Potential energy surface hopping algorithms for polyatomic molecules: Theoretical study

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ABSTRACT

The applicability of a computer simulation technique for investigating photoinduced dynamics of polyatomic molecules, based on a combination of classical dynamics and a quantum surface hopping algorithm is discussed. The Wigner representation of a molecule's time-dependent density matrix is calculated and the corresponding approximation of the molecule's dynamics as a series of quantum jumps between the electronic states with classical movement on single electronic levels between jumps is presented. The effectiveness of this approach in computer simulations of a molecule's photodissociation dynamics in the presence of a strong laser field is shown and computer simulation results on IR photostimulated dissociation in HCl$^+$ molecule are reported.

1. Introduction

Molecules present unique challenges to theoreticians because they straddle the border of the classical/quantum correspondence. Although the dynamics of a single electronic level can often be treated as predominantly classical, the dynamics of electronic transitions is essentially quantum. Any calculations involving polyatomic molecules and taking into account all $3N - 6$ vibrational degrees of freedom (N is the number of atoms) can only be performed practically within a classical approach to the atoms' dynamics. A simple way to introduce the quantum dynamics of the electronic subsystem was proposed by Tully and Preston.[1] It is based on a representation of the electronic dynamics as a series of quantum jumps between the electronic levels. For a two-electronic-state system with electronic states $|0\rangle$ and $|1\rangle$, the method consists of first integrating the classical mechanical equations of motion for the nuclei, then quantum mechanically propagating the electronic wave function along the calculated piece of trajectory and determining the probabilities a_{jj}^2 for the system to be in each of the electronic states $|j\rangle$ ($j = 0, 1$). Switching from one surface to another occurs if the switching probability is larger than a generated random number between 0 and 1.

There have been many specific problems investigated with the Tully's algorithm and its modifications. These include applications to: collision dissociation dynamics of simple molecules, cluster dynamics, photoinduced dissociation dynamics in matrices, electron solvation dynamics and photoinduced conformational dynamics in polyatomic molecules.

Blais and Truhlar[2] have used a surface hopping procedure to calculate the cross section for the collision induced process $H+H_2(\nu, j) \rightarrow 3H$, where ν and j denote selected vibrational and rotational quantum numbers. The effect of the first excited electronic state which has a conical intersection with the ground state, is included. It is shown that the surface hopping mechanism increases the cross section and rate constants for production of unbound states by 2% – 44%. The calculation is performed using two different direction vectors to adjust the molecule's momentum so as to conserve the total energy for a single trajectory. It is shown that the two directions are nearly perpendicular, but nevertheless the calculation results are not sensitive to the choice. A closely related variance of surface hops has been introduced by Kuntz[3]. Here, the surface-hopping procedure is applied to an explanation of the large observed cross-section for a well studied collision induced predissociation $Ne+He_2^+ \rightarrow Ne^+ +He+He$ where vibration in the entrance channel $Ne+He_2^+$ leads to strong nonadiabatic behavior. In Ref. 4 the same computational method was applied to study the dissociation of singly charged argon trimer-ions produced in the ionization process $Ar_3^+ \rightarrow Ar_2^+ +Ar$. There the different dynamical mechanisms are interpreted in terms of charge

migration and nonadiabatic effects, and applicability of the method to the dynamics of Ar_n^+ clusters is shown. Stine and Muckerman[5] have compared several different modifications of the surface hopping algorithm, including one proposed by them and based on a specific criterion for surface hop, with respect to the dynamics of $H_2^+ + H_2$ collision. It is argued that the modification presented by the authors corresponds to the original approach of Tully and Preston, and both treated the problem within the same accuracy.

The molecular dynamics of photodissociation of HCl and Cl_2 in Xe-crystal matrices was investigated by Gersonde and Gabriel[6]. They show that nonadiabatic transitions between the adiabatic states occur on a subpicosecond time scale and induce fast recombination of the fragments, reducing the quantum yield of permanent dissociation. It is especially pointed out that, in such systems, a specific mechanism of suppressing coherence between the adiabatic states does exist.

Another application of surface-hopping algorithms is concerned with a calculation of nonadiabatic rates in condensed phases.[7,8] The key idea of the method is to apply a molecular dynamics simulation method to the calculation of nonadiabatic rates, based on the golden rule expression. The latter is introduced in an equivalent form through the temporal dynamic evolution, investigated within the frame of a classical approach modified with the use of frozen Gaussian packets.[9] It is shown that for this specific case, a direct application of the Tully–Preston algorithm does not provide exact results.

