COMMUNICATIONS TO THE EDITOR

Discrete-time Quantum Dynamics for Non-perturbative Study of Matter-Light Interactions

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In this communication, we propose a new non-perturbative method for the study of interactions of arbitrarily strong radiations with matters. The method will be addressed to the problem of converting operator differential equations (Heisenberg equations of motions) into a set of finite-difference operator equations which exactly preserve the equal time commutation relation $[q(t_n), p(t_n)] = i\hbar$ at each time step. The expectation values of operators can be obtained at each time step by solving the difference equations iteratively. The method provides an alternative approach for the numerical study of quantum dynamics of time-dependent Hamiltonian systems.

For time-independent hamiltonians, the operator difference equations have been studied by Bender,[1] *et al.*, and Moncrief.[2] When the Hamiltonian depends on time explicitly, however, the solution of problem is not straightforward.

We consider the one dimensional system driven by time dependent force $-f(t)$. The Hamiltonian takes the form

$$H = H_o(q, p) + qf(t) \tag{1}$$

where $H_o(q,p) = p^2/2m + V_o(q)$, the time independent part. The time evolution of observables can be obtained by solving Heisenberg equations of motion.

$$i\hbar\dot{q} = [q, H],\ i\hbar\dot{p} = [p, H]. \tag{2}$$

Equivalently, the evolution should be expressed in terms of unitary operator

$$\begin{aligned} \dot{q}(t) &= U^+(t, t_0)\, q(t_0)\, U(t, t_0) \\ p(t) &= U^+(t, t_0)\, p(t_0)\, U(t, t_0). \end{aligned} \tag{3}$$

In general, the unitary operator $U(t, t_o)$ contains all the information of the system, although it is difficult to express it in a closed form. For small time displacement, however, *i.e.*, $t = t_o + \epsilon$, ϵ is small, one can look for a tractable form of $U(t_o+\epsilon, t_o)$. The unitarity of $U(t_o+\epsilon, t_o)$ is essential for the equal time commutation relations.

In order to examine the $U(t_o+\epsilon, t_o)$, it is convenient to work in the interaction picture. The unitary operator in the interaction picture $U_I(t_o+\epsilon, t_o)$ is defined by

$$\begin{aligned} U_I(t_0+\epsilon, t_0) = \exp\left[\frac{i(t_0+\epsilon)}{\hbar}\right] H_0(t_0+\epsilon, t_0) \\ \exp\left[\frac{-it_0}{\hbar} H_0(t_0)\right]. \end{aligned} \tag{4}$$

The $U_I(t_o+\epsilon, t_o)$ should be obtained by solving certain evolution equation whose solution is expressed formally in terms of time ordered products,

$$\begin{aligned} U_I(t_0+\epsilon, t_0) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i}{n}\right)^n \int_0^\epsilon d\tau_1 \cdots \\ \int_0^\epsilon d\tau_n T_D[V_I(t_0+\tau_1) \cdots V_I(t_0+\tau_n)] \end{aligned} \tag{5}$$

where

$$\begin{aligned} V_I(t_0+\tau_n) = \exp\left[\frac{i(t_0+\tau_n)}{\hbar} H_0(t_0)\right] q(t_0) f(t_0+\tau_n) \\ \exp\left[\frac{-i(t_0+\tau_n)}{\hbar} H_0(t_0)\right]. \end{aligned} \tag{6}$$

and T_D stands for Dyson time-ordered product which means operators in the bracket after T_D rearranged so that time decreases from left to right. The use of (5) for the (3) gives a set of exact evolution equations of q and p, at least formally. However, they constitute infinite series with increasing powers of ϵ. In a practical sense, one can cut off higher order terms of the series taking first three, four, or even more terms. Then one sees that the q and p do not satisfy the commutation relation due to the absence of higher order terms. Alternatively, one can look for an approximate form of (5) which gives approximate evolution equations of q and p while they are closed and the commutation relation should be preserved exactly, not approximately, during the time evolution. Here we propose an approximate form of $U_I(t_o+\epsilon, t_o)$

$$U_I(t_0+\epsilon, t_0) = \exp\left[\frac{-i}{\hbar} \int_0^\epsilon V_I(t_0+r)\, dr\right] \tag{7}$$

Table 1. Convergence of Energy Expectation Values at $t = 1000$ a.u..

