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Quantum Molecular Dynamics with Wave Packets

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Quantum effects are prominent in the dynamics of many molecular systems. Simulating quantum molecular dynamics, the wave packet approach is an efficient tool to solve time-dependent and time-independent Schrödinger equations. The article reviews standard methods employed in wave packet calculations: different type of grid representations for wave functions and propagation schemes for solving the time-dependent Schrödinger equation are described. Iterative diagonalization schemes and filter diagonalization approaches for the time-independent Schrödinger equation are also discussed within the framework of the wave packet dynamics approach. Following the review of the standard methods for wave packet dynamics, an efficient approach for the description of larger systems, the multi-configurational time-dependent Hartree (MCTDH) approach, is presented.

1 Introduction

Quantum mechanics is not only essential for the understanding of the electronic structure of molecules, quantum effects also strongly influence the nuclear motion of many molecular systems. Tunneling is a key issue in the understanding of hydrogen or proton transfer reactions. Vibronic coupling determines the outcome of many photochemical reactions. Zero point energy effects are important for the structure and dynamics of van der Waals-clusters. Many other examples could be found.

In the absence of strong laser fields, molecular system can typically be described by time-independent Hamiltonians. Thus, the system dynamics can be studied by solving the time-independent Schrödinger equation. The solution of a linear eigenvalue problem might therefore be viewed as the most direct approach for studying quantum dynamics of molecular systems: the Hamiltonian is represented in a finite basis set and the resulting matrix is numerically diagonalized. However, two problems associated with this approach should be mentioned. The CPU time required for the (complete) matrix diagonalization is proportional to the cube of the basis size and the required memory is proportional to the square of the basis size. Since the basis set size scales exponentially with the dimensionality of the system, the computation becomes easily infeasible if the system size increases. Second, the interpretation of the numerical results is a formidable task if larger systems are considered. The number of relevant eigenstates is enormous and the spectra typically can not be assigned using simple and physically meaningful patterns.

The wave packet approach, which has become increasingly popular in the last two decades, can reduce both problems. First, the motion of wave packets obtained from the solution of the time-dependent Schrödinger equation can typically be understood using classical-mechanical and semiclassical ideas. This can considerably simplify the interpretation of the numerical results. Second, while in the above diagonalization approach the dynamics of all states are computed at once, the wave packet approach typically describes only the motion of individual wave packets. The initial conditions defining these wave

packets are tailored to the specific experiment in question. This reduction of the required information yields a numerically more efficient scheme. In wave packet dynamics calculations, CPU time and memory requirements scale approximately proportional to the basis set size. It should be noted that these numerical advantages are not limited to time-dependent wave packet calculations. Analogous arguments are valid also for the calculation of individual energy eigenstates by iterative diagonalization or filter diagonalization approaches.

The present article reviews the methods employed in modern wave packet dynamics calculations. Standard schemes for an efficient spatial representation of wavefunctions are described: the Fast Fourier Transform (FFT) approach¹ and the Discrete Variable Representation (DVR)²⁻⁴. Concepts for the efficient temporal integration of the time-dependent Schrödinger equation are discussed and examples of widely used integrators are given⁵⁻⁷. The connection between these propagation schemes and iterative diagonalization techniques is discussed. The description of the filter diagonalization technique⁸ finally highlights the connection between time-dependent and energy-dependent methods.

Due to the numerical effort, presently standard wave packet calculations are not feasible for systems with more than six dimensions. Even four atom systems can be studied in their full dimensionality only under favorable circumstances. Therefore also a scheme which is tailored to the description of multi-dimensional systems will be presented: the multi-configurational time-dependent Hartree (MCTDH) approach^{9,10}. The MCTDH approach employs a two layer scheme for the representation of the wavefunction. The multi-dimensional wavefunction is represented in a time-dependent basis set. The time-dependent basis functions employed are products of one-dimensional wave packets represented in a standard time-independent (FFT or DVR) basis. The MCTDH approach can give an accurate description of multi-dimensional systems which are beyond the scope of standard wave packet calculations. Recent applications include a 24-dimensional calculation on the absorption spectrum of pyrazine^{11,12} and a 12-dimensional investigation of the $H + CH_4 \rightarrow H_2 + CH_3$ reaction^{14,15}.

2 Spatial Representation of Wavefunctions

The dynamics of a wave packet is given by the Schrödinger equation

$$i \frac{\partial}{\partial t} \psi(x_1, \dots, x_f, t) = \hat{H} \psi(x_1, \dots, x_f, t) \quad (1)$$

(atomic units, i.e. $\hbar=1$, are used).

Representing the wavefunction in a finite time-independent basis set,

$$\psi(x_1, \dots, x_f, t) = \sum_n A_n(t) \phi_n(x_1, \dots, x_f), \quad (2)$$

the equations of motions for the time-dependent expansion coefficient are a linear system of first order differential equations:

$$i \frac{\partial}{\partial t} A_n(t) = \sum_m H_{nm} A_m(t). \quad (3)$$

Thus, the solution of the time-dependent Schrödinger equation can be decomposed into two different task. The first task is the computation of the matrix elements H_{nm} or, alternatively, the calculation of the action of the Hamiltonian operator on the wavefunction. Second, the resulting differential equation have to be integrated in time. The present section focuses on the first task, while the time propagation will be discussed in the next section.