Recently, we presented a comprehensive $3N$-dimensional (N is a number of atoms) study of the photoinduced isomerization of isolated cis- stilbene, including all 72 vibrational degrees of freedom, using quasiclassical molecular dynamics (MD) simulation method.[10] For modeling the internal conversion process we have used a modification of the Tully–Preston algorithm. Since evaluation of the electronic wave functions and their time dependencies is not feasible for such a large system we have used an approximate formulae, given by Miller and George,[11] for the probability of transitions between the electronic states along the nuclear trajectories. In this case, the probability of a transition at a given moment depends only on the energy difference between the electronic states and its second derivative, both of which can be directly calculated along a classical trajectory. The point in phase space at which switching occurs plays an important role in determining the subsequent dynamics in the ground state and the final disposition of photoproducts in the reaction. It is therefore important, that a representation of the internal conversion molecule's dynamics as a well-defined quantum stochastic process is justified with quantum considerations, providing a rigorous basis for semiclassical calculations. At present, most theoretical investigations are based on wave function dynamics,[11−15] which is not feasible for the case of polyatomic molecules or other cases where the stochastic nature of the quantum transitions is important.

In this paper we present a corresponding approach based on a representation of molecular dynamics in the frame of density matrix, with the use of the Wigner representation (Sec. 2). Finally, we obtain the proper approximation for the density matrix, which indicates the validity of the quantum jumps picture, however reveals also some essential corrections to the Tully– Preston algorithm. In particular, our investigation leads to a different interpretation of the energy conservation law during the process of quantum jumps. A formulae for the transition probability is also derived which is similar to the approximation of Miller–George, but is more precise.

In Sec. 3 we apply our analytical results to the computer simulation of molecular dynamics in the presence of a highly intense non-resonant laser field which produces strong electronic coupling via the transition dipole moment.

2. Semiclassical Stochastic Representation of Quantum Dynamics

In molecular dynamics there are two common types of quantum scenarios. The first one is concerned with the dynamics on a single electronic state, that is with vibrational dynamics. Another one is concerned with electronic coupling, that is with electronic dynamics between different electronic states. In studying fast molecular processes on a femtosecond time scale vibrational dynamics may be correctly treated within a classical approach, in contrast to the electronic one, demanding essentially quantum description. The key point of this approach can be represented in terms of Wigner representation of quantum dynamics, as follows.

In this section we introduce a stationary problem, which may be also applied to the case of a highly intense IR field.[16] In the total Hamiltonian of a molecule $\hat{\mathcal{H}} = \hat{T} + \hat{V}$, the kinetic energy operator can be written in the form

$$\hat{T} = \hat{T}_{11} + \hat{T}_{22} + \hat{T}_{12} + \hat{T}_{21}, \quad \hat{T}_{kl} = \hat{P}_k \hat{T} \hat{P}_l \quad , \tag{1}$$

where $\hat{P}_k = P_k(\hat{q})$ are coordinate-dependent orthogonal projectors onto k-th electronic eigenstate ψ_k of the adiabatic

potential $\hat{V} = V_1\hat{P}_1 + V_2\hat{P}_2$ depending on the vibrational coordinates $\hat{q}$ and time t. The diagonal terms

$$\hat{\mathcal{H}}_{kk} = \hat{P}_k\hat{\mathcal{H}}\hat{P}_k \tag{2}$$

correspond to movement on single adiabatic states, while the off-diagonal ones $\hat{\mathcal{H}}_{kl} = \hat{T}_{kl}$ correspond to $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |1\rangle$ electronic transitions due to non-adiabatic coupling. They are non-zero due to non-commutativity of the operators $\hat{T}$ and $\hat{q}$, which means the corresponding perturbation parameter is proportional to Planck constant $\hbar$ and may be expected to be small if the single-level dynamics is quasiclassical. In this representation, non-adiabatic coupling looks like a generally weak perturbation, though a specific dimensionless parameter responsible for the reliability of the corresponding perturbation theory approach should be estimated for any specific case. As far as dynamics within a single level described by the operator (2) is concerned, its major approximation is thence of classical dynamics governed by the Hamiltonian $\hat{\mathcal{H}}_k = \hat{T} + \hat{V}_k$, which ignores a small interplay of non-adiabatic coupling to a single-level dynamics. Several general approaches for the investigation of the nonadiabatic coupling problem that also take into account the effects of quantum vibrational dynamics have been suggested.[17] Here we restrict our approach to the demands of computer simulation of polyatomic molecules.

