

Propagation of 3D Wave Packets for Nonzero Total Angular Momentum Using the Split Operator Method[†]

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Received: March 20, 2001

Three-dimensional wave packet calculations for total angular momentum quantum number $J \geq 0$ have been performed in Jacobi coordinates. To be able to use the split operator propagator together with the fast Fourier transform method, the wave function is transformed and a modified Hamiltonian obtained. The filter diagonalization method has been used to determine a few rovibrational eigenstates of the H₂O molecule on the lowest potential energy surface. Good agreement with previous work is obtained.

1. Introduction

The time-dependent Schrödinger equation (we use atomic units throughout)

$$i\frac{\partial}{\partial t}\Psi(\mathcal{R}, t) = \hat{H}(\mathcal{R}, t)\Psi(\mathcal{R}, t) \quad (1)$$

together with the initial condition

$$\Psi(\mathcal{R}, t = 0) = \Psi_0(\mathcal{R}) \quad (2)$$

where \mathcal{R} describes all spatial coordinates, provides a physically clear picture of a system's evolution in time and allows us to connect experimental properties, such as absorption¹ and Raman^{2,3} spectra, with details in the dynamical process. The time-dependent approach is the natural choice when dealing with time-dependent potentials, as in the case of interaction with a laser field.

At present, several methods of propagating the solution to the time-dependent Schrödinger equation, such as the split operator method, the Lanczos algorithm, and the Chebyshev polynomial expansion technique, are known.^{4,5} Different coordinate systems, such as Cartesian, Jacobi, hyperspherical, etc.,⁶ are used, as there is no ideal coordinate system for every molecule or task and the optimal system should be chosen for the problem at hand.

In our previous work^{7,8} the split operator method has been applied to study 3D quantum dynamics of nonlinear triatomic molecules for total angular momentum quantum number $J = 0$ using a modified version of Johnson's hyperspherical coordinate system. Advantages of the split operator method are its simplicity and the possibility to use it with time-dependent Hamiltonians. It exploits the speed of the fast Fourier transform (FFT), scaling as favorably as $N \ln N$ with increasing grid size N .

Unfortunately, the modified version of Johnson's hyperspherical coordinates has singularities at certain T-shaped configurations which may cause numerical problems for some molecules. For example, the H₂O ground-state wave function is nonzero close to singular geometries. This slows down the

convergence of the calculations significantly. Therefore, other curvilinear coordinate systems, such as Radau or Jacobi coordinates, could be more efficient in this case.

To be able to use the split operator method together with FFT in curvilinear coordinates, the Hamiltonian must obey certain requirements.⁷ These are fulfilled for the modified version of Johnson's hyperspherical coordinates but do not hold in general. Therefore, the question of the applicability of the method to other curvilinear coordinate systems arises. In the present study we show that for triatomic systems the split operator method together with FFT can be applied using the Jacobi coordinate system for problems with nonzero total angular momentum if a transformation of the Hamiltonian is made.

Inclusion of nonzero total angular momentum complicates the calculations considerably. This inclusion may, however, be necessary for accurate calculations, for example, when studying photoexcitation where the $J = 0 \rightarrow J' = 0$ transition usually is not allowed.

2. Jacobi Coordinate System

The set of Jacobi coordinates for a triatomic molecule ABC is given by three internal coordinates R, r, θ , where r is the distance between B and C, R is the distance from the BC mass center to the A atom, and θ is the angle between R and r . Three Euler angles α, β, γ describe rotations of the molecule. We can write the wave function as a sum of products of internal functions and angular momentum eigenfunctions⁹

$$\Psi_J(R, r, \theta, \alpha, \beta, \gamma, t) = \sum_{k=-J}^{k=J} \psi_{Jk}(R, r, \theta, t) \sqrt{\frac{2J+1}{8\pi^2}} D_k^J(\alpha, \beta, \gamma) \quad (3)$$

where D_k^J are eigenfunctions of the total angular momentum operator J , and k is a quantum number corresponding to the projection of the total angular momentum on the z axis. Inserting the wave function, eq 3, into the Schrödinger equation, eq 1, multiplying by $(D_k^J)^*$, and integrating over the Euler angles, one can verify that the original problem is reduced for every value of J from a six-dimensional to a four-dimensional problem in R, r, θ, k space.

[†] This paper was originally submitted for the Aron Kuppermann issue of *The Journal of Physical Chemistry A* (March 22, 2001).

