PRAMANA
— journal of
physics

Vol. 62, No. 4
April 2004
pp. L983–L991

A time-dependent Fourier grid Hamiltonian-based formulation of time-dependent multi-configuration Hartree method

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MS received 8 September 2003; revised 16 January 2004; accepted 17 January 2004

Abstract. We propose a variant of the time-dependent multi-configuration Hartree method within the framework of Fourier grid Hamiltonian method. The workability of the method proposed is demonstrated with a well-known coupled two-mode problem.

Keywords. Quantum dynamics; time-dependent Fourier grid Hamiltonian; multi-configuration time-dependent Hartree method; relaxation dynamics.

PACS No. 33.80

1. Introduction

A large number of time-dependent quantum mechanical methods are currently available in literature for handling a wide variety of dynamical problems [1,2]. One of these methods is the time-dependent Fourier grid Hamiltonian (TDFGH) method which evolved naturally as the time-dependent generalization [3,4] of the time-independent one-dimensional Fourier grid Hamiltonian (FGH) method developed by Marston and Balint-Kurti [5,6]. The multi-dimensional variant of FGH, both in the time-dependent and time independent moulds were subsequently developed and used in a wide variety of problems [7–9]. Very recently, the scope of its applicability was further enhanced to cover the dynamics on coupled potential energy surfaces [10].

For quite sometime, we have been trying to generalize our TDFGH recipe further to include the time-dependent multi-configuration Hartree (TDMCH) method in its framework. The most popular version of the TDMCH methods has been due to Mayer *et al* [11,12]. A TDMCH with built-in multilayered time-dependence has also been proposed very recently [13]. We demonstrate, in what follows, that TDFGH method can handle the multi-configuration Hartree problem quite easily and elegantly and has some advantages over other realizations of TDMCH.

2. The method

Let us consider a coupled two-dimensional system represented by the Hamiltonian H where

$$\begin{aligned} H &= -\frac{1}{2}\nabla_x^2 + V(x) - \frac{1}{2}\nabla_y^2 + V(y) + \lambda V(x,y) \\ &= H_x^0 + H_y^0 + \lambda V(x,y). \end{aligned} \tag{1}$$

The eigenstates of H_x^0 and H_y^0 are supposed to be known through separate FGH calculations:

$$\begin{aligned} H_x|\phi_i(x)\rangle &= \epsilon_{ix}|\phi_i(x)\rangle, \\ H_y|\chi_j(y)\rangle &= \epsilon_{jy}|\chi_j(y)\rangle. \end{aligned} \tag{2}$$

In the FGH method, the eigenfunctions are represented on uniformly discretized coordinate grids $x_i = i\Delta x$, $y_j = j\Delta y$ as follows [5,6]:

$$\begin{aligned} |\phi_i(x)\rangle &= \sum_{p=1}^{n_x} w_{pi}^x |x_p\rangle \Delta x, \\ |\chi_j(y)\rangle &= \sum_{q=1}^{n_y} w_{qj}^y |y_p\rangle \Delta y. \end{aligned} \tag{3}$$

The orthonormality conditions on the grids are

$$\begin{aligned} \langle x_p|x_r\rangle \Delta x &= \delta_{pr}, \\ \langle y_q|y_s\rangle \Delta y &= \delta_{qs}, \end{aligned} \tag{4}$$

and the grid-point amplitudes (w_{pi}^x, w_{qj}^y) are obtained variationally. In a time-dependent problem, the grid-point amplitudes are implicit functions of time and that imparts great flexibility to the single-particle basis.

