

On the theory and MD-simulation of one-photon electronic excitation
of multi-atomic molecules

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ABSTRACT

Quantum description of the molecular dynamics under laser excitation of electronic transitions is reduced to an equivalent classical form. This classical treatment is applied to the molecular dynamics problem and some specific results for one-dimensional case are demonstrated. Absorption probability and laser induced quantum coordinate displacement spectra are calculated.

1. INTRODUCTION

Classical MD methods^{1,2} are in the evident contradiction with the quantum peculiarity of laser molecule excitation. Quantum methods are necessary for description of the initial stage of excitation. If the first stage of the excitation and further evolution can be described separately, classical MD-analyses of further evolution can be employed (Fig. 1). It has been also demonstrated that laser pulse in a two-level electronic molecular system excites essentially delocalized rovibronic states only if pulse duration is not extremely short.³ A good number of calculations of excited states have been produced in a fully quantum manner by computation of the wave functions. This approach however is good only for small molecules and is not effective for multi-atomic molecules which are also of great interest now for example, for biomacromolecules such as rhodopsin, bacteriorhodopsin,⁴ stilbene.⁵

In this work we present a partially analytical way of calculating of excited states characteristics of harmonic systems. The Gaussian operator form technique⁶ is used for the representation of quantum dynamics as oscillations of classical coordinate-momentum pair $X = (x, p)$. Thus we have classical concept that is completely adequate to the quantum description and it can put in accordance the quantum and classical concepts.

2. BASIC FORMULAE

Excited state can be described by the formula of the first order perturbation theory respective to the laser field for the quantum density matrix of the upper electronic state |2>:

$$\hat{\rho}_{22} = \frac{|d_{12}|^2}{4\hbar^2} \iint d\tau_1 d\tau_2 E_L(\tau_1) E_L^*(\tau_2) e^{-i\hat{\delta}_2(t-s)} \hat{\rho}_{22}^0(\tau) e^{i\hat{\delta}_2(t-s)}, \quad (1)$$

where $\tau = \tau_2 - \tau_1$, $s = (\tau_2 + \tau_1)/2$, $E_L(\tau_k)$ is a complex wave function of the laser field with amplitude E_L , d_{12} is an electronic transition dipole moment, \hbar is the Plank constant;

$$\hat{\rho}_{22}^0(\tau) = e^{-i\hat{\delta}_2\tau/2} e^{i\hat{\delta}_1\tau/2} \hat{\rho}_{11}^T e^{i\hat{\delta}_1\tau/2} e^{-i\hat{\delta}_2\tau/2} \quad (2)$$

is generalized density matrix of the vibronic state that excited at a medium moment s starting from the ground electronic state |1> and then being formed during time interval τ by combining dynamics of the both terms |1>, |2>; $\hat{\rho}_{11}^T$ is initial ground equilibrium state with a temperature T ;

$$\hat{\delta}_{1,2} = [\hat{p}^T m^{-1} \hat{p}/2 + U_{1,2}(\hat{x})]/\hbar \quad (3)$$