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An effective Hamiltonian operator for a system with its z axis parallel to R is given by⁹

$$\hat{H}_{k,k} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu'} \frac{\partial^2}{\partial r^2} - \frac{1}{2} \left(\frac{1}{\mu R^2} + \frac{1}{\mu' r^2} \right) \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{k^2}{\sin^2 \theta} \right) + \frac{1}{2\mu R^2} [J(J+1) - 2k^2] + V(R, r, \theta, t) \quad (4)$$

$$\hat{H}_{k,k\pm 1} = \frac{1}{2\mu R^2} [(J \pm k + 1)(J \mp k)]^{1/2} \left[(k \pm 1) \frac{\cos \theta}{\sin \theta} \pm \frac{\partial}{\partial \theta} \right] \quad (5)$$

where μ is the reduced mass of the A–BC system and μ' is the reduced mass of the BC fragment. $V(R, r, \theta, t)$ is a potential energy term that includes any external fields which may be time dependent. The volume element for this Hamiltonian is given by $\sin \theta dR dr d\theta$.

In order not to mix local and nonlocal operators of the same coordinate (e.g., $\sin \theta$ and ∂/θ),⁷ a transformation of the wave function $\psi_{jk} = \phi_{jk} \sin^{-1/2} \theta$ is made. This allows the use of the split operator propagator together with FFT. The new Hamiltonian is given by

$$\hat{H}_{k,k} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu'} \frac{\partial^2}{\partial r^2} - \frac{1}{2} \left(\frac{1}{\mu R^2} + \frac{1}{\mu' r^2} \right) \left(\frac{\partial}{\partial \theta} + \frac{1 - 4k^2}{4 \sin^2 \theta} + \frac{1}{4} \right) + \frac{1}{2\mu R^2} [J(J+1) - 2k^2] + V(R, r, \theta, t) \quad (6)$$

$$\hat{H}_{k,k\pm 1} = \frac{1}{2\mu R^2} [(J \pm k + 1)(J \mp k)]^{1/2} \left[\left(k \pm \frac{1}{2} \right) \frac{\cos \theta}{\sin \theta} \pm \frac{\partial}{\partial \theta} \right] \quad (7)$$

with the volume element $dR dr d\theta$.

The Hamiltonian can be simplified for the special case $J = k = 0$:

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu'} \frac{\partial^2}{\partial r^2} - \frac{1}{2} \left(\frac{1}{\mu R^2} + \frac{1}{\mu' r^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{4 \sin^2 \theta} + \frac{1}{4} \right) + V(R, r, \theta, t) \quad (8)$$

There are singularities at $\theta = 0$ and $\theta = \pi$. Therefore, one must be careful when using this Hamiltonian for cases where collinear geometries occur.

3. Propagation

Because of the nonlocal character of quantum mechanics, the wave function is in principle required at every point in space. In practice this is not required, as in most numerical implementations the wave packet is discretized and propagated on a grid.

To evaluate the action of the time evolution operator \hat{U} (the exponential of the Hamiltonian operator) on ϕ_{jk} , the split operator method is used:^{7,10}

$$\hat{U}(R, r, \theta, \Delta t) = e^{-i\Delta t[\hat{T}_R + \hat{T}_r + T_\theta + \hat{U}(R, r, \theta, t)]} = e^{-i\Delta t \hat{T}_R/2} e^{-i\Delta t \hat{T}_r/2} e^{-i\Delta t T_\theta/2} e^{-i\Delta t \hat{U}(R, r, \theta, t)} e^{-i\Delta t \hat{T}_r/2} e^{-i\Delta t \hat{T}_r/2} e^{-i\Delta t \hat{T}_R/2} \quad (9)$$

where \hat{T}_R is made up of terms containing R derivatives in eqs

6 and 7 and correspondingly for \hat{T}_r and \hat{T}_θ . The operator \hat{U} collects all terms that do not contain any derivative.

For each kinetic energy operator, \hat{T}_R , \hat{T}_r , \hat{T}_θ , its derivatives are found using one-dimensional FFT, keeping the other two coordinates fixed.⁷ The operators \hat{T}_R and \hat{T}_r are diagonal, but for $J > 0$ operators \hat{U} and \hat{T}_θ are not diagonal in k . Different k components of the $\hat{U}(R, r, \theta, t)$ operator are coupled by the $\hat{H}_{k,k\pm 1}$ terms of the Hamiltonian as seen in eq 7. Therefore, the $\hat{U}(R, r, \theta, t)$ operator must be diagonalized at each R , r , and θ grid point. \hat{T}_θ is diagonalized in the Fourier space (see Appendix A). The diagonalizations are performed before the propagation in time begins. The results are stored, which does not require much memory but reduces the computational effort.