The time-dependent Schrödinger equation for $|\Psi\rangle$ is

$$i\hbar \frac{\partial|\Psi(x,y)\rangle}{\partial t} = \hat{H}|\Psi(x,y)\rangle. \tag{5}$$

In the multiconfiguration time-dependent Hartree method in a time-dependent Fourier grid Hamiltonian framework, the general form of $|\Psi(x,y)\rangle$ is $\Psi(x,y,t)\rangle = \sum_{ij} C_{ij}(t)|\phi_i(x,t)\chi_j(y,t)\rangle \equiv \sum_{ij} C_{ij}(t) \sum_{p=1}^{n_x}\sum_{q=1}^{n_y} w_{pi}^x(t) w_{qj}^y(t)|x_p y_q\rangle \Delta x \Delta y$ and the most general form of variation allowed is

$$\begin{aligned} |\delta\Psi(x,y,t)\rangle = \sum_{ij} [&\delta C_{ij}(t)|\phi_i(x,t)\chi_j(y,t)\rangle \\ &+ C_{ij}(t)\left[|\delta\phi_i(x,t)\chi_j(y,t)\rangle + |\phi_i(x,t)\delta\chi_j(y,t)\rangle\right]], \end{aligned} \tag{6}$$

where $|\delta\phi_i(x,t)\rangle = \sum_{p=1}^{n_x} \delta w_{pi}^x(t)|x_p\rangle\Delta x$ and $|\delta\chi_j(y,t)\rangle = \sum_{q=1}^{n_y} \delta w_{qj}^y(t)|y_q\rangle\Delta y$. That means, we now have two types of variational parameters – the configuration interaction coefficients (C_{ij}s) and the grid-point amplitudes (w_{pi}^xs, w_{qj}^ys). The

advantages of introducing the FGH formulation in developing MCTDH are two-fold. First, the single-particle basis now becomes completely and comprehensively time-dependent through the time-dependence of the grid-point amplitudes so that a small number of configurations could represent the dynamics of evolution accurately and effectively. The evolution of w^x_{pi}s or w^y_{qj}s, are coupled with evolution of C_{ij}s, and the overall changes in wave function during evolution are partly due to changes in the configuration mixing coefficients and partly due to the changes in the grid-point amplitudes. In other realizations of MCTDH, one relies heavily on the configuration mixing coefficients for introducing major changes in the wave function and only minor changes are allowed in the single-particle basis. Most often, the single-particle basis functions are expanded in a harmonic oscillator basis and the linear expansion coefficients are allowed to vary, thereby making the single-particle basis time-dependent. This is in sharp contrast to our recipe. Secondly, though the grid-point amplitudes in the present realization vary for all the single-particle basis functions, even the kinetic energy operators are to be constructed only once for each mode (in the coordinate basis) through the analytical fast Fourier transform of the FGH method while time displacement, in case of time-dependent potentials needs to be effected only for the diagonal terms of V, V being a diagonal matrix in the coordinate representation used in the FGH formulation.

The Dirac–Frenkel time-dependent variational principle can now be invoked to demand that

$$\langle \delta\Psi(x,y,t)|H - i\frac{\partial}{\partial t}|\Psi(x,y,t)\rangle = 0, \tag{7}$$

for arbitrary variation $|\delta\Psi\rangle$, subject to auxilary conditions

$$\begin{aligned}
&\langle \phi_i(x,t)|\phi_j(x,t)\rangle = \delta_{ij},\\
&\langle \chi_k(y,t)|\chi_l(y,t)\rangle = \delta_{kl},\\
&\langle \phi_i(x,t)|\dot{\phi}_j(x,t)\rangle = 0,\\
&\langle \chi_k(y,t)|\dot{\chi}_l(y,t)\rangle = 0,
\end{aligned} \tag{8}$$

for all times. In order to make the subsequent manipulations transparent we restrict the expansion in (6) to the minimal set of configurations so that we have a four-configuration wave function

$$\begin{aligned}
|\Psi(x,y,t)\rangle = {} & C_{00}|\phi_0(x,t)\chi_0(y,t)\rangle + C_{01}|\phi_0(x,t)\chi_1(y,t)\rangle\\
& + C_{10}|\phi_1(x,t)\chi_0(y,t)\rangle + C_{11}|\phi_1(x,t)\chi_1(y,t)\rangle.
\end{aligned} \tag{9}$$