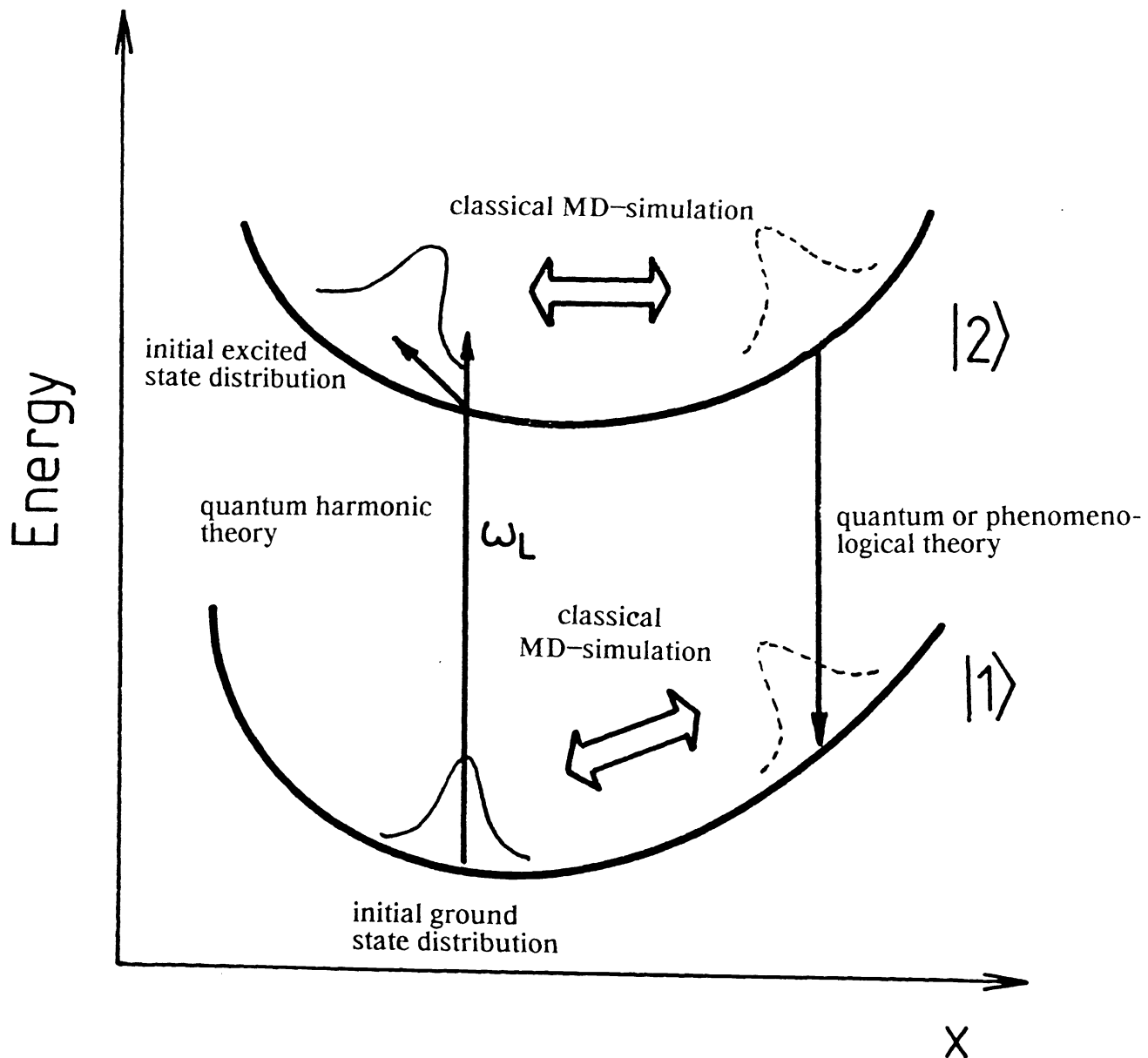


Fig. 1. Stages of MD calculations of molecule dynamics under electronic excitation by laser pulse (ω_L is a laser frequency).

are molecular terms energy operators in frequency units. Due to the harmonicity of both terms expression (2) determines the generalized Gaussian density matrix (see below) and so the correspondent state can be classically interpreted as a result of oscillations of the classical coordinates x and momenta p , initially uncertain because of vacuum and temperature fluctuations given by the Plank formula. Any characteristics of this state may be represented analytically by proper matrix expressions using the frequency and mass matrices for the both molecular terms. In this article we present only calculations of average values of density matrix (2) itself and coordinate-momentum pair x, p .

In expression (1) the transformation $e^{-i\hat{\delta}_2(t-s)}$ determines the free evolution of the upper state by the time $t-s$. This evolution is nothing but classical harmonic oscillations of the upper term only. It may be omitted if the final result depends on the evolution at time intervals, much greater than a laser pulse duration τ_p . Sometimes it is possible for a certain class of problems studied by MD such as isomerization. For the purpose of absorption spectrum calculations it is always possible because of the conservation of the excited state probability at short times $t \sim \tau_p$.

In these cases the subject of interest is the effective density matrix

$$\hat{\rho}_{22}^0 = \frac{|d_{12}|^2}{4\hbar^2} \iint d\tau_1 d\tau_2 E_L(\tau_1) E_L^*(\tau_2) \hat{\rho}_{22}^0(\tau). \quad (4)$$

It is initial density matrix for MD problems connected with the excited state. It is the integral of Gaussian generalized density matrix $\hat{\rho}_{22}^0(\tau)$ if the ground state is Gaussian. It differs mainly from the ground state by average values of coordinates $x_q \neq x_1$ due to the photon energy excess $\hbar\omega_L - (U_2 - U_1)$, where $U_{1,2}$ is calculated for $\hat{x} = x_1$ (the potential energy minimum point of the ground state). So, the full set of the $\hat{\rho}_{22}^0$ -matrix characteristic parameters are:

- $P(\omega_L)$ — quantum transition probability to the excited state |2);
- $\Delta x(\tau)$ — instantaneous mean displacement of X ;
- $X_q = (x_q, p_q)$ — average value of X over pulse duration;
- $K(\tau) = (\langle \dot{X}_i \dot{X}_j - \dot{X}_j \dot{X}_i \rangle_\tau)$ — instantaneous correlation matrix corresponding to $\hat{\rho}_{22}^0(\tau)$;
- \mathbf{K} — average correlation matrix, produced as a result of averaging $K(\tau)$;
- \mathcal{K} — full correlation matrix including fluctuations of displacements, $\mathcal{K} = \mathbf{K} + \langle \Delta x(\tau) \Delta x(\tau) \rangle$.

