{T}\right) + a_{21}\frac{t}{T} \end{bmatrix} \tag{37}$$

Time integration over the Hamiltonian results in the forms

$$\int_0^T \mathrm{d}t\alpha(t)\left(1 - \frac{t}{T}\right)^{2-n}\left(\frac{t}{T}\right)^n \equiv \alpha(n) \quad n = 0,1,2 \tag{38}$$

where an additional notation is introduced. The relevant matrices in eq 10 and the following are then

$$\begin{aligned} \mathbf{A}_{00} &= \alpha(0)\sigma_0 + \beta_x(0)\sigma_x + \beta_y(0)\sigma_y + \beta_z(0)\sigma_z \\ \mathbf{A}_{01} &= \left[\alpha(1) + \frac{i\hbar}{2}\right]\sigma_0 + \beta_x(1)\sigma_x + \beta_y(1)\sigma_y + \beta_z(1)\sigma_z \\ \mathbf{A}_{11} &= \alpha(2)\sigma_0 + \beta_x(2)\sigma_x + \beta_y(2)\sigma_y + \beta_z(2)\sigma_z \end{aligned} \tag{39}$$

It cannot be assumed that the vectors $\{\beta(0), \beta(1), \beta(2)\}$ are parallel and thus there is no basis which diagonalizes all three matrices (eq 39). The average action matrix, see eq 30, appears as

$$\begin{aligned} \mathbf{A} &= [\bar{\alpha} + \hbar\sin(\phi)]\sigma_0 + \bar{\beta}_x\sigma_x + \bar{\beta}_y\sigma_y + \bar{\beta}_z\sigma_z \\ \bar{\alpha} &= \alpha(0)|\kappa|^2 + 2\alpha(1)\cos(\phi) + \alpha(0)|\kappa|^{-2} \\ \kappa\mu^* &= \cos(\phi) + i\sin(\phi) \end{aligned} \tag{40}$$

where the average notation applies to all parameters. It follows that the eigenvalues are

$$s_\pm(\kappa,\mu) = \bar{\alpha} + \hbar\sin(\phi) \pm |\bar{\beta}| \tag{41}$$

and the unitary transformation comes as

$$\mathbf{U} = \frac{z_+}{2|\bar{\beta}|}[|\bar{\beta}|\sigma_0 + \bar{\beta}\cdot\sigma] + \frac{z_-}{2|\bar{\beta}|}[|\bar{\beta}|\sigma_0 - \bar{\beta}\cdot\sigma] \tag{42}$$

which can be reduced in the case of a constant Hamiltonian to be of the similar form as the one state problem dealt with in the previous section.

Conclusions

Development of variational methods in the time domain of quantum mechanics promises effective numerical algorithms when implemented in the finite element method framework. The rather simple examples given in this article demonstrate the feasibility of the approach and will be further exploited in the context of control mechanisms as employed in magnetic resonance experiments.[7] Greater challenges are provided by the chemical reactions where the single potential surface picture breaks down and multistate propagation is required. Such problems are on our agenda.

Acknowledgment. Generous hospitality has been extended to us at the Henry Eyring Center for Theoretical Chemistry at the University of Utah. We are grateful to Professor Jack Simons for scientific and economic stimulus during our extended stay at Salt Lake City. He and the other organizers of the workshop at Brian Head receive our thanks for the support for participation and for the creation of a congenial atmosphere. Professor Greg Voth, the director of the Henry Eyring Center, and Professor Thanh Truong maintain with Simons the excellent working environment. Travel support was obtained by one of us (B.R.J.) from the Faculty of Natural Science, Aarhus University under the graduate student program.

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