A corresponding approach may be based on first and second order perturbation theory with respect to non-adiabatic coupling. For the case of a two-electronic-level molecule initially produced in electronic state $|1\rangle$ we obtain the expression for the diagonal density matrix element

$$\hat{\rho}_{22}(t) = \frac{1}{\hbar^2}\int_0^t\int_0^t d\tau_1 d\tau_2 \mathcal{U}_2^{-1}(\tau_1)\hat{T}_{21}\mathcal{U}_1(\tau_1)\hat{\rho}_{11}^0\mathcal{U}_1^{-1}(\tau_2)\hat{T}_{12}\mathcal{U}_2(\tau_2) \quad . \tag{3}$$

Here $\hat{\rho}_{kk}$ are kk-th diagonal elements of a molecule's density matrix $\hat{\rho}$ and $\mathcal{U}_k(\tau)$ are time evolution operators within a single k-th electronic levels governed with Hamiltonian $\hat{\mathcal{H}}_k$.

To obtain a specific quasiclassical dynamics approach we must first introduce an appropriate representation of quantum dynamics within a single electronic level. One possible representations is that of Wigner[18] based on a specific representation $\hat{f} \rightarrow f(X)$ of quantum operators $\hat{f}$ with classical functions f of coordinates and momenta $X = (q, p)$. Operator products are represented in accordance to the rule[19]

$$\hat{f}\hat{g} \rightarrow \mathcal{N}_{X,\partial/\partial X} f\left(X + \frac{1}{2}C\frac{\partial}{\partial X^{\mathrm{T}}}\right)g(X) \quad , \tag{4}$$

where an ordering symbol $\mathcal{N}$ indicates that operators $\partial/\partial X$ are applied before the product of X, symbol T indicates transposition of vector X and C is a commutation matrix of operators $\hat{X}$ of the classical canonic variables X. This representation presents the simplest way to describe the quasiclassical limit used in our computer simulations. The possibilities provided by other representations as well as a perspective specific representation are discussed elsewhere.[20]

Within this representation and the second order perturbation theory approach (3), the two most important transformations for a system with classical scalar Hamiltonian $\mathcal{H}(X)$ arise while calculating dynamical processes. They correspond to the two evolution processes expressed by the two time variables $s = (t_1 + t_2)/2$ and $\tau = t_2 - t_1$ where t_1, t_2 are the time arguments arising in the second order approach with respect to $\hat{T}_{12}(t), \hat{T}_{21}(t)$ in combinations like $\hat{T}_{21}(t_1) \odot \hat{T}_{12}(t_2)$. The substitution symbol $\odot$ indicates where the transformed density matrix operator $\hat{\rho}$ is to be inserted. These main dynamical transformations are represented by operators

$$\mathcal{L}_- = -\frac{i}{\hbar}\mathcal{N}_{X,\partial/\partial X}\left[\mathcal{H}\left(X + \frac{1}{2}C\frac{\partial}{\partial X^{\mathrm{T}}}\right) - \mathcal{H}\left(X - \frac{1}{2}C\frac{\partial}{\partial X^{\mathrm{T}}}\right)\right], \tag{5}$$

$$\mathcal{L}_+ = -\frac{i}{2\hbar}\mathcal{N}_{X,\partial/\partial X}\left[\mathcal{H}\left(X + \frac{1}{2}C\frac{\partial}{\partial X^{\mathrm{T}}}\right) + \mathcal{H}\left(X - \frac{1}{2}C\frac{\partial}{\partial X^{\mathrm{T}}}\right)\right]. \tag{6}$$

Here $\mathcal{L}_-$ represents a quantum Liouvillian, that is a transformation $(-i/\hbar)[\hat{H}\odot - \odot\hat{H}]$ of density matrix operators $\hat{\rho}$. $\mathcal{L}_-$ may represent also the Heisenberg equations of motion. Its eigenfunctions correspond to the transition projectors $\hat{P}_{kl} = |k\rangle\langle l|$ with the corresponding eigen values $-i\omega_{kl} = i(E_l - E_k)/\hbar$. Its major approximation with respect to $\hbar$ is the classical Poisson bracket $\mathcal{L}_1 = \{\mathcal{H}, \odot\}$ obtained from Eq. 5 in the first order with respect to $C \sim \hbar$. $\mathcal{L}_+$ is given by $(-i/2\hbar)[\hat{H}\odot + \odot\hat{H}]$ with eigenvalues $-i\omega_{kl} = -i(E_l + E_k)/2\hbar$. The key approximations made here are $\mathcal{L}_0 = -i\mathcal{H}(X)/\hbar$ in zeroth order and $\mathcal{L}_2 = (-i/\hbar)\left[\hbar^2\mathcal{D}_2/8 + \mathcal{H}(X)\right]$ in second order, where

$$\mathcal{D}_n = -\left(\frac{i}{\hbar}\right)^n \frac{\partial^n\mathcal{H}}{\partial X_1...\partial X_n}C_1\cdots C_n\frac{\partial}{\partial X_1^{\mathrm{T}}}\cdots\frac{\partial}{\partial X_n^{\mathrm{T}}} \quad ,$$