Using these data one can associate exact MD analyses of molecules excited by a laser pulse. It is useful to note that in contrast to real density matrix $\hat{\rho}_{22}$, the effective one $\hat{\rho}_{22}^0$ is not the eigen state for Hamiltonian $\hbar/\hat{\delta}_2$ even for the stationary conditions at the exact resonance (as in Ref. 3). Somehow it not worth while marking specially the stationary states of the excited level in case of short picosecond pulses.

3. RESULTING FORMULAE

Calculating the value $Tr \hat{\rho}_{22}^0$ for $t \gg \tau_p$ we obtain the following expression for transition probability

$$P(\omega_L) = (\Omega_L^2/4) \int d\tau f_p(\tau) \exp \{i[\omega_L - (\delta_2 - \delta_1)]\tau\} \chi(\tau), \quad (5)$$

where $\Omega_L = E_L d_{12}$ is the Rabi frequency; $f_p(\tau) = \int ds u_p(s - \tau/2) u_p^*(s + \tau/2)$ is the autocorrelation function of complex normalized amplitude u_p ; δ_1, δ_2 are calculated in the point x_1 .

$$\chi(\tau) = \frac{\det \left[\sinh \left(\frac{\hbar\omega_1}{2kT} \right) (sh_1 sh_2)^{-1} \right]}{\det^{1/2}(cth_1/\omega_1 + cth_2/\omega_2) \det^{1/2}(cth_1\omega_1 + cth_2\omega_2)} \times \exp \left\{ -\frac{1}{\hbar} (x_2 - x_1)^T m^{1/2} (cth_1/\omega_1 + cth_2/\omega_2)^{-1} m^{1/2} (x_2 - x_1) \right\} \quad (6)$$

is a generalized function of transition probability for time t while photon excitation of upper term $|2\rangle$ is being formed, x_2 — energy minimum point of the term $|2\rangle$, m is $3N \times 3N$ -mass-matrix if the considered system is N -atomic molecule;¹

$$\begin{aligned} \text{sh}_1 &= \sinh[\omega_1(\hbar/kT - i\tau)/2], & \text{sh}_2 &= \sinh(i\omega_2\tau/2), & \text{ch}_2 &= \cosh(i\omega_2\tau/2), \\ \text{cth}_1 &= \coth[\omega_1(\hbar/kT - i\tau)/2], & \text{cth}_2 &= \coth(i\omega_2\tau/2) \end{aligned}$$

are complex or pure imaginary expressions with ω_1 , ω_2 — frequency matrices for terms $|1\rangle$, $|2\rangle$ (for dissociative term $|2\rangle$ ω_2 is imaginary) and k is the Boltzman constant.

This generalized probability is not actually positive despite the classical character of initial vibrational state ($\Delta x_{\text{vac}} \sim 0.1\text{\AA}$) because of actually quantum interaction with the electron states, but it is definitely positive as an operator kernel and its Fourier transformation is always positive. These resulting formulae give the exact one-photon expression and include vacuum shifts due to vacuum term energies $\hbar\omega_1/2$, $\hbar\omega_2/2$ in contrast to a semiclassical statistical approach including only the exponential factor of Eq. (6).

For average x -coordinate we have:

$$x_q = x_2 + \int p(\tau) \Delta x(\tau) d\tau / P(\omega_L), \quad (7)$$

where $p(\tau)$ is time density of $P(\omega_L)$ (see Eq. (5));

$$\Delta x(\tau) = -m^{-1/2} \omega_2^{-1} \text{sh}_2^{-1} (\text{cth}_1/\omega_1 + \text{cth}_2/\omega_2)^{-1} m^{1/2} (x_2 - x_1) \quad (8)$$

is the displacement at the moment τ respectively to x_2 . For average momenta we have $p_q = 0$. Instantaneous correlation matrix $K(\tau)$ is given by the following expression:

$$K(\tau) = \begin{pmatrix} K_{xx}(\tau) & 0 \\ 0 & K_{pp}(\tau) \end{pmatrix},$$