2.1 Grid and Basis Representations

Wave packet calculations utilize different representations of the wavefunction to evaluate different terms in the Hamiltonian. Consider a Hamiltonian

$$\hat{H} = \hat{H}_0 + V. \quad (4)$$

If the wavefunction represented in the basis $|\phi_n\rangle$ of eigenstates of \hat{H}_0 with the corresponding eigenvalues E_n , the action of \hat{H}_0 on the wavefunction can be evaluated immediately,

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle, \quad (5)$$

$$\langle \phi_n | \hat{H}_0 | \psi \rangle = E_n c_n. \quad (6)$$

Analogously a discrete grid representation based on the grid point states $|X_n\rangle$ can be employed to evaluate the action of the potential on the wavefunction:

$$|\psi\rangle = \sum_n k_n |X_n\rangle, \quad (7)$$

$$\langle X_n | V | \psi \rangle = V(X_n) k_n. \quad (8)$$

If the transformation between the basis and the grid representation, i.e. the matrix $\langle X_n | \phi_m \rangle$, is known, the action of the Hamiltonian can be evaluated by transforming from one representation to the other:

$$\hat{H} = \sum_n |\phi_n\rangle E_n \langle \phi_n| + \sum_n |X_n\rangle V(X_n) \langle X_n|, \quad (9)$$

$$\langle \phi_n | \hat{H} | \psi \rangle = E_n c_n + \sum_m \langle \phi_n | X_m \rangle V(X_m) \left(\sum_j \langle X_m | \phi_j \rangle c_j \right), \quad (10)$$

$$\langle X_n | \hat{H} | \psi \rangle = \sum_m \langle X_n | \phi_m \rangle E_m \left(\sum_j \langle \phi_m | X_j \rangle k_j \right) + V(X_n) k_n. \quad (11)$$

To define this dual representation scheme, the two bases $|\phi_n\rangle$ and $|X_n\rangle$ have to be chosen and the transformation between the two set, $\langle X_n | \phi_m \rangle$, has to be specified. Two different schemes are frequently used for this propose: the discrete variable representation (DVR)⁴ and the fast Fourier transform (FFT)¹ approach. These schemes will be discussed below in more detail.

The above discussion has not explicitly considered the dimensionality of the wavefunction. The transformation between the two bases requires a matrix multiplication. In

principle, the numerical effort of this operation would be proportional to the square of the basis set size. In multi-dimensional calculations the numerical effort can be drastically reduced if the basis sets and grids are direct products of one-dimensional functions:

$$\phi_n(x_1, x_2, \dots, x_f) = \phi_{n_1}^{(1)}(x_1) \cdot \phi_{n_2}^{(2)}(x_2) \cdot \dots \cdot \phi_{n_f}^{(f)}(x_f), \quad (12)$$

$$|X_n\rangle = |(X_1)_{n_1}\rangle | (X_2)_{n_2}\rangle \dots | (X_f)_{n_f}\rangle, \quad (13)$$

where the index n should be read as multi-index n_1, n_2, \dots, n_f and the multi-dimensional coordinate X as X_1, X_2, \dots, X_f . Then the transformation matrix $\langle X_n | \phi_m \rangle$ factorizes:

$$\langle X_n | \phi_m \rangle = \langle (X_1)_{n_1} | \phi_{m_1}^{(1)} \rangle \langle (X_2)_{n_2} | \phi_{m_2}^{(2)} \rangle \dots \langle (X_f)_{n_f} | \phi_{m_f}^{(f)} \rangle. \quad (14)$$

The transformation from the basis grid to the grid representation and vice versa can be calculated for each coordinate separately:

$$k_{n_1, n_2, \dots, n_f} = \langle X_{n_1, n_2, \dots, n_f} | \psi \rangle = \quad (15)$$

$$\left(\sum_{m_1} \langle (X_1)_{n_1} | \phi_{m_1}^{(1)} \rangle \left(\sum_{m_2} \langle (X_2)_{n_2} | \phi_{m_2}^{(2)} \rangle \dots \right. \right.$$

$$\left. \left. \dots \left(\sum_{m_f} \langle (X_f)_{n_f} | \phi_{m_f}^{(f)} \rangle c_{m_1, m_2, \dots, m_f} \right) \dots \right) \right).$$

If N_i basis functions or grid points are employed in the i -th coordinate, then the numerical effort of this operation is proportional to $(N_1 + N_2 + \dots + N_f) \prod_{i=1}^f N_i$. Thus, in a multi-dimensional direct product basis the numerical effort of the transformation scales approximately linear with the basis set size $N = \prod_{i=1}^f N_i$.