All matrices to be diagonalized are tridiagonal of order $(2J + 1) \times (2J + 1)$. For large values of the total angular momentum, it may be worthwhile to separate the matrix into two smaller matrices using initial wave functions of odd and even parities.¹¹ In this case the matrices will have orders $(J + 1) \times (J + 1)$ and $J \times J$, depending on the parity.

An attractive feature of the split operator method is that it is simple and it has been used successfully together with time-dependent external fields. However, it should be pointed out that in comparing it to the Chebyshev and Lanczos methods,^{4,5} the necessity to diagonalize a nondiagonal Hamiltonian matrix is specific to the split operator method. This is due to the fact that in the split operator method we evaluate the exponent of the Hamiltonian matrix, whereas in the Chebyshev and Lanczos methods the nondiagonal Hamiltonian matrix acts directly on a wave function.

The split operator method has also been used by J. Z. H. Zhang and co-workers for $J > 0$ calculations, see for instance ref 13. In their approach, the total wave function is expanded in a basis of vibrational eigenfunctions for the r coordinate and angular momentum eigenfunctions for angular coordinates. Due to construction, this method¹³ should be effective when applied to problems that can be well described by vibrational basis functions for the r coordinate. Fourier functions, on the other hand, are eigenfunctions of the kinetic energy operator and are therefore expected to describe free particle motion and dissociating coordinates well.

The operator \hat{T}_θ is often handled by a Gauss–Legendre DVR. In this case, the \hat{T}_θ operator becomes nondiagonal in the angle θ through the DVR basis set, whereby it acquires an extra dimension. Propagation thereby becomes very expensive, see ref 12. The problem of diagonalization in θ does not arise using FFT, as \hat{T}_θ remains diagonal in this coordinate in the Fourier basis set.

4. Calculations of H₂O Eigenstates

Time-dependent methods can be used to find eigenvalues and eigenfunctions of the stationary Schrödinger equation.¹⁰ Since eigenvalue problems of small polyatomic molecules are studied by many researchers and many results are available, we have chosen to test our propagation method by finding eigenvalues for a previously well-studied system.

The procedure developed above is applied to the H₂O molecule in the ground state using an empirical PES constructed by Jensen.¹⁴ Eigenstates for $J = 0, 1, 2$ are calculated using the filter diagonalization method¹⁵ in order to separate closely lying eigenstates. For $J = 2$, each vibrational level has rotational states with an energy separation ΔE of only 1.1 cm⁻¹. It can be estimated from the time–energy uncertainty principle (more precisely, from the Fourier integral theorem or the sampling theorem) $T \geq \pi/\Delta E$,¹⁷ that using spectral methods the total

propagation time T must be larger than 15 ps. The filter diagonalization method has been devised to overcome the uncertainty principle¹⁵ and our hope was that it would allow us to reduce this long propagation time.

To find eigenstates using the filter diagonalization (FD) method a small set of basis functions is first obtained. This can be done by propagating an arbitrary wave packet on the potential energy surface.

Functions

$$|\Phi(E_i)\rangle = \int_{-\infty}^{\infty} g(t) e^{iE_i t} \Psi(t) dt \quad (10)$$

where $g(t)$ is a filtering function, can be calculated at different energies E_i and used as a basis set for the expansion of the trial wave function. By construction, the functions $\Phi(E_i)$ are optimized to find eigenstates whose energies are close to E_i .

In constructing the Hamiltonian, \mathbf{H} , and overlap, \mathbf{S} , matrices over $|\Phi(E_i)\rangle$, two time integrals result from eq 10. Using a Gaussian damping function,¹⁵ a step function, or cosine based functions¹⁶ in eq 10 allows the Hamiltonian and overlap matrices to be constructed knowing only the correlation function:

$$C(t) \equiv (\Psi(0)| e^{-i\hat{H}t} |\Psi(0)) = (\Psi(0)|\Psi(t)) \quad (11)$$

where $(\Psi(0)|\Psi(t)) \equiv \langle \Psi^*(0)|\Psi(t) \rangle$. This is made possible by calculating one of the two time integrals in the \mathbf{H} and \mathbf{S} matrices analytically. We have tried all three damping functions mentioned above. The cosine-based and the Gaussian damping functions give similar convergence of the results, the former being slightly better, in agreement with ref 16. The cosine based filtering function,¹⁶ which is used for the present work, is

$$g_1(t) = \cos\left(\frac{\pi t}{2T}\right) \Theta(1 - t^2/T^2) \quad (12)$$

where T is the total propagation time and $\Theta(1 - t^2/T^2)$ is the Heaviside step function. The Hamiltonian matrix elements and the overlap matrix elements are given in Appendix B.