C_k, X_k are copies of C, X. Transformation $\mathcal{L}_+$ represents the Schrödinger equation in terms of variables X instead of more accustomed standard quantum representation in terms of Hilbert space with elements $\psi(q)$ depending only on coordinates q.

Let us assume that, at the moment $t = 0$, a molecule is in electronic state $|1\rangle$. Then, based on the second order perturbation theory result, we obtain

$$\Delta w_{22}(X,t) = \int_0^t ds\, \mathcal{S}_-^2(t-s)\mathcal{P}(s)\mathcal{S}_-^1(s)w_{11}(X,0). \tag{7}$$

Here w_{kl} are the Wigner representation of the respective density matrix elements, $\mathcal{S}_\pm^k(t) = \exp\left(\mathcal{L}_\pm^k t\right)$ are time evolution operators for k-th level introduced by generators Eq. (5), Eq. (6) and

$$\mathcal{P} = \frac{1}{\hbar^2}\int_{-s}^s d\tau\, \mathcal{S}_+^2(-\tau)(\hat{T}_{21} \odot \hat{T}_{12})\mathcal{S}_+^1(\tau) \tag{8}$$

is a transition operator where the quantum transformation $(\hat{T}_{21} \odot \hat{T}_{12})$ is to be represented in the Wigner form and integration actually may be extended to infinite limits. Expressions (7) and (8) present a more general approach than the quasiclassical one.[11] Eq. (8) represents a transition probability rate calculated over a classical trajectory. Nevertheless, when the quasiclassical approximation is valid, both lead to the common approximation (see the Appendix):

$$\mathcal{P}(s) = \langle \dot{2}|1\rangle_s^2 \mathcal{T}(X_s) \tag{9}$$

where $\langle \dot{2}|$ is the time derivative of the vector $\langle 2|_s$ depending on coordinates $q(s)$, and $\mathcal{P}(s)$ now is simply the time density of the jump probability which can be written as the product of a squared matrix element of the transition rate and the effective interaction time $\mathcal{T}(X_s)$ between the levels at the point X_s. The latter is represented by the formula (see also Ref. 11):

$$\mathcal{T}(X) = \frac{2\hbar}{\sqrt{3}\pi V_{12}}K_{1/3}(\chi) \approx \frac{2\sqrt{2\pi}}{3^{1/6}}\frac{\hbar^{1/3}}{\dot{V}_{12}^{1/3}}\frac{e^{-\chi}}{\chi^{1/2}}, \quad \chi(X) = \frac{4\sqrt{2}}{3\hbar}\frac{V_{12}^{3/2}}{\dot{V}_{12}^{1/2}}. \tag{10}$$

Here the approximate expression is based on the approximation of Bessel function $K_{1/3}(\chi)$ valid for large values χ.

For off-diagonal elements we use first order perturbation theory. After similar calculations we obtain within the classical approach for single-level dynamics:

$$w_{21}(t) = \int_0^t \langle \dot{2}|1\rangle_s \mathcal{S}^{21}(t-s)w_{11}(X,s)ds. \tag{11}$$

Here

$$\mathcal{S}^{21}(\tau) = \exp\left[\frac{-i}{\hbar}(V_{21}\tau - \{\mathcal{H}_2, \mathcal{H}_1\}\,\tau^2/2)\right]\bar{\mathcal{X}}^{21}(\tau) \tag{12}$$

is a dynamical transformation due to the combined action of the potentials of the two electronic levels, where the exponential describes the phase factor including energy gap V_{21} and

$$\bar{\mathcal{X}}^{12}(\tau) = \exp\left[\{(\mathcal{H}_1 + \mathcal{H}_2)/2, \odot\}\,\tau\right]$$

is a classical dynamical transformation, corresponding to movement under the average potential of the two levels $|1\rangle, |2\rangle$. If off-diagonal terms may be neglected, Eq. 7 corresponds to the QJ model of molecular dynamics illustrated in Fig. 1 within a semiclassical approach for $\mathcal{S}^k(\tau)$. An argument for the validity of the incoherent approach for different cases has been presented elsewhere[1,21] as well as the description of specific cases when the coherence is essential.[22,23]