2.2 DVR

In the discrete variable representation (DVR), the optimally localized grid point states $|X_n\rangle$ are obtained from the eigenstates of the coordinate operator represented in the given finite basis $|\phi_n\rangle$ ²:

$$\langle \phi_n | x | \phi_m \rangle = \sum_j \langle \phi_n | X_j \rangle X_j \langle X_j | \phi_m \rangle. \quad (16)$$

The eigenvalue X_j are grid points of the one-dimensional grid and the eigenstates $\langle \phi_n | X_j \rangle$ are the grid-to-basis transformation matrix employed in the DVR scheme. Considering all bases $|\chi_n\rangle$ which can be obtained by a unitary transformation of the original $|\phi_n\rangle$ basis, the $|X_n\rangle$ basis minimizes the localization criterion

$$\sum_n (\langle \chi_n | x^2 | \chi_n \rangle - \langle \chi_n | x | \chi_n \rangle^2) \rightarrow \text{minimum}. \quad (17)$$

The evaluation of the potential energy integrals

$$\langle \phi_n | V(x) | \phi_m \rangle = \sum_j \langle \phi_n | X_j \rangle V(X_j) \langle X_j | \phi_m \rangle \quad (18)$$

within the DVR corresponds to a Gaussian quadrature if the basis $|\phi_n\rangle$ consists of orthogonal polynomials multiplied by a weight function³. Since the wavefunction is typically

more structured than the potential energy function, the numerical inaccuracy resulting from this Gaussian quadrature scheme is usually small compared to the truncation error resulting from the representation of the wavefunction in the finite basis $|\phi_n\rangle$. Thus, the number of grid points can be equal to the number of basis functions without relevant loss of accuracy⁴.

Typical basis sets employed in DVR schemes are the harmonic oscillator eigenfunctions for distance coordinates (Hermite DVR) and Legendre polynomials for angular variables (Legendre DVR). Employing the eigenstates of H_0 operator specifically adjusted to the system under investigation is another interesting possibility (often called potential optimized DVR). Thus, the DVR approach offers maximal freedom for tailoring the basis sets and grids to any specific system.

If the grid representation is employed as a primary representation, explicit transformations to the basis representation can be avoided⁴. The kinetic energy operator is employed in its grid representation:

$$\hat{T} = \hat{H}_0 + V_0, \quad (19)$$

$$\langle X_n | \hat{T} | X_m \rangle = \sum_j \langle X_n | \phi_j \rangle E_j \langle \phi_j | X_m \rangle - V_0(X_n) \delta_{nm}. \quad (20)$$

Since usual kinetic energy operators show a simple structure, the application of the total kinetic energy operator can be performed by subsequent application of the different one-dimensional kinetic energy matrices of the respective coordinates. Thus, two matrix multiplies for the forward and backward basis transformations can be replaced by a single matrix multiply with the kinetic energy matrix in coordinate representation. Moreover, these DVR schemes are no longer restricted to direct product type grid. Unnecessary grid points can be dropped in the representation of the wavefunction and the kinetic energy operator^{4,16} which reduces the basis set size.

2.3 FFT

While the DVR approach provides a flexible choice of basis sets and grids, the fast Fourier transform (FFT) scheme¹ focuses on the numerical efficiency of the transformation between the different basis sets employed. The FFT approach employs an evenly spaced grid in a given interval $[x_i, x_f]$ of the coordinate space. The N grid points in this interval are connected via a discrete Fourier transform with an evenly spaced momentum grid in the interval $[p_i, p_i + \frac{2\pi}{\Delta x}]$, where $\Delta x = \frac{x_f - x_i}{N}$ is the grid spacing in coordinate space. The transformation between the discrete coordinate representation $|X_n\rangle$ and the discrete momentum representation $|P_m\rangle$ is given by:

$$|X_n\rangle = \frac{1}{\sqrt{N}} \sum_{m=1}^N e^{iP_m X_n} |P_m\rangle, \quad (21)$$

$$|P_m\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-iP_m X_n} |X_n\rangle. \quad (22)$$

Fast Fourier transform algorithms can be employed to compute these transformation. They provide a numerical efficient scheme if N can be split into many prime factors. N being a power of two is the most favorable case. Then the numerical effort of the transformation is proportional to $\log_2 N \cdot N$.

Connecting to the description of section 2.1, the plane waves $\phi_n(x) = \frac{1}{\sqrt{N}} e^{iP_n x}$ can be viewed as the basis functions employed in the FFT approach. The momentum values P_n are evenly spaced in the interval $[p_i, p_i + \frac{2\pi}{\Delta x}]$ and the grid states are placed on evenly spaced points in the interval $[x_i, x_f]$. The transformation matrix between this basis and the grid representation reads:

$$\langle X_n | P_m \rangle = \frac{1}{\sqrt{N}} e^{iP_m X_n} . \quad (23)$$

Any operator diagonal in the momentum representation, e.g. $\frac{1}{2m} \frac{\partial^2}{\partial x^2}$, can be used as H_0 .

Due to the Fourier representation employed, the resulting wavefunction is $(x_f - x_i)$ -periodic in coordinate space and $\frac{2\pi}{\Delta x}$ -periodic in momentum space. Thus, a converged description of the wavefunction is obtained if it vanishes outside the interval $[x_i, x_f]$ in coordinate space and outside the interval $[p_i, p_i + \frac{2\pi}{\Delta x}]$ in momentum space or obeys the corresponding periodicity requirements.