	A = 0.1			A = 1.0		
	$\epsilon = 0.05$	$\epsilon = 0.025$	$\epsilon = 0.0125$	$\epsilon = 0.05$	$\epsilon = 0.025$	$\epsilon = 0.0125$
N = 8	1.193569	1.183913	1.181416	1.483652	1.228425	1.167532
N = 12	1.193459	1.183843	1.181356	1.429381	1.134994	1.066114
N = 16	–	–	–	1.429351	1.134959	1.066084
N = 32	–	–	–	1.429351	1.134959	1.066084

and employ the approximation which has been introduced by Moncrief,[2]

$$\exp\left(\frac{-i\epsilon}{\hbar}H_0\right) = \exp\left(\frac{-i\epsilon}{\hbar}\frac{V_0(q)}{2}\right)\exp\left(\frac{-i\epsilon}{\hbar}\frac{p^2}{2m}\right)\exp\left(\frac{-i\epsilon}{\hbar}\frac{V_0(q)}{2}\right) \tag{8}$$

It can be shown that the approximations (7) and (8) converge to exact results in the limit in which the time-step size tends to zero. Moreover, they are indistinguishable from exact expressions up to $O(\epsilon^2)$ when they are expanded around $\epsilon = 0$. After some rearrangements of (4), (6), (7) and (8), the unitary operator $U(t, t_0)$ for a small time step is written by

$$U(t_0+\epsilon, t_0) = U_0(t_0+\epsilon, t_0)\exp\left\{\frac{-i}{\hbar}\left[f_0 q + \frac{f_1}{m}p + \frac{1}{2m}f_2 F_0(q)\right]\right\} \tag{9}$$

where

$$f_0 = \int_0^\epsilon f(t_0+\tau)\,d\tau \tag{10a}$$

$$f_1 = \int_0^\epsilon \tau f(t_0+\tau)\,d\tau \tag{10b}$$

$$f_2 = \int_0^\epsilon \tau^2 f(t_0+\tau)\,d\tau \tag{10c}$$

$$F_0(q) = -\frac{d}{dq}V_0(q) \tag{10d}$$

and the operators q and p are the values measured at t_0. The unitary operator, (9), yields a set of finite-difference evolution equations which constitute the recurrence relations for quantum operators, q and p, at time step $t_0+\epsilon$ in terms of those at time step t_0 preserving the commutation relation.

$$q(t_0+\epsilon) = q(t_0) + \frac{\epsilon}{m}p(t_0) + \frac{\epsilon^2}{2m}F_0[q(t_0)] + \frac{f_1}{m} - \frac{\epsilon}{m}\Pi(t_0) \tag{11a}$$

$$p(t_0+\epsilon) = p(t_0) + \frac{\epsilon}{2}\{F_0[q(t_0)] + F_0[q(t_0+\epsilon)]\} - \Pi(t_0) \tag{11b}$$

where

$$\Pi(t_0) = f_0 + \frac{1}{2}\left(\frac{f_2}{f_1} - \epsilon\right)\left\{F_0[q(t_0)] + \frac{f_1}{m}\right] - F_0[q(t_0)]\} \tag{12a}$$

$$\doteq f_0 + \frac{1}{2m}(f_2 - \epsilon f_1)\frac{d}{dq}F_0[(t_0)] \tag{12b}$$

Since the unitarity and the infinitesimal of time step are only requirements for obtaining the finite difference equations, there is no restrictions on the strength of external time-dependent force.

In order to apply the present method to a particular problem, it is essential to examine the error accumulations of iterations due to the finite size of time step and the numerical instabilities due to the truncations of basis vectors which represent quantum operators. These questions have been studied for the time-independent Hamiltonian system.[2] They are highly nontrivial for the time dependent case. A simple minded way to examine them is to resort to numerical experiments. One sees that numerical errors are more serious when the time-dependent forces are strong.

As an illustration, the time evolution of an electron captured in the 1-dimensional quartic potential, $(1/4)q^4$, and driven by the oscillating electric field, $A\cos\omega t$, that is switched on at t=0, will be calculated. All the physical quantities in this illustration are in atomic units. The recurrence relations for the quantum operators at time step $n+1$ in terms of those at time step n are

$$q_{n+1} = q_n + \epsilon p_n + \frac{1}{2}\epsilon^2 q_n^3 + \frac{3}{2}\epsilon(f_{2n} - \epsilon f_{1n})q_n^2 + f_{1n} - \epsilon f_{0n} \tag{13a}$$

$$p_{n+1} = p_n + \frac{1}{2}\epsilon(q_n^3 + q_{n+1}^3) + \frac{3}{2}(f_{2n} - \epsilon f_{1n})q_n^2 - f_{0n} \tag{13b}$$

with

$$f_{0n} = -\frac{A}{\omega}[\sin(n+1)\omega\epsilon - \sin n\omega\epsilon] \tag{14a}$$

$$f_{1n} = -\frac{A}{\omega^2}[\omega\epsilon\sin(n+1)\omega\epsilon + \cos(n+1)\omega\epsilon - \cos n\omega\epsilon] \tag{14b}$$

$$f_{2n} = -\frac{A}{\omega^3}[(\omega\epsilon)^2\sin(n+1)\omega\epsilon + 2\omega\epsilon\cos(n+1)\omega\epsilon - 2\sin(n+1)\omega\epsilon + 2\sin n\omega\epsilon] \tag{14c}$$