3. Quantum Jumps Stimulated by an Intense Laser Field

The present approach is well-suited to the simulation of molecular dynamics induced by an intense laser field when the vibrational quantum structure is of no significance and quantum properties result only from coupling between
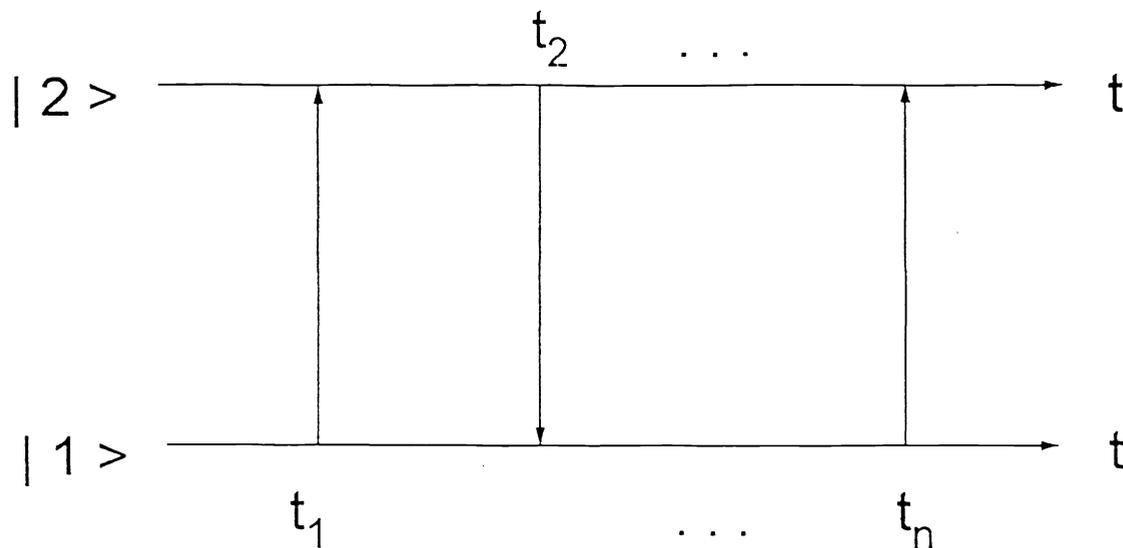
Fig. 1. Simulation of the molecule's quantum electronic dynamics by means of the Quantum Jumps (QJ) model. Quantum jumps take place at the random time instants $t_1, t_2, \ldots, t_n \ldots$. The dynamics between the consecutive jumps at t_n and t_{n+1} are treated classically.
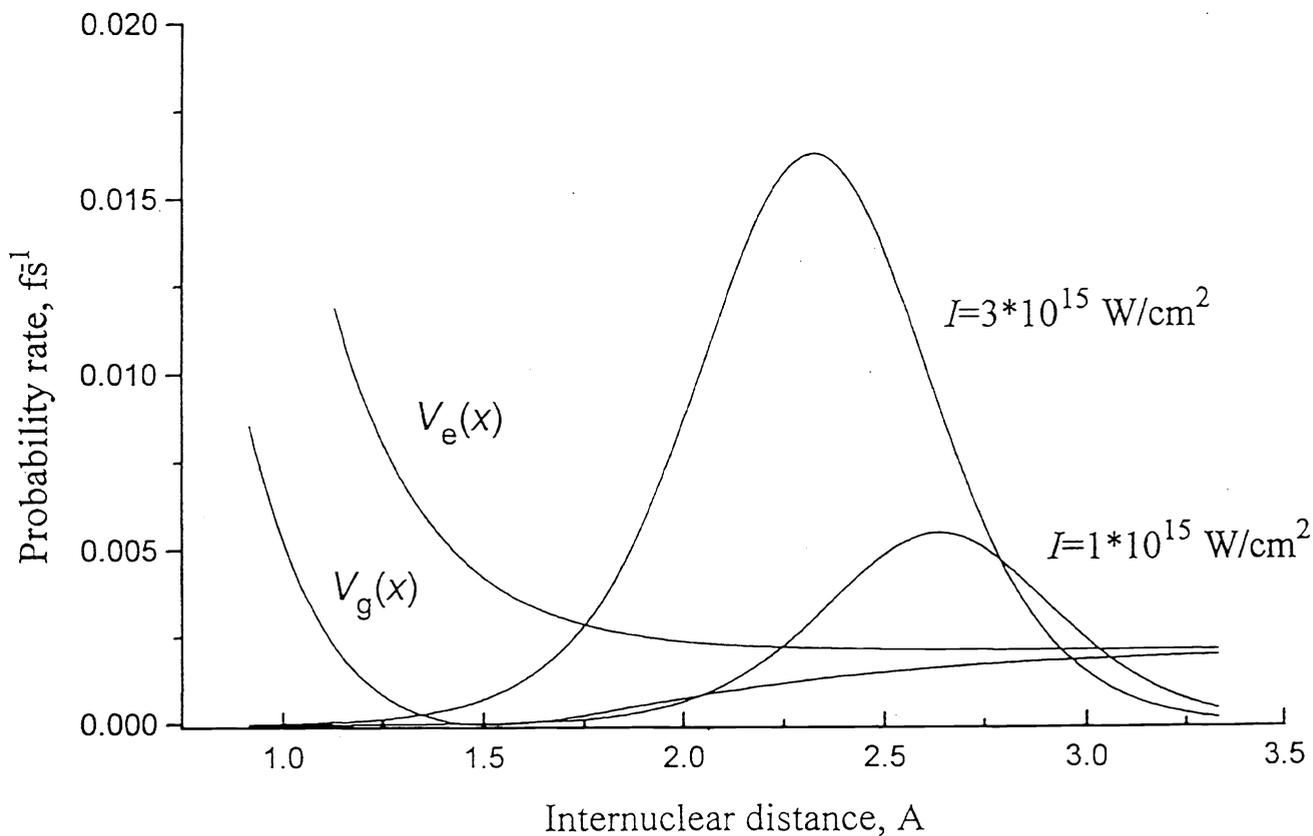
Fig. 2. The expected probability rate of quantum jump $|1\rangle \rightarrow |2\rangle$. The corresponding energies of the field-dressed electronic levels are presented in arbitrary units.