Also non-evenly space grids can be employed in the FFT scheme. To this end, a coordinate transformation $\tilde{x} = f(x)$ is made in the Hamiltonian. The evenly spaced grid of \tilde{x} points then corresponds to a non-evenly spaced grid in the original coordinate x (mapped FFT¹⁷).

3 Propagation of Wave Packets

Solving Eq.(3) requires to evaluate the action of the Hamiltonian on the wavefunction, which has been discussed in the preceding section, and to integrate the set of linear differential equations. Of course, any general purpose integration scheme, e.g. Runge-Kutta or predictor-corrector algorithms, could be used. However, integration schemes specifically developed for this particular type of equations are considerably more efficient. In the following, different integrations schemes widely used in modern computations will be described and compared.

3.1 Split Operator Propagation

The split operator scheme⁵ explicitly utilizes the dual representation approach. The Hamiltonian is splitted into two parts and each is represented in its eigenstate representation (see Sect.2.1).

$$\hat{H} = \hat{H}_0 + V = \sum_n |\phi_n \rangle E_n \langle \phi_n| + \sum_n |X_n \rangle V(X_n) \langle X_n| \quad (24)$$

Employing a Trotter formula

$$e^{-i\hat{H}\Delta t} = e^{-i\hat{V}\Delta t/2} e^{-i\hat{H}_0\Delta t} e^{-i\hat{V}\Delta t/2} + 0(\Delta t^3) \quad (25)$$

and evaluating each resulting propagator in its eigenstate representation, a second order short time integrator can be constructed:

$$e^{-i\hat{H}\Delta t} = \left(\sum_n |X_n \rangle e^{-iV(X_n)\Delta t/2} \langle X_n| \right) \cdot \left(\sum_n |\phi_n \rangle e^{-iE_n\Delta t} \langle \phi_n| \right) \cdot \left(\sum_n |X_n \rangle e^{-iV(X_n)\Delta t/2} \langle X_n| \right) + 0(\Delta t^3) . \quad (26)$$

Thus, the operator $\exp(-i\hat{V}\Delta t/2)$ is evaluated in the coordinate representation, where it is diagonal. Then the wavefunction is transformed from the coordinate to the basis representation. The operator $\exp(-i\hat{H}_0\Delta t)$, which is diagonal in this representation, is now applied. After a change back to coordinate representation and application of $\exp(-i\hat{V}\Delta t/2)$, the result of a Δt integration step is obtained. Repeating these steps, the integration can be continued for any required period of time:

$$e^{-i\hat{H}t} = \prod_{n=1}^{\frac{t}{\Delta t}} \left(e^{-i\hat{V}\Delta t/2} e^{-i\hat{H}_0\Delta t} e^{-i\hat{V}\Delta t/2} \right) + O(\Delta t^2). \quad (27)$$

The integration scheme is unitary and strictly conserves the norm of the wavefunction. Analyzing the numerical propagator in its eigenstate representation,

$$e^{-i\hat{V}\Delta t/2} e^{-i\hat{H}_0\Delta t} e^{-i\hat{V}\Delta t/2} \chi_n = u_n \chi_n, \quad (28)$$

one finds that the discretisation on the finite time step Δt effects only the phase of u_n (since $|u_n| = 1$). This guarantees the long time stability of the integration scheme. However, it is only a low order scheme. Thus, the results tend not to be particularly accurate. High precision results can only be obtained with a prohibitively small time step Δt .

The above discussion has been limited to a specific implementation of the split operator scheme for a simple Hamiltonian. It aimed only on presenting the basic idea. The scheme has been applied to several different type of Hamiltonians and used in different variants.

3.2 Polynomial Expansions

Higher order integration schemes are based on a polynomial expansion of the propagator:

$$e^{-i\hat{H}\Delta t} = \sum_{n=0}^N c_n(\Delta t) \hat{H}^n + O(\Delta t^{N+1}). \quad (29)$$

The action of the propagator on the wavefunction is computed by successive application of the Hamiltonian,

$$\psi_n = a_n \hat{H} \psi_{n-1} + \sum_{j=0}^{n-1} b_{n,j} \psi_j, \quad (30)$$

where a_n and b_j are coefficients which characterize the particular scheme. Employing orthogonal polynomials, the above recursion relation usually reduces to a three term series: $b_{n,j} = 0$ for $j < n - 2$.