In this four-dimensional subspace,

$$\begin{aligned}
|\delta\Psi\rangle = {} & (|C_{00}\chi_0\rangle + |C_{01}\chi_1\rangle)|\delta\phi_0\rangle + (|C_{10}\chi_0\rangle + |C_{11}\chi_1\rangle)|\delta\phi_1\rangle\\
& + (|C_{00}\phi_0\rangle + |C_{10}\phi_1\rangle)|\delta\chi_0\rangle + (|C_{01}\phi_0\rangle + |C_{11}\phi_1\rangle)|\delta\chi_1\rangle\\
& + \sum_{ij}\delta C_{ij}|\phi_i\chi_j\rangle.
\end{aligned} \tag{10}$$

Using eqs (6) and (10) in eq. (7) and invoking the arbitrariness and independence of variations δC_{ij}, $\delta\phi_i$ and $\delta\chi_j$, we have the following sets of equations for describing

the evolution of the expansion coefficients $(C_{ij}(t))$, and the single-particle basis functions (ϕ_0, ϕ_1) and (χ_0, χ_1):

$$\langle \phi_i(x,t)\chi_j(y,t)|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0, \;\; i = 0,1; \; j = 0,1, \tag{11}$$

$$\langle C_{00}\chi_0 + C_{10}\chi_1|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0, \tag{12a}$$

$$\langle C_{01}\chi_0 + C_{11}\chi_1|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0, \tag{12b}$$

$$\langle C_{00}\phi_0 + C_{01}\phi_1|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0, \tag{12c}$$

$$\langle C_{10}\phi_0 + C_{11}\phi_1|H - i\frac{\partial}{\partial t}|\Psi\rangle = 0. \tag{12d}$$

We now impose the orthonormality conditions summarized in eqs (8) on each of the equations in (11) and (12). From eq. (11), this leads to the evolution equations for the expansion coefficients

$$i\dot{C}_{ij}(t) = \sum_{kl}\langle \phi_i\chi_j|H|\phi_k\phi_l\rangle C_{kl}(t) \quad \text{for all } i,j. \tag{13}$$

These equations can be integrated, once $C_{kl}(0)$ are specified. The construction of H matrix is very simple in the FGH mode so that equations in (13) can be integrated easily, even if H has explicit time-dependence. From (12a) and (12b), on the other hand, we get

$$C^\star_{00}\langle\chi_0|H|\Psi\rangle + C^\star_{10}\langle\chi_1|H|\Psi\rangle - i\{C^\star_{00}\langle\chi_0|\dot{\Psi}\rangle + C^\star_{10}\langle\chi_1|\dot{\Psi}\rangle\} = 0$$

and

$$C^\star_{01}\langle\chi_0|H|\Psi\rangle + C^\star_{11}\langle\chi_1|H|\Psi\rangle - i\{C^\star_{01}\langle\chi_0|\dot{\Psi}\rangle + C^\star_{11}\langle\chi_1|\dot{\Psi}\rangle\} = 0, \tag{14}$$

while eqs (12c) and (12d) yield

$$C^\star_{00}\langle\phi_0|H|\Psi\rangle + C^\star_{01}\langle\phi_1|H|\Psi\rangle - i\{C^\star_{00}\langle\phi_0|\dot{\Psi}\rangle + C^\star_{01}\langle\phi_1|\dot{\Psi}\rangle\} = 0$$

and

$$C^\star_{10}\langle\phi_0|H|\Psi\rangle + C^\star_{11}\langle\phi_1|H|\Psi\rangle - i\{C^\star_{10}\langle\phi_0|\dot{\Psi}\rangle + C^\star_{11}\langle\phi_1|\dot{\Psi}\rangle\} = 0. \tag{15}$$