two or more electronic levels. As an example, we consider a two-state one-dimensional model investigated using the approach of random quantum jumps. The potential energy of such a system can be represented by the 2×2-matrix

$$\hat{U}(t) = \left(\begin{array}{cc} U_2(\hat{x}, t) & \Delta V(\hat{x}, t) \\ \Delta V(\hat{x}, t) & U_1(\hat{x}, t) \end{array} \right).$$

(13)

Here $U_{1,2}(\hat{x}, t) = [V_{1,2}(\hat{x}) - d_{1,2}(\hat{x})E_L(t)]$, $\Delta V(\hat{x}, t) = -E_L(t)d_{12}(\hat{x})$; $V_{1,2}(\hat{x})$ and $d_{1,2}(\hat{x})$ are the potential energies and dipole moments of the electronic levels; $E_L(t)$ is the magnitude of the laser field. The matrix elements are functions of the position operator $\hat{x}$. The off-diagonal elements in (13) describe generally the non- resonant interaction of the laser field with the transition dipole moment $d_{12}(\hat{x})$ of the electronic transition. In this case potentials $V_{1,2}(q)$ introduced in Sec. 3 correspond to the eigenvalues $V_{g,e}(x, t)$ of matrix (13), which depend on time through the magnitude of the laser field. At times $t_k = 2\pi k/\omega_L$ the field goes to zero and $V_{g,e}(x, t_k) = V_{g,e}(x, 0)$, which does not depend on the field estimating the coupling in Eq. (13). At the same time the second time derivative, $\ddot{V}_{eg} \sim V''_{eg}\dot{x}^2 + V'_{eg}\ddot{x}$, which determines the transition probability in Eqs. (7,9), depends essentially on the field through the acceleration $\ddot{x}$, that is the non-adiabatic coupling is proportional to the field's magnitude $E_L(t)$. Moreover, for non-zero dipole diagonal moments $d_{1,2}(\hat{x})$, the energy gap $V_{g,e}(x, t)$ for some specific time instants t may be essentially smaller then the non-perturbed one, if the difference $\Delta d = d_2 - d_1$ is larger than the transition dipole moment. Thus, an intense laser field is a natural stimulator of quantum electronic transitions at the times corresponding to zero field magnitude.