A short polynomial expansion (typically with $N \leq 10$) provides efficient propagators for limited time steps Δt . These integration steps are repeated until the propagation is completed:

$$\psi(M\Delta t) = \left(\prod_{m=1}^M e^{-i\hat{H}\Delta t} \right) \psi(0) + O(\Delta t^N). \quad (31)$$

The Lanczos scheme is mostly employed to define the coefficients in the polynomial expansion⁷. In the Lanczos scheme, the Hamiltonian matrix is represented in the Krylov

space $\{\psi, \hat{H}\psi, \dots, \hat{H}^N\psi\}$. The resulting $(N+1)$ -dimensional model Hamiltonian H_{model} is diagonalized,

$$H_{model} \chi_j = E_{model,j} \chi_j , \quad (32)$$

and the propagator is evaluated in the model space:

$$e^{-i\hat{H}\Delta t}\psi = \sum_{j=1}^{N+1} \chi_j \cdot e^{-iE_{model,j}\Delta t} \cdot \langle \chi_j | \psi \rangle + 0(\Delta t^{N+1}) . \quad (33)$$

The resulting propagation scheme is numerically unitary. Thus, it provides the same long time stability as the split operator propagation. Its main advantage is the increased accuracy since the error is of higher order: $0(\Delta t^{N+1})$. Practical experience indicates that N should be chosen between 6 and 10 in most applications. The required length of integration step Δt is closely related to the spectrum of the Hamiltonian. Typically $\Delta t/N$ roughly equals the inverse spectral range of Hamiltonian.

Alternatively, the full propagation can be done employing a single polynomial expansion⁶. Then very high expansion orders N are required. Chebychev polynomials provide an expansion which is stable even for very high orders. Employing Chebychev polynomials T_n of the normalized Hamiltonian

$$\hat{H}_{norm} = \frac{\hat{H} - \bar{E}}{\Delta E} \quad (34)$$

and corresponding n -th order wavefunctions $\psi_n = T_n(\hat{H}_{norm})\psi(0)$ generated by the recursion relation

$$\psi_n = 2\hat{H}_{norm}\psi_{n-1} - \psi_{n-2} , \quad (35)$$

the wavefunction $\psi(t)$ is given as

$$\psi(t) = \sum_{n=0}^N a_n(t)\psi_n . \quad (36)$$

with

$$a_n(t) = (2 - \delta_{n0})e^{-i\bar{E}t}(-i)^n J_n(\Delta Et) . \quad (37)$$

The spectrum of the normalized Hamiltonian should be in the interval $[-1, 1]$. The J_n denote the Bessel functions. The above series converges exponentially if the order N exceeds ΔEt . Thus, the number of Hamiltonian multiplies is directly connected to the spectra range of the Hamiltonian \hat{H} . Due to the very high order of the scheme, the Chebychev method can efficiently produce extremely accurate results. However, extracting information at intermediate times, e.g. the evolution of expectation values with time, is not straightforward within the Chebychev method. The wavefunction would have to be calculated for all desired times simultaneously causing a significant storage problem.

4 Iterative Diagonalization

Considering time-independent Hamiltonians, time-dependent and energy-dependent representation are equivalent. However, direct matrix diagonalization and wave packet propagation schemes employ different computational strategies to solve the Schrödinger equation. In contrast, iterative matrix diagonalization approaches are closely related to wavepacket propagation. To highlight this connection, two examples will be discussed in the following.

The Lanczos scheme is frequently used to directly compute spectra in the energy domain. The first applications to molecular spectra^{18–20} preceded the development of the integration schemes discussed above. While in the short iterative Lanczos scheme for time propagation only a low order expansion is employed, these computations use high order expansions. Since the Lanczos recursion relation is a three term series, the resulting Hamiltonian matrix is tridiagonal. This tridiagonal matrix can be diagonalized numerically efficient. As a result, the eigenvalues of H_{model} and the overlap of the eigenvalues with the initial vector ψ is obtained:

$$H_{model} \chi_j = E_{model,j} \chi_j, \quad (38)$$

$$\sigma(E) = \sum_j \delta(E_{model,j} - E) \cdot |\langle \chi_j | \psi \rangle|^2. \quad (39)$$

The envelop of the absorption spectrum $\sigma(E)$ converges with the increasing Lanczos order. However, due to the numerical instability of the Lanczos recursion at high orders, only convoluted spectra (and not individual eigenvalues) can be converged easily. Computing the spectrum via the autocorrelation function $\langle \psi | \exp(-i\hat{H}_{model}t) | \psi \rangle$, the connection between the time and energy-dependent approach becomes obvious:

$$\sigma(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \langle \psi | e^{-i\hat{H}_{model}t} | \psi \rangle e^{iEt}, \quad (40)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_j \langle \psi | \chi_j \rangle e^{-iE_{model,j}t} \langle \chi_j | \psi \rangle e^{iEt}, \quad (41)$$

$$= \sum_j \langle \psi | \chi_j \rangle \delta(E_{model,j} - E) \langle \chi_j | \psi \rangle. \quad (42)$$

Due to accumulating roundoff errors, high order Lanczos expansions are numerically unstable. In contrast, Chebychev polynomials facilitate arbitrarily accurate expansions at all orders. Thus, virtually any energy-dependent quantity can be directly expanded in Chebychev polynomials:

$$f(\hat{H})\psi = \sum_{n=0}^N c_n T_n(\hat{H})\psi. \quad (43)$$

The expansion coefficient can be obtained from the expansion coefficients $a_n(t)$ of the time propagator. For a normalized Hamiltonian they read

$$c_n = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt a_n(t) \int dE e^{iEt} f(E). \quad (44)$$

Since a Chebychev expansion of order N yields a converged description of the time-dependent wavefunction for propagation time of about $N/\Delta E$, the expansion index N

could be viewed as a transformed propagation time. In scattering problems the computation of the action of the Greens function

$$\frac{1}{E - (\hat{H} - i\epsilon)}\psi \quad (45)$$

is a central task. This Greens function includes a negative imaginary potential $-i\epsilon$. The modified Hamiltonian $\hat{H} - i\epsilon$ is not hermitian. To obtain a convergent expansion in polynomial of this non-hermitian Hamiltonian, a modified Chebychev recursion has to be used²¹.