The orthonormality conditions can now be brought in to simplify the preceding four equations in (14) and (15). Thus,

$$\begin{aligned} C^\star_{00}\langle\chi_0|\dot{\Psi}\rangle + C^\star_{10}\langle\chi_1|\dot{\Psi}\rangle &= C^\star_{00}\{C_{00}\langle\chi_0|\chi_0\rangle|\dot{\phi}_0\rangle \\ &\quad + c_{10}\langle\chi_0|\chi_0\rangle|\dot{\phi_1}\rangle \;\; + \dot{C}_{00}|\phi_0\rangle + \dot{C}_{10}|\phi_1\rangle\} \\ &\quad + C^\star_{10}\{C_{01}\{\langle\chi_1|\chi_1\rangle|\dot{\phi}_0\rangle + C_{11}\langle\chi_1|\chi_1\rangle|\dot{\phi}_1\rangle \\ &\quad + \dot{C}_{01}|\phi_0\rangle + \dot{C}_{11}|\phi_1\rangle\} \\ &= (C^\star_{00}C_{00} + C^\star_{10}C_{01})|\dot{\phi}_0\rangle + (C^\star_{00}C_{10} + C^\star_{10}C_{11})|\dot{\phi}_1\rangle \\ &\quad + (C^\star_{00}\dot{C}_{00} + C^\star_{10}\dot{C}_{01})|\phi_0\rangle + (C^\star_{00}\dot{C}_{10} + C^\star_{10}\dot{C}_{11})|\phi_1\rangle \end{aligned} \tag{16}$$

and

$$\begin{aligned} C^{\star}_{01}\langle\chi_0|\dot{\Psi}\rangle + C^{\star}_{11}\langle\chi_1|\dot{\Psi}\rangle &= C^{\star}_{01}\{C_{00}\langle\chi_0|\chi_0\rangle|\dot{\phi_0}\rangle + c_{10}\langle\chi_0|\chi_0\rangle|\dot{\phi_1}\rangle \\ &\quad +\dot{C_{00}}|\phi_0\rangle + \dot{C_{10}}|\phi_1\rangle\} \\ &\quad +C^{\star}_{11}\{C_{01}\{\langle\chi_1|\chi_1\rangle|\dot{\phi_0}\rangle + C_{11}\langle\chi_1|\chi_1\rangle|\dot{\phi_1}\rangle \\ &\quad +\dot{C}_{01}|\phi_0\rangle + \dot{C}_{11}|\phi_1\rangle\} \\ &= (C^{\star}_{01}C_{00} + C^{\star}_{11}C_{00})|\dot{\phi_0}\rangle + (C^{\star}_{01}C_{10} + C^{\star}_{11}C_{11})|\dot{\phi_1}\rangle \\ &\quad +(C^{\star}_{01}\dot{C}_{00} + C^{\star}_{11}\dot{C}_{01})|\phi_0\rangle + (C^{\star}_{01}\dot{C}_{10} + C^{\star}_{11}\dot{C}_{11})|\phi_1\rangle. \quad (17) \end{aligned}$$

Similarly, we also have

$$\begin{aligned} C^{\star}_{00}\langle\phi_0|\dot{\Psi}\rangle + C^{\star}_{01}\langle\phi_1|\dot{\Psi}\rangle &= (C^{\star}_{00}C_{00} + C^{\star}_{01}C_{10})|\dot{\chi}_0\rangle + (C^{\star}_{00}C_{01} + C^{\star}_{01}C_{11})|\dot{\chi}_1\rangle \\ &\quad +(C^{\star}_{00}\dot{C}_{00} + C^{\star}_{01}\dot{C}_{10})|\chi_0\rangle + (C^{\star}_{00}\dot{C}_{01} + C^{\star}_{01}\dot{C}_{11})|\chi_1\rangle \quad (18) \end{aligned}$$