To evaluate the effectiveness of this mechanism we calculated the $|g\rangle \rightarrow |e\rangle$ transition probability with use of Eq. (9) for different points x, assuming that at any point a molecule moves with the velocity corresponding to the kinetic energy which the molecule would gain in the absence of the internal potential. The corresponding time t is chosen so as to obtain the maximum probability. The results of these illustrative calculations are presented in Fig. 2. They show that transition probability for time intervals of ~ 1 fs and field intensities $I \sim 10^{15}$ W/cm^2 are in range $\sim 10^{-2}$, confirming the validity of the perturbation theory approximation used. Nevertheless, these estimates are not able to describe the exact dynamics because they are not in rigorous correspondence with real trajectories and strict dynamics calculations are needed. These results indicate that the dynamics can be represented as combination of classical movement on each electronic level and fast random quantum jumps between the levels with probabilities described by Eq. 9. This conclusion is based also on Eq. 11, which shows that off-diagonal density matrix elements include a fast phase factor changing dramatically just at the time of quantum jump. These matrix elements can then be neglected as there is no specific mechanism producing time coherence. These are the theoretical foundations of the quantum jumps approach.

This approach has been applied[16] to the investigation of a two-electronic-state and one-dimensional model of a photodissociation dynamics of HCl$^+$ in IR laser field. As in the case of isolated surface hops, discussed in Sec. 3, the calculation results show that the semiclassical approach of random quantum jumps in the case of non-resonant highly intense field is also suitable if only limited number of active electronic levels are responsible for the molecule's dynamics. The dynamics in the latter case is essentially stochastic due to numerous random jumps and is therefore a specific example of a stochastic dynamics due to non-zero probability of non-adiabatic electronic transitions at each time instant (closely related examples of stochastic dynamics induced by localized quantum jumps have been discussed elsewhere[22,24]).

4. Conclusions

It is shown in Sec. 2, that the dynamics of a free molecule in a presence of a non-adiabatic perturbation due to levels' nearly crossing at isolated points is actually a stochastic process, well represented by combination of a series of random quantum jumps and classical movement on single electronic levels, as has been commonly suggested. Nevertheless, the postulate of conservation of vibrational energy of a molecule in the changing potential during a single electronic jump is not necessary in the present approach (see Appendix). The nature of the jumps is consistent with the idea of conservation of average energy of the incoherent ensemble of trajectories, and in this way it is similar to the nature of quantum jumps used to simulate Markovian dynamics of a quantum system in terms of wave functions.[25]

The semiclassical approach of random quantum jumps is also applicable to the non-adiabatic photodissociation dynamics of a molecule in a strong non-resonant field when a limited number of electronic levels is essential. This provides an effective method of computer simulation of photodissociation processes in polyatomic molecules.

Acknowledgments

Appendix

The exact expression (8) for the transition operator is too general for the purpose of quasiclassical approach. The major and simplest approximation is to neglect the operator character of $\hat{T}_{21} \odot \hat{T}_{12}$ and reduce the operator superposition $\mathcal{S}_+^{12}(\tau) = \mathcal{S}_+^2(-\tau)\mathcal{S}_+^1(\tau)$ to a non-operator factor which after integration over τ results as T in Eq. (9). The function $\mathcal{S}_+^{12}(\tau)$ may be obtained from the equation for its time derivative

$$\frac{d}{dt}\mathcal{S}_+^{12}(\tau) = e^{-\mathcal{L}_2^{(2)}\tau}[\mathcal{L}_2^{(1)} - \mathcal{L}_2^{(2)}]e^{\mathcal{L}_2^{(1)}\tau} \quad , \tag{A1}$$

where, according to Sec. 2

$$\mathcal{L}_2^{(k)} = -\frac{i}{\hbar}\left[V_k(q) + \frac{p^2}{2m} - \frac{\hbar^2}{8}\left(V_k''\frac{\partial^2}{\partial p^2} + \frac{1}{m}\frac{\partial^2}{\partial q^2}\right)\right]. \tag{A2}$$

For the difference in Eq. (A1) we obtain the expression

$$\mathcal{L}_2^{(1)} - \mathcal{L}_2^{(2)} = -\frac{i}{\hbar}\left[V_{12}(q) - \frac{\hbar^2}{8}V_{12}''(q)\frac{\partial^2}{\partial p^2}\right] \tag{A3}$$

where the only operator term is the second one. The approximation leading to approach (9) corresponds to neglecting in Eq. (A2) all the operators including factor $\hbar^2$ and using $\mathcal{L}_2^{(2)} = -(i/\hbar)[V_2(q) + p^2/2m]$. Taking into account the non-commutativity of p and operator $\partial^2/\partial p^2$ in Eq. (A3) we have, after the commutation of the first exponential in Eq. (A1) and the corresponding term, the replacement

$$\partial/\partial p \rightarrow \partial/\partial p - ip\tau/(\hbar m). \tag{A4}$$