5 Filter Diagonalization

Formally time-dependent and energy-dependent representations are equivalent. However, depending on the particular phenomenon, either the time-dependent or the energy-dependent picture can yield a more intuitive interpretation of the process. The energy-dependent description seems favorable if a small number of individual states dominates the process under investigation. Non-overlapping sharp resonances are an example where a energy-dependent picture might be preferable. In contrast, the time-dependent picture is very suitable for the description of rapid dissociation processes showing broad spectra. In many systems both situation are simultaneously present: few resonances are embedded in a moderately structured background. Then the filter diagonalization approach²²⁻²⁴ which combines time-dependent and energy-dependent descriptions yields an effective description of the system.

In the filter diagonalization approach²², a set of wavefunctions $\psi_1, \psi_2, \dots, \psi_N$ corresponding to N energies $E_n = E_0 + n \Delta E$ in the interval $[E_1, E_N]$ is obtained by wave packet propagation:

$$\psi_n = \int_{-T}^T dt e^{iE_n t} e^{-i\hat{H}t} \psi, \quad (46)$$

$$= \hat{F}(E_n)\psi. \quad (47)$$

The propagation time T should be sufficiently large to separate the the different ψ_n , i.e. $\Delta E \cdot T \geq 1$. If the energy grid is sufficiently fine, i.e. N exceeds the number of energy eigenstates in the interval $[E_1, E_N]$, the set of wavefunctions $\psi_1, \psi_2, \dots, \psi_N$ forms a complete basis for the representation of the energy eigenstates in the interval. The eigenstates and eigenvalues can be computed by representing the Hamiltonian in this basis and diagonalizing the resulting N-dimensional Hamiltonian matrix.

In the filter diagonalization approach, the required propagation time is given by the averaged density of states $\rho(E)$:

$$T \geq \frac{N}{E_N - E_1} \geq \frac{1}{E_N - E_1} \int_{E_1}^{E_N} \rho(E) . \quad (48)$$

Since the propagation is followed by an numerically exact diagonalization of the Hamiltonian matrix $\langle \psi_j | \hat{H} | \psi_n \rangle$, accurate energy eigenvalue are obtained. The energy resolution is not limited by the propagation time. In a simple wave packet propagation scheme, the energy resolution would have been Fourier limited to $1/T$. In contrast to a full diagonalization of the Hamiltonian, the filter diagonalization approach reduces the size of the problem

by limiting the representation to a small energy window. The projection into this window is obtained from a wave packet propagation for a limited time T .

The filter diagonalization approach can also directly address the autocorrelation function^{23,24}. Then the explicit construction of the wavefunctions ψ_n can be avoided and the memory requirements are reduced. Also other choices for the filter operators $\hat{F}(E_n)$ are possible. The only principal requirement for $\hat{F}(E_n)$ is to project on states with an energy E_n if N goes to infinity.

6 MCTDH

The wave packet propagation schemes described above employ multi-dimensional time-independent grids or basis sets to represent the wavefunction. The numerical effort of these schemes increases exponentially with the number of degrees of freedom. Given the computational resources presently available, only systems with up to four atoms can be treated accurately. The extension of numerically exact calculations towards larger systems therefore requires other schemes for the solution of the Schrödinger equation. The multi-configurational time-dependent Hartree (MCTDH) approach^{9,10} utilizes optimized time-dependent expansion functions to represent the wavefunction. The numerical effort of the MCTDH approach scales exponentially with the number of degrees of freedom but the effort increases less dramatically with dimensionality than in standard wave packet propagation schemes. Thus, the MCTDH approach facilitates the description of systems with are beyond the range of conventional wave packet propagation. Recent applications include a 24-dimensional calculation on the absorption spectrum of pyrazine^{11,12} and a 12-dimensional investigation of the $H + CH_4 \rightarrow H_2 + CH_4$ reaction^{14,15}.