In order not to have to store the initial wave function, eq 11 can be rewritten as¹⁸

$$C(t) = (e^{-i\hat{H}t/2} \Psi(0)| e^{-i\hat{H}t/2} \Psi(0)) = (\Psi(t/2))^2 \quad (13)$$

The Hamiltonian and overlap matrices give the generalized eigenvalue equation

$$\mathbf{H}\mathbf{B} = \mathbf{S}\mathbf{B}\mathbf{E} \quad (14)$$

Solving eq 14, eigenvalues and eigenstates can be found in selected energy ranges provided that these eigenstates are contained in the wave packet.

In our calculations, we have used 32 grid points for every coordinate and a time step $\Delta t = 0.05$ fs. Separate calculations for each J have been performed. An arbitrary, but smooth, initial wave packet with no symmetry restrictions has been chosen in order to obtain all relevant eigenstates from one run. The rotational eigenenergies have been converged to 0.005 cm^{-1} accuracy. This corresponds to a relative error smaller than 10^{-6} . The required number of propagation steps to converge all rotational eigenstates is $N_0 = 1500$, $N_1 = 30\,000$, and $N_2 = 50\,000$ for $J = 0$, $J = 1$, and $J = 2$, respectively.

In Tables 1–3, the eigenenergies obtained are compared with eigenenergies found in the theoretical study by Fernley et al.¹⁹ using the variational method. Results from the recent study of Acioli et al.²⁰ using the correlation function quantum Monte Carlo (CFQMC) method are also included. The same potential

TABLE 1: Calculated Vibrational Energies ($J = 0$) of the H_2O Molecule in the Ground Electronic State (denoted FD)^a

(ν_1, ν_2, ν_3)	FD	DVR	CFQMC
0 1 0	1594.3	1594.3	1594.4
0 2 0	3152.0	3152.0	3151.4
1 0 0	3657.1	3656.5	3657.8
0 0 1	3755.5	3756.0	3756.6

^a Reference energies are taken from Fernley et al.¹⁹ (DVR) and Acioli et al.²⁰ (CFQMC). All energies are given in cm^{-1} relative to the (0, 0, 0) state.

TABLE 2: Calculated Rovibrational Energies ($J = 1$) of the H_2O Molecule in the Ground Electronic State (denoted FD)^a

(ν_1, ν_2, ν_3)		$\tau = -1$	$\tau = 0$	$\tau = 1$
0 0 0	FD	23.80	37.08	42.32
	DVR	23.80	37.08	42.33
	CFQMC	22.25	36.04	41.61
0 1 0	FD	23.82	40.17	45.72
	DVR	23.82	40.18	45.72
	CFQMC	22.78	41.24	44.86
0 2 0	FD	23.82	44.39	50.23
	DVR	23.82	44.39	50.22
	CFQMC	22.52	47.08	52.24
1 0 0	FD	23.43	36.24	41.45
	DVR	23.43	36.24	41.45
	CFQMC	23.42	35.97	42.05
0 0 1	FD	23.60	35.80	41.09
	DVR	23.60	35.80	41.09
	CFQMC	23.64	39.31	42.64

^a Reference energies are taken from Fernley et al. (DVR)¹⁹ and Acioli et al. (CFQMC).²⁰ All energies are relative to the $J = 0$ state.

TABLE 3: Calculated Rovibrational Energies ($J = 2$) of the H_2O Molecule in the Ground Electronic State (FD)^a

(ν_1, ν_2, ν_3)		$\tau = -2$	$\tau = -1$	$\tau = 0$	$\tau = 1$	$\tau = 2$
0 0 0	FD	70.11	79.45	95.16	134.70	135.97
	DVR	70.11	79.45	95.17	134.70	135.98
	CFQMC	71.40	79.45	99.51	135.81	137.13
0 1 0	FD	70.23	82.27	98.88	147.38	148.57
	DVR	70.23	82.27	98.88	147.39	148.57
	CFQMC	74.12	84.48	104.36	150.52	151.57
0 2 0	FD	70.36	86.24	103.68	164.24	165.31
	DVR	70.36	86.23	103.69	164.25	165.32
	CFQMC	72.52	89.68	99.82	170.16	175.84
1 0 0	FD	68.97	77.89	93.50	131.63	132.92
	DVR	68.97	77.89	93.50	131.63	132.92
	CFQMC	72.25	79.74	102.96	130.94	134.28
0 0 1	FD	69.39	77.73	93.58	129.89	131.27
	DVR	69.39	77.73	93.58	129.89	131.27
	CFQMC	71.86	78.48	98.74	133.46	137.94