After that, omitting the terms with $\partial/\partial p$ (that are concerned with the corresponding small transformation of the wave packet) we obtain the non-operator equation

$$\frac{d}{dt}\mathcal{S}_+^{12}(\tau) = -\frac{i}{\hbar}\mathcal{S}_+^{12}(\tau)\left[V_{12}(q) + \frac{1}{8}V_{12}''(q)\frac{p^2}{m^2}\tau^2\right]. \tag{A5}$$

The solution after integration over τ leads in an obvious way to the expression for T presented in Sec. 2, after taking into account the following representation for operator $\hat{T}_{21} \odot \hat{T}_{12} = |2\rangle\langle 2|\hat{T}|1\rangle\langle 1| \odot |1\rangle\langle 1|\hat{T}|2\rangle\langle 2| = \langle 2|\hat{T}|1\rangle^2|2\rangle\langle 1| \odot |1\rangle\langle 2| = [(\hbar p/m)\langle 2|d/dq|1\rangle]^2|2\rangle\langle 1| \odot |1\rangle\langle 2|$ where the last term includes the operator for the quantum jump treated as a non-operator one with respect to vibrational coordinates.

One may note a contradiction between the calculations presented above and Tully's calculation scheme.[1] In the present calculations there is no requirement for energy conservation during each electronic jump as postulated in Tully's work.[1] From our point of view, such an interpretation of the energy conservation law is not correct due to the uncertainty of the electronic energy during the process of a non-adiabatic electronic jump. This uncertainty provides a reason for the jump and does not require any additional energy source. A change in the vibrational kinetic energy can be revealed based on transformation (A4) where, in particular, the term with $\partial/\partial p$ corresponds to a shift of the momentum. Nevertheless, the meaning of this term is different from Tully's conservation law. It takes into account only a momentum shift under the influence of the force produced by the electronic levels' potential difference acting at the time of electronic jump. Yet, this specific quantum shift is not concerned with the usual energy conservation and it is rather an analog of relatively weak quantum effects such as the Lamb frequency shift. It does not forbid energy jumps and obviously does not lead to an essential influence on the total dynamics.

The modification of the transition operator (9) including a momentum shift is due to the additional term $(1/4)V_{12}''\dot{q}\tau\partial/\partial p$ in Eq. (A5) arising from Eq. (A3) after the above mentioned time transformation (A4) of $\partial/\partial p$:

$$\mathcal{P}(s) = \langle 2|1\rangle_s^2 \int_{-\infty}^{+\infty} d\tau \exp\left\{-\frac{i}{\hbar}\left[V_{12}(q)\tau + \frac{1}{24}V_{12}''(q)\dot{q}^2\tau^3\right]\right\} \mathcal{S}_p(V_{12}''\dot{q}\tau^2/8) \quad , \tag{A6}$$

where $\dot{q} = p/m$ and $\mathcal{S}_p(\eta)$ indicates the momentum shift transformation $p \rightarrow p + \eta$. Eq. (A6) introduces an interference structure in the molecule's excitation after a jump. The greater the momentum shift is, the more rapid phase oscillations accompany the corresponding contribution to the excited state. The mechanism for the disappearance of the large shift is the averaging over fast oscillations, although any value of the shift at any fixed time τ can be represented by the same intensity. The typical momentum shift value may be evaluated as

$$\Delta p \approx \frac{1}{8} V_{12}'' \dot{q} T^2 \quad , \qquad (A7)$$

that with the use of Eq. (10) for T leads to the following estimation for the corresponding kinetic energy: $\Delta E_{\text{kin}} \sim V_{12}'' a^2/8$ where a is the dimension of the transition region. Although this value is the same order as V_{12}, there are no indication to that it does equal to V_{12}, that is energy conservation for a single trajectory breaks down. To conclude the problem of momentum shift, we may state, basing on Eqs. (5), (6) that at the time of the quantum jump, the dynamics is governed only by the difference of the levels' potentials and not with their time sequence as has been previously postulated.[11] Actually, we have two different time variables, that is $s = (t_1 + t_2)/2$, $\tau = t_2 - t_1$, where s corresponds to the dynamics within a single level and τ corresponds to a transition. Discussion of the jump's dynamics in terms of a classical one with respect to s is consistent only within a Markovian approach when jumps are treated as instantaneous, because the dynamics with respect to time τ has principally quantum nature and is an analog of wave function dynamics rather than the dynamics of any classical variable.

5. References

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