In the multi-configurational time-dependent Hartree (MCTDH) approach^{9,10}, the wavefunction $\psi(x_1, \dots, x_f, t)$ is represented as

$$\psi(x_1, \dots, x_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \cdot \phi_{j_1}^{(1)}(x_1, t) \cdot \dots \cdot \phi_{j_f}^{(f)}(x_f, t), \quad (49)$$

The $A_{j_1 \dots j_f}(t)$ are time-dependent expansion coefficients. The time-dependent expansion functions $\phi_{j_\kappa}^{(\kappa)}(x_\kappa, t)$ are called single-particle functions. Standard DVR or FFT-schemes can be used to represent these single-particle functions:

$$\phi_{j_\kappa}^{(\kappa)}(x_\kappa, t) = \sum_{l=1}^{N_\kappa} c_{j_\kappa l}^{(\kappa)}(t) \cdot \chi_l(x_\kappa), \quad (50)$$

where the χ_l denote the time-independent basis functions (or grid points) employed in the DVR or FFT scheme. Based on the above ansatz, equations of motion can be derived from the Dirac-Frenkel variational principle^{9,10}. Analogous to standard wave packet propagation, the expansion coefficients A are propagated by the Hamiltonian represented in the basis employed (which here is time-dependent):

$$i \frac{\partial}{\partial t} A_{l_1 \dots l_f}(t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} \langle \phi_{l_1}^{(1)} \dots \phi_{l_f}^{(f)} | \hat{H} | \phi_{j_1}^{(1)} \dots \phi_{j_f}^{(f)} \rangle \cdot A_{j_1 \dots j_f}(t). \quad (51)$$

The differential equations for the single-particle functions ϕ are more involved:

$$i \frac{\partial}{\partial t} \phi_n^{(\kappa)}(x_\kappa, t) = (1 - \hat{P}_\kappa) \sum_m \rho_{nm}^{(\kappa)-1} \sum_j \langle \psi_m^{(\kappa)} | \hat{H} | \psi_j^{(\kappa)} \rangle \phi_j^{(\kappa)}. \quad (52)$$

The above equations include a projection operator on the space spanned by the single-particle functions,

$$\hat{P}_\kappa = \sum_j |\phi_j^{(\kappa)} \rangle \langle \phi_j^{(\kappa)}|, \quad (53)$$

the matrix of mean-field operators acting only on the coordinate x_κ ,

$$\langle \psi_m^{(\kappa)} | \hat{H} | \psi_j^{(\kappa)} \rangle, \quad (54)$$

which employs the the single-hole functions

$$\begin{aligned} \psi_j^{(\kappa)}(x_1, \dots, x_{\kappa-1}, x_{\kappa+1}, \dots, x_f) &= \sum_{j_1} \dots \sum_{j_{\kappa-1}} \sum_{j_{\kappa+1}} \dots \sum_{j_f} A_{j_1 \dots j_{\kappa-1} j_{\kappa+1} \dots j_f}(t) \cdot \\ &\cdot \phi_{j_1}^{(1)}(x_1, t) \cdot \dots \cdot \phi_{j_{\kappa-1}}^{(\kappa-1)}(x_{\kappa-1}, t) \cdot \phi_{j_{\kappa+1}}^{(\kappa+1)}(x_{\kappa+1}, t) \cdot \dots \cdot \phi_{j_f}^{(f)}(x_f, t), \end{aligned} \quad (55)$$

and the inverse of the single-particle density matrix $\rho_{ij}^{(\kappa)}$,

$$\rho_{ij}^{(\kappa)} = \langle \psi_i^{(\kappa)} | \psi_j^{(\kappa)} \rangle. \quad (56)$$

The MCTDH-representation (49) of the wavefunction should be compared to the representation of the wavefunction employed in a standard wave packet scheme:

$$\psi(x_1, \dots, x_f, t) = \sum_{l_1=1}^{N_1} \dots \sum_{l_f=1}^{N_f} \tilde{A}_{l_1 \dots l_f}(t) \cdot \chi_{l_1}^{(1)}(x_1) \cdot \dots \cdot \chi_{l_f}^{(f)}(x_f). \quad (57)$$

The standard scheme expands the wavefunction in a time-independent basis while the MCTDH-approach employs an optimized set of time-dependent expansion functions. Thus, n , the number of single-particle functions required, can be much smaller than N , the number of underlying time-independent basis functions. Assuming equal basis set sizes in all f degrees of freedom, the numerical effort of a standard wavepacket propagation is approximately proportional to N^{f+1} . In the MCTDH-approach, there are two different contributions to the numerical effort which scale differently with dimensionality. The numerical effort resulting from the A-coefficients is proportional to n^{f+1} while the effort resulting from the representation of the single-particle function approximately equals $f \cdot n \cdot N^2$. For larger systems, the n^{f+1} component dominates. Thus, the numerical effort of the standard wave packet propagation as well as the effort of the MCTDH scheme scales exponentially with the number of degrees of freedom. However, for multi-dimensional problems, the MCTDH is more efficient than the standard wavepacket propagation since n can be considerably smaller than N . Typically N values are of the order of 10^2 while n is often smaller than 10.

In contrast to standard wave packet propagation, the differential equations (51,52) describing the propagation of the MCTDH wavefunction are nonlinear. Thus, the integration schemes discussed in Sect.3 are not directly applicable. However, instead of resorting to

general purpose integrator, an efficient integration scheme developed particularly for integrating the MCTDH equations^{26,27} can be used. This scheme views eq.(51) as set a linear differential equations with a time-dependent Hamiltonian matrix and employs a short iterative Lanczos scheme to integrate these equations.