For the representation of operators, the N-truncated eigen vectors of unperturbed Hamiltonian are used as the baisis. Then, the expectation values of q and p at each time step are calculated by iterating $N \times N$ matrix arithmetics. At the nth time step, the energy expectation value of electron which is initially in the ground state is given by

$$\langle 0|H_{0n}|0\rangle = \frac{1}{2}\sum_{k=0}^{N-1}\langle 0|p_n|k\rangle\langle k|p_n|0\rangle + \frac{1}{4}\sum_{k=0}^{N-1}\sum_{l=0}^{N-1}\sum_{m=0}^{N-1}\langle 0|q_n|k\rangle\langle k|q_n|l\rangle\langle l|q_n|m\rangle\langle m|q_n|0\rangle \tag{15}$$

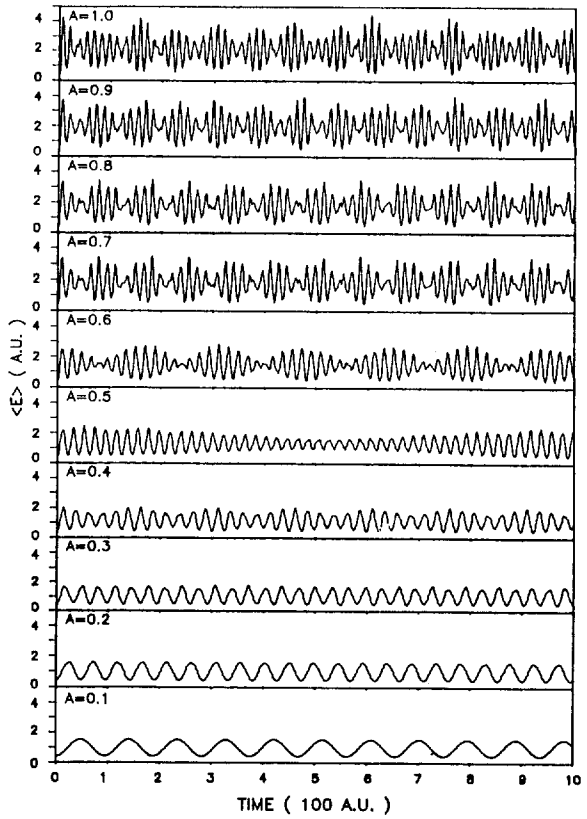

Figure 1. Energy expectation values *vs.* time.

The $\omega = 1.0871$ is taken, that is the resonance frequency of (0–1) transition of quartic oscillator. To see the effect of field strength on the energy absorption, ten cases of A values ringing from 0.1 to 1.0 are studied.

The convergence of calculations as a function of ϵ and N should be studied for A–1.0 which is the most serious case in this illustrative example as shown in Table 1. Taking $N = 8$, one sees that for $\epsilon = 0.05$, at least one significant figure; for $\epsilon = 0.025$, two significant figures are stable by comparing to the results for $\epsilon = 0.0125$ unit $t = 1000$. Next, keeping $\epsilon = 0.05$, and increasing the matrix size by $N = 16,32$ and so on, the infinite N–limit is studied. For $N = 16$, there are no appreciable truncation errors in the results. Finally, taking the values of $\epsilon = 0.025$ and $N = 16$, one confirms that two significant figures are accurate in the calculation when $t \leq 1000$.

In Figure 1, the numerical results for energy expectation values are displayed. For the cases of weak radiations, *i.e.*, $A = 0.1$ and 0.2, energy absorptions show two-state Rabi oscillation of (0–1) transition with frequency $\omega_R = 0.674A$. When the intensity of radiation is increased, the simple oscillatory behavior disappears but multiple modes of oscillations are intermixed because of the contributions of non-resonant multiphoton transitions.

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Convenient Method for the Preparation of Precursors of Tandem Cope–Claisen Rearrangement

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Germacrane sesquiterpenes are of interest not only because of their important role as biogenetic and synthetic precursors to a variety of sesquiterpene lactones but also because of their anti-tumor, cytotoxic, anti-microbial and phytotoxic activity.[1] However, the efforts culminating in the total synthesis[2] of germacrane have been relatively few in number despite the biological importance of the germacrane sesquiterpene lactones. This fact reflects the substantial difficulties in constructing a 10-membered ring with the control of stereochemistry.

We[3] recently reported that the first successful application of the tandem Cope-Claisen rearrangement[4] strategy for the total synthesis of the germacrane sesquiterpene (+)-dihydrocostunolide (**1**). Our investigations to extend the application of this strategy for the synthesis of various germacranolides have necessitated a convenient procedure for the preparation of the requisite precursors **2** and **3**. Since the stereochemical difference between the precursors might be crucial for the success of the tandem Cope-Claisen rearrangement and/or subsequent transformations, our efforts have been focused on the synthesis of each precursor which is completely free of other stereoisomers.

We now wish to report an useful method for the preparation of the precursors **2** and **3**.