^a Reference energies are taken from Fernley et al. (DVR)¹⁹ and Acioli et al. (CFQMC).²⁰ All energies are relative to the $J = 0$ state.

used in those studies was used in the present study. As the H_2O molecule is an asymmetric rotor, k is not a good quantum number and eigenenergies corresponding to some particular value of J are numbered by τ rather than by k . Our calculated zero point energy is 4630.4 cm^{-1} . Acioli et al.²⁰ found it to be 4628.2 cm^{-1} .

From the tables, we see that the agreement with the results of Fernley et al. is very good, whereas the agreement with the results of Acioli et al. is poorer. There is, however, a discrepancy of about 0.5 cm^{-1} between our energy values and those of Fernley et al. for the (1,0,0) and (0,0,1) $J = 0$ vibrational levels, see Table 1. The origin of this disagreement is not clear.

To resolve the $J = 2$ rovibrational states, the required total propagation time is 2.5 ps. Thus, there is some gain compared to the 15 ps propagation time, which is dictated by the time–energy uncertainty principle, though the improvement is not very

large. The gain is even smaller for the $J = 0$ and $J = 1$ states. One possible explanation for the slow convergence of the filter diagonalization method that we find for this problem could be the specific structure of the rovibrational spectrum, where rotational energy levels are grouped in dense packs for each vibrational level. We note that in a recent paper Vijay and Wyatt find that the FD method does not always bypass the time–energy uncertainty constraint.²¹ Certainly, one must conclude that for the particular problem treated here, the use of basis set methods or iterative approaches, for instance employing the Lanczos algorithm, would be computationally less expensive for finding the eigenvalues, see ref 22 for a discussion.

5. Concluding Remarks

A wave packet representing a rotating triatomic molecule is propagated in Jacobi coordinates for total angular momentum quantum number J equal to 0,1,2. The propagation is performed using the split operator method combined with the fast Fourier transform technique, which is made possible by a simple transformation of the molecular Hamiltonian. We test this propagation method by calculating rovibrational eigenstates of the H_2O molecule, which are found to be in good agreement with those found by Fernley et al. using the discrete variable representation approach.¹⁹

The nonzero total angular momentum calculations could be of interest to photoexcitation processes. As a short-time propagator is used in this work, the method can be applied to studies of triatomic molecules interacting with femtosecond laser fields. However, application of the method to transitions other than $J = 0 \rightarrow J' = 1$ may be difficult, due to problems of finding an initial wave function (different J and k states may contribute to the initial wave function). Another problem for application to transitions involving large values of J could be that the computer memory required increases with the total angular momentum. Therefore, some approximations, such as restriction of the initial state to certain J and k (or τ) values, may be necessary in such a case.

Acknowledgment. This project has been supported by the Swedish Natural Science Research Council (NFR), the Swedish Council for Planning and Coordination of Research (FRN), and the Wallenberg Foundation.

Appendix A

To illustrate the evaluation of the action of the exponential of the kinetic energy operator \hat{T}_θ on ϕ_{Jk} , we consider the simple case $J = 1/2$. Then k can take two values, which we denote by subscripts and write

$$\exp\left\{-i\Delta t \begin{pmatrix} -\frac{1}{2}\left(\frac{1}{\mu R^2} + \frac{1}{\mu r^2}\right)\frac{\partial^2}{\partial\theta^2} & \frac{1}{2\mu R^2}[(J+k_{-1/2}+1)(J-k_{-1/2})]^{1/2}\frac{\partial}{\partial\theta} \\ -\frac{1}{2\mu R^2}[(J-k_{1/2}+1)(J+k_{1/2})]^{1/2}\frac{\partial}{\partial\theta} & -\frac{1}{2}\left(\frac{1}{\mu R^2} + \frac{1}{\mu r^2}\right)\frac{\partial^2}{\partial\theta^2} \end{pmatrix}\right\} \\ \equiv \exp\begin{pmatrix} f_1(R, r)\frac{\partial^2}{\partial\theta^2} & f_2(R)\frac{\partial}{\partial\theta} \\ -f_2(R)\frac{\partial}{\partial\theta} & f_1(R, r)\frac{\partial^2}{\partial\theta^2} \end{pmatrix} \quad (15)$$