and

$$\begin{aligned} C^{\star}_{10}\langle\phi_0|\dot{\Psi}\rangle + C^{\star}_{11}\langle\phi_1|\dot{\Psi}\rangle &= (C^{\star}_{10}C_{00} + C^{\star}_{11}C_{10})|\dot{\chi}_0\rangle + (C^{\star}_{10}C_{01} + C^{\star}_{11}C_{10})|\dot{\chi}_1\rangle \\ &\quad +(C^{\star}_{10}\dot{C}_{00} + C^{\star}_{11}\dot{C}_{00})|\chi_0\rangle + (C^{\star}_{10}\dot{C}_{01} + C^{\star}_{11}\dot{C}_{10})|\chi_1\rangle. \quad (19) \end{aligned}$$

Let us now define a matrix $C(2\times 2)$ and D where

$$C = \begin{pmatrix} C_{00} & C_{01} \\ C_{10} & C_{11} \end{pmatrix}, \quad C^{\dagger} = \begin{pmatrix} C^{\star}_{00} & C^{\star}_{10} \\ C^{\star}_{01} & C^{\star}_{11} \end{pmatrix}', \quad D = \left(C^{\dagger}C\right). \quad (20)$$

Using these three matrices, equation can be given a condensed representation:

$$\begin{aligned} &\mathbf{D} \equiv \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \\ &i\mathbf{D}\begin{pmatrix} |\dot{\phi}_0\rangle \\ |\dot{\phi}_1\rangle \end{pmatrix} = C^{\dagger}\begin{pmatrix} \langle\chi_0|H|\Psi\rangle - i(\dot{C}_{00}|\phi_0\rangle + \dot{C}_{10}|\phi_1\rangle) \\ \langle\chi_1|H|\Psi\rangle - i(\dot{C}_{01}|\phi_0\rangle + \dot{C}_{11}|\phi_1\rangle) \end{pmatrix}, \quad (21) \end{aligned}$$

which leads to the resolved time evolution equations for the single-particle functions associated with the X-mode:

$$\begin{pmatrix} |\dot{\phi}_0\rangle \\ |\dot{\phi}_1\rangle \end{pmatrix} = \frac{1}{i}\mathbf{D}^{-1}C^{\dagger}\begin{pmatrix} \langle\chi_0|H|\Psi\rangle - i(\dot{C}_{00}|\phi_0\rangle + \dot{C}_{10}|\phi_1\rangle) \\ \langle\chi_1|H|\Psi\rangle - i(\dot{C}_{01}|\phi_0\rangle + \dot{C}_{11}|\phi_1\rangle) \end{pmatrix}. \quad (22)$$

We note here that both $\langle\chi_0|H|\Psi\rangle$ and $\langle\chi_1|H|\Psi\rangle$ are operators acting in the space spanned by basis functions of mode x. A similar resolution occurs for $|\dot{\chi_0}\rangle$ and $|\dot{\chi_1}\rangle$ also in terms of matrices D_1, C_1 and $C_1^{\dagger}$, the definitions of which follow easily from eqs (18) and (19). Noting now that in the TDFGH representation the time-dependence of the single-particle basis function $\{\phi_i,\ \chi_j\}$ comes through the time-dependence of grid amplitudes w^x_{pi} and w^y_{qj}:

$$|\dot{\phi_0}\rangle = \sum_{p=1}^{n} \dot{w}^x_{p_0}|x_p\rangle\Delta x, \quad |\dot{\phi_1}\rangle = \sum_{q=1}^{n} \dot{w}^x_{q_1}|x_q\rangle\Delta x, \quad (23)$$

$$|\dot{\chi}_0\rangle = \sum_{r=1}^{n} \dot{w}^y_{r_0}|y_r\rangle\Delta y, \quad |\dot{\chi}_1\rangle = \sum_{s=1}^{n} \dot{w}^y_{s_1}|y_s\rangle\Delta y, \tag{24}$$