A difficulty in the MCTDH approach is the evaluation of the potential energy matrix elements

$$\left\langle \phi_{l_1}^{(1)} \cdots \phi_{l_f}^{(f)} \left| V \right| \phi_{j_1}^{(1)} \cdots \phi_{j_f}^{(f)} \right\rangle . \quad (58)$$

The direct integration of these matrix elements using the DVR or FFT grid employed for the representation of the single-particle functions ϕ is prohibitive, since it would require a multi-dimensional grid of the size N^f . The problem can be avoided if the potential can be specified as a sum of products of one-dimensional functions¹⁰

$$V(x_1, x_2, \dots, x_f) = \sum_{j=1}^J c_j \cdot v_j^{(1)}(x_1) \cdot v_j^{(2)}(x_2) \cdots v_j^{(f)}(x_f) . \quad (59)$$

Then the above multi-dimensional integral can be decomposed into one-dimensional components

$$\begin{aligned} & \left\langle \phi_{l_1}^{(1)} \cdots \phi_{l_f}^{(f)} \left| V \right| \phi_{j_1}^{(1)} \cdots \phi_{j_f}^{(f)} \right\rangle = \\ & \sum_{j=1}^J c_j \left\langle \phi_{l_1}^{(1)} \left| v_j^{(1)} \right| \phi_{j_1}^{(1)} \right\rangle \cdots \left\langle \phi_{l_f}^{(f)} \left| v_j^{(f)} \right| \phi_{j_f}^{(f)} \right\rangle . \end{aligned} \quad (60)$$

However, for many potentials this decomposition can not be achieved with a reasonable number of terms J .

Alternatively, the problem can be resolved by employing the correlation DVR (CDVR) approach²⁵ to evaluate the above integrals. The CDVR scheme employs time-dependent grids obtained by diagonalizing the coordinate matrix represented in the basis of the time-dependent single-particle functions

$$\langle \phi_n^{(\kappa)} | x_\kappa | \phi_m^{(\kappa)} \rangle = \sum_{l=1}^{n_\kappa} \langle \phi_n^{(\kappa)} | X_l^{(\kappa)} \rangle X_l^{(\kappa)} \langle X_l^{(\kappa)} | \phi_m^{(\kappa)} \rangle . \quad (61)$$

However, these grids can not be used for the quadrature of the potential integrals without an essential modification. In the MCTDH-approach, the coefficients $A_{j_1 \dots j_f}(t)$ describe mainly the correlation between the different degrees of freedom, while the motion of the time-dependent basis functions $\phi_{j_\kappa}^{(\kappa)}(x_\kappa, t)$ accounts for the separable dynamics. Thus, the size of the time-dependent basis depends only on the amount of correlation, it is independent of any separable dynamics. The time-dependent basis is small compared with the size of the underlying primitive grid. Due to the small size of the time-dependent basis, a quadrature based on this basis can properly describe only those parts of the potential which only result in correlations. The number of time dependent grid points $X_j^{(\kappa)}(t)$ is too small to also result in an accurate evaluation of the separable parts of the potential. This problems can be solved by explicitly accounting for separable parts of the potential in the quadrature²⁵.

As noted above, the numerical effort of the MCTDH approach scales exponentially with the dimensionality. Employing directly the ansatz (49), MCTDH calculations are limited to 10-20 degrees of freedom. Even if only two single-particle function per degree of freedom are used, $2^{20} \approx 10^6$ A-coefficients would be required in a 20-dimensional calculation. To overcome this limitation, several physical coordinates have to be grouped together and treated as a single logical coordinate (“mode combination”)^{11,27}. If the coordinates $\{x_1, \dots, x_f\}$ are grouped as

$$\{(x_1, x_2, \dots, x_{p_1}), (x_{p_1+1}, \dots, x_{p_2}), \dots, (x_{p_{F-1}+1}, \dots, x_f)\} \quad (62)$$

the corresponding MCTDH wavefunction reads

$$\begin{aligned} \psi(x_1, \dots, x_f, t) = & \sum_{j_1=1}^{n_1} \dots \sum_{j_F=1}^{n_F} A_{j_1 \dots j_F}(t) \cdot \phi_{j_1}^{(1)}(x_1, x_2, \dots, x_{p_1}, t) \cdot \phi_{j_2}^{(2)}(x_{p_1+1}, \dots, x_{p_2}, t) \\ & \dots \cdot \phi_{j_F}^{(F)}(x_{p_{F-1}+1}, \dots, x_f, t) . \end{aligned} \quad (63)$$

Employing this scheme, converged 24-dimensional MCTDH wave packet calculations on the $S_0 \rightarrow S_2$ excitation in pyrazine^{11,12} and up to 80-dimensional calculations on the spin-boson model¹³ have been reported. However, this mode combination approach presently can not be combined with the CDVR scheme for potential evaluation. Thus, these calculations can only study wave packet motion on potential energy surfaces which can be represented in the form analogous to eq.(59).

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