The following property is used

$$\exp\begin{pmatrix} +f_1(R, r)\frac{\partial^2}{\partial\theta^2} & f_2(R)\frac{\partial}{\partial\theta} \\ -f_2(R)\frac{\partial}{\partial\theta} & f_1(R, r)\frac{\partial^2}{\partial\theta^2} \end{pmatrix} = \widehat{FT}(p_\theta, \theta)^{-1} \exp\begin{pmatrix} -f_1(R, r)p_\theta^2 & -if_2(R, r)p_\theta \\ if_1(R, r)p_\theta & -f_1(R, r)p_\theta^2 \end{pmatrix} \widehat{FT}(\theta, p_\theta), \quad (16)$$

where $\widehat{FT}(p_\theta, \theta)^{-1}$ is the inverse Fourier transform, which is defined as

$$\Psi(\theta) = \widehat{FT}(p_\theta, \theta)^{-1}\Phi(p_\theta) = \frac{1}{\sqrt{2\pi}} \int \Phi(p_\theta) e^{ip_\theta\theta} dp_\theta \quad (17)$$

if the forward Fourier transform is defined as

$$\Phi(p_\theta) = \widehat{FT}(\theta, p_\theta)\Psi(\theta) = \frac{1}{\sqrt{2\pi}} \int \Psi(\theta) e^{-ip_\theta\theta} d\theta \quad (18)$$

The kinetic energy operator $\hat{T}_\theta(p_\theta)$, defined by eqs 4 and 5, is diagonalized in Fourier space

$$\hat{T}_\theta(p_\theta) = U^{-1}\hat{D}_\theta U \quad (19)$$

where \hat{D}_θ is a diagonal matrix and U is unitary, whereby

$$\exp(-it\hat{T}_\theta) = U^{-1}\exp(-it\hat{D}_\theta)U \quad (20)$$

can be used to propagate the wave packet. Generalization to cases of larger values of J is straightforward.

Summarizing, the action of \hat{T}_θ for $J > 0$ cases is evaluated in three steps. First, the 1D Fourier transform of the wave function is performed. Second, the exponential of the operator $\hat{T}_\theta(p_\theta)$, eq 20, is applied. The \hat{T}_θ operator can be split into a commuting diagonal part and a noncommuting nondiagonal part. The required diagonalization of the nondiagonal part is then done at each R and p_θ . Third, the 1D inverse Fourier transform of the wave function is found.

Appendix B

The overlap matrix elements $S_{ll'}$ for the cosine filtering function are given by

$$S_{ll'} = \frac{1}{4} \int_{-T}^T \left[2\cos\left(\frac{\pi t}{T}\right) \sin((T-|t|)\Delta E)/\Delta E + \sin((\pi/T + \Delta E)(T-|t|))/(\pi/T + \Delta E) + \sin((-\pi/T + \Delta E)(T-|t|))/(-\pi/T + \Delta E) \right] \times C(t) \exp[i(E_l + E_r)t/2] dt \quad (21)$$

where $\Delta E = (E_l - E_r)/2$. This expression is analogous to the one derived by M. H. Beck et al. in ref 16, where details of the derivation can be found.

To find the Hamiltonian matrix elements $H_{ll'}$, the following relationship¹⁵ has been used:

$$(\Psi(0)|\hat{H}|\Psi(t)) = (\Psi(0)\left| i\frac{d}{dt} \right|\Psi(t)) \quad (22)$$

giving

$$\begin{aligned}
H_W = & -\frac{i}{2} \int_{-T}^T \left[-\frac{\pi}{T} \sin\left(\frac{\pi t}{T}\right) \sin((T - |t|)\Delta E)/\Delta E + \right. \\
& \left. \cos\left(\frac{\pi t}{T}\right) \sin((T - |t|)\Delta E)/\Delta E + \frac{1}{2} \sin((\pi/T + \Delta E) \right. \\
& (T - |t|)/(\pi/T + \Delta E) + \frac{1}{2} \sin((-\pi/T + \Delta E)(T - |t|)/ \\
& \left. (-\pi/T + \Delta E)) \right] i(E_l + E_r)/2 \times C(t) \exp[i(E_l + E_r)t/2] dt
\end{aligned} \tag{23}$$

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