we proceed to resolve eq. (22) into their grid amplitude counterparts by projecting each row of eqs (22) on the fixed coordinate vectors $\{\langle x_l|\}_{l=1,n_x}$. The process leads to required resolved evolution equations for each grid-point amplitude along the X-mode for the single-particle states $|\phi_0\rangle$ and $|\phi_1\rangle$:

$$\begin{pmatrix} \dot{w}^x_{l_0} \\ \dot{w}^x_{l_1} \end{pmatrix} = \frac{1}{i}\mathbf{D}^{-1}C^\dagger \begin{pmatrix} \langle x_l\chi_0|H|\Psi\rangle - i(\dot{C}_{00}\langle x_l|\phi_0\rangle + \dot{C}_{10}\langle x_l|\phi_1\rangle) \\ \langle x_l\chi_1|H|\Psi\rangle - i(\dot{C}_{01}\langle x_l|\phi_0\rangle + \dot{C}_{11}\langle x_l|\phi_1\rangle) \end{pmatrix}, \quad l = 1, 2, \ldots, n_x \tag{25}$$

and a similar set of equations for $\dot{w}^y_{s_0}$ and $\dot{w}^y_{s_1}$ are obtained by projecting on $\{\langle y_s|\}_{s=1,n_y}$. We note here that the structure of FGH representation enables us to evaluate the right-hand side of equation easily and efficiently. The $i\dot{C}_{ij}$ terms in eqs (25) can be replaced by the corresponding right-hand side in eq. (13) and the evolution equations integrated by predictor–corrector method. Adam-Moulton or Adam Bashforth methods can be conveniently used. Equations (13) on the other hand can be integrated by the sixth order Runge–Kutta method (instead of a predictor–corrector method). In other realization of the TDMCH method, eqs (22) would have to be converted into evolution equations for the parameters in ϕ_i or χ_j (linear or non-linear or both) but a comprehensive time-dependent variation would have been difficult to implement. This has been sought to be achieved by the multilayered time-dependent method of [13]. In the TDFGH-based realization described here the comprehensive time-dependence of single-particle basis appears naturally. However, that comes with a cost in the sense that the number of equations to be integrated increases. Even then, the method enjoys an edge over others because of the structure of the FGH method.

3. Results and discussion

We consider a coupled oscillator problem defined by the Hamiltonian [14]

$$H = \frac{1}{2}(P_x^2 + P_y^2 + x^2 + y^2) + \lambda\left(xy^2 - \frac{1}{3}x^2\right) + \frac{1}{16}\lambda^2(x^2 + y^2)^2$$

with λ=0.2. The starting single-particle functions were generated by preliminary Hartree mean-field calculations and the initial wave packet was constructed from the Hartree product of the mean-field eigenfunctions for each mode. For example, the initial wave packet could be chosen as follows: $|\Psi(x, y, 0)\rangle \approx |\phi_1(x, 0)\chi_1(y, 0)\rangle$. The initial coefficient matrix for this choice of $\Psi(x, y, 0)$ is singular, viz.

$$C \equiv \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{26}$$

To start the calculations C was replaced by $\overline{C}$ where

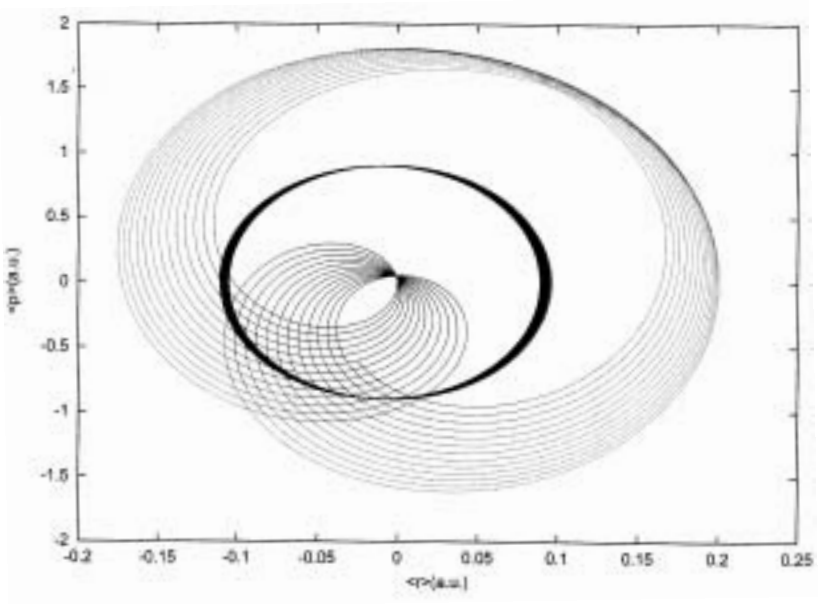

Figure 1. The 'quantum phase space' accessed by the particle when the initial wave packet is constructed from lowest mean-field eigenfunctions $\phi_1\chi_1$.

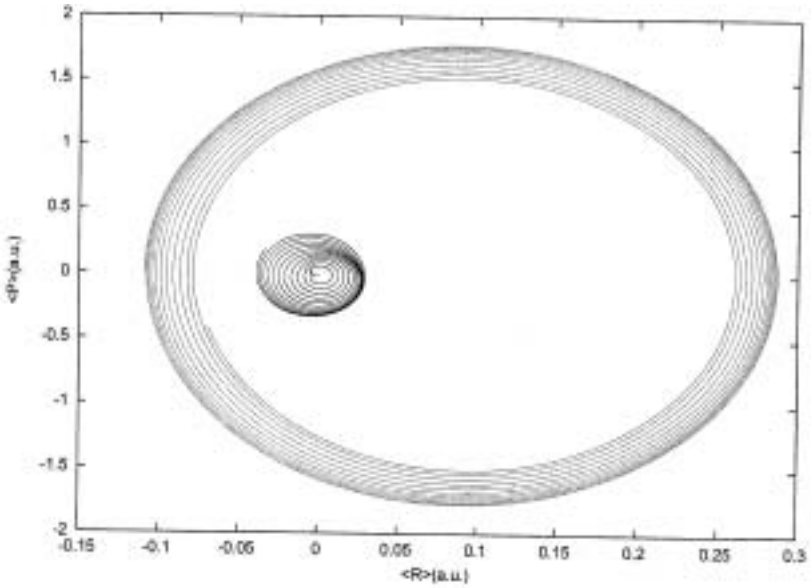

Figure 2. The 'quantum phase space' accessed by the particle when the initial wave packet is constructed from mean-field eigenfunctions as $\frac{1}{\sqrt{2}}[|\phi_0(x,0)\chi_0(y,0)\rangle + |\phi_1(x,0)\chi_1(y,0)\rangle]$.

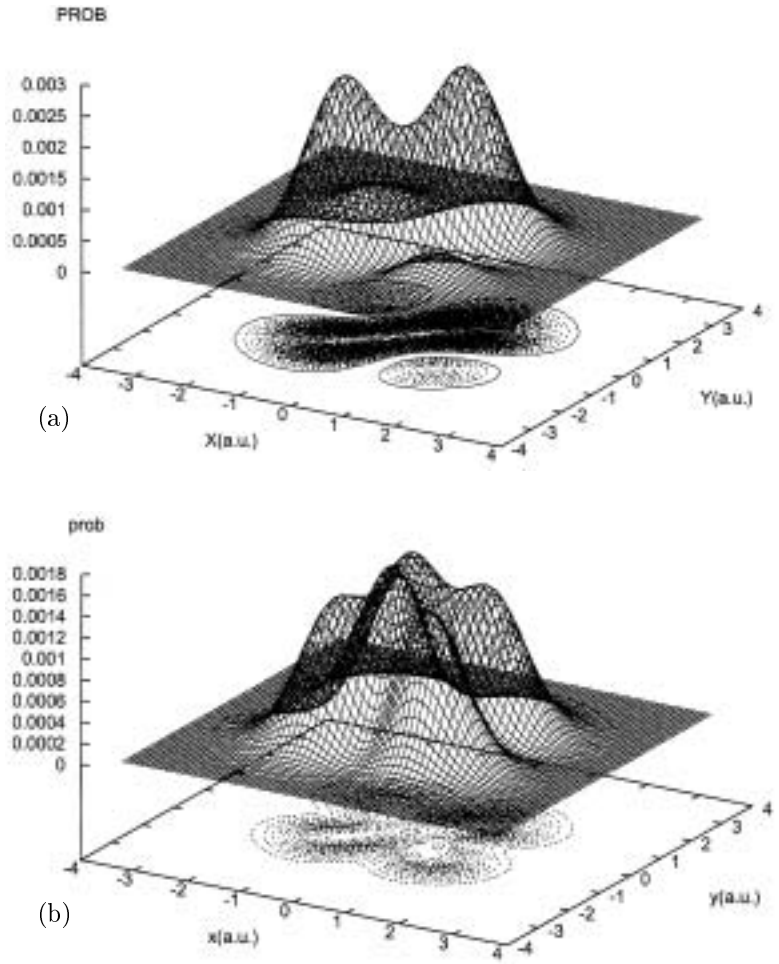

Figure 3. (a) The form of the wave function at $t = 0$ corresponding to the initial conditions used for figure 2. **(b)** The form of the wave function after time propagation for 20 fs with 10^{-3} fs time steps. It evolves no further.

$$\overline{C} = \begin{pmatrix} \delta & 0 \\ 0 & 1 \end{pmatrix}, \quad \delta \sim 10^{-12}\text{–}10^{-15}. \tag{27}$$

Figure 1 shows the evolution of the 'quantum phase space' dynamics obtained by plotting $\langle p_x \rangle$ vs. $\langle x \rangle$ and $\langle p_y \rangle$ vs. $\langle y \rangle$ at different times. It is clearly seen that as the system relaxes, one mode gains energy at the expense of the other till an equilibrium is reached. The dynamics of the approach to equilibrium depends strongly on the initial state. Thus figure 2 shows the 'phase space' dynamics when $|\Psi(x, y, 0)\rangle$ is chosen in the following form: $\frac{1}{\sqrt{2}}[|\phi_0(x, 0)\chi_0(y, 0)\rangle + |\phi_1(x, 0)\chi_1(y, 0)\rangle]$. The relaxation path here turns out to be quite different from what was seen in figure 1. We have also computed the fully relaxed wave function corresponding to the second choice of $|\Psi(x, y, t)\rangle$. In figure 3a we have displayed the converged wave

function obtained after a time propagation of 20 fs while in figure 3b we have shown the initial form of the wave function. Like all other realizations of MCTDH, the evolution conserves norm. The orthonormality of the single-particle functions is conserved during the propagation ($S_{\max} \leq 10^{-6}$). The relaxation or reorganization seems to be over in 20 fs as no further evolution of Ψ seems to take place.

4. Conclusion

It appears that the TDFGH-based realization of time-dependent MCH method can be profitably utilized to probe a wide variety of dynamical phenomena. It is easy to implement the recipe. The fully time-dependent grid-point amplitudes make the wave function flexible so that one can use fewer configurations ($\phi_i \chi_j$) to represent Ψ. The diagonality of the potential part of $\hat{H}$ and the need to fast Fourier transform *only once for each mode* to construct the kinetic energy operators in the TDFGH formulation make it rather straightforward to use it for time-propagation. However, one needs to have accurate and stable integrators for long-time propagation. We are in the process of making much larger scale applications of the methodology proposed. We hope to return to these applications in the near future.

Acknowledgements

One of us (KM) thanks the CSIR, Government of India, New Delhi, for the award of a Junior Research Fellowship.

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