where

$$K_{xx}(\tau) = \frac{\hbar}{2} m^{-1/2} (\text{cth}_1/\omega_1 \omega_2 \text{sh}_2 + \text{ch}_2)^{-1} (\text{sh}_2/\omega_2 + \text{cth}_1/\omega_1 \text{ch}_2) m^{-1/2}, \quad (9)$$

$$K_{pp}(\tau) = \frac{\hbar}{2} m^{1/2} (\text{cth}_1 \omega_1 / \omega_2 \text{sh}_2 + \text{ch}_2)^{-1} (\text{sh}_2 \omega_2 + \text{cth}_1 \omega_1 \text{ch}_2) m^{1/2}. \quad (10)$$

Eqs. (7)–(10) describe the superposition of the quantum initial fluctuations and the free classical vibrations in the ground state $|1\rangle$ with the following classical vibrations in upper state $|2\rangle$. Using these formulae we can calculate all characteristics of generalized density matrix (2) as for Gaussian case they all can be expressed by resulting $\Delta x(\tau)$ and $K(\tau)$.

In one-dimensional case the mean values x_q , \mathbf{K} for distribution (4) may be easily expressed by the combinations of values $P(\omega_L \pm n\omega_1 \pm l\omega_2)$ due to the periodicity of the corresponding time dependencies. For the case $T = 0$ and $\omega_1 = \omega_2 = \omega$ after integration over time we have

$$x_q - x_1 = (x_2 - x_1) \frac{P(\omega_L) - P(\omega_L - \omega/2)}{P(\omega_L)}. \quad (11)$$

¹Zero subspaces due to the conservation of transitional and rotational integrals must be excluded but corresponding spectrum effects can also be taken into account after adding proper terms.

This expression gives zero displacement for frequencies $\omega_L \simeq \omega_{\max} + \omega/4$ and infinite one for zero absorption. For the correlation matrix at $T = 0$ we have the following expression:

$$\mathbf{K}_{xx} = \frac{\hbar}{2} m^{-1} \omega_1^{-1} \sum k_n(\omega_2/\omega_1) \frac{P(\omega_L) - P(\omega_L - n\omega_2)}{P(\omega_L)}, \quad (12)$$

$$\mathbf{K}_{pp} = \frac{\hbar}{2} m\omega_1 \sum k'_n(\omega_2/\omega_1) \frac{P(\omega_L) - P(\omega_L - n\omega_2)}{P(\omega_L)}, \quad (13)$$

where k_n is the Fourier-coefficients for periodic function $f(\tau) = (1 + \omega_1/\omega_2 \text{th}_2)(1 + \omega_2/\omega_1 \text{th}_2)^{-1}$, $\text{th}_2 = \text{th}(i\omega_2 \tau/2)$, and k'_n — for function $1/f(\tau)$. The corresponding instantaneous fluctuations $K_{xx}(\tau)$, $K_{pp}(\tau)$ are vacuum ones but they do not correspond to the vacuum state of term |2). They are oscillating in a complex region with the values $\hbar/(2m\omega_1)$, $\hbar m\omega_1/2$ at $\tau = 0$ and $\hbar\omega_1/(2m\omega_2^2)$, $\hbar m\omega_2^2/(2m\omega_1)$ at $\tau = \pi/\omega_2$; minimum of the Heisenberg uncertainty conserved but the proper states in a general case are squeezed. These latter equations are valid only for zero temperature, for which the initial states before excitation are illustrated by Fig. 2a. For $T \neq 0$ we can simplify the interpretation of the phenomenon using the representation of T -fluctuations as a result of random displacements of vacuum state (see Fig. 2b). So, in the following operator equations we must use representation $\hat{\rho}_{11}^T = \int p_T(X) U_X \hat{\rho}_{11}^0 U_X^{-1} dX$ with the Gaussian distribution of temperature fluctuation $p_T(X)$ and shift transformation U_X .

The described formulae are the corollary of the the well-known composition rule for operators \hat{X} and Gaussian exponents:

$$\hat{X} e^{-\hat{X}^T Q \hat{X}} = e^{2CQ} e^{-\hat{X}^T Q \hat{X}} \hat{X},$$

where \hat{X} is a vector set of operators \hat{X}_i with scalar commutator

$$C = (\hat{X}_i \hat{X}_j - \hat{X}_j \hat{X}_i).$$

For N -atomic molecules \hat{X} is a $6N$ -vector and Q , C are $6N \times 6N$ -matrices in a vector space of phase coordinates X . For $\Delta X(\tau) = \text{Tr} \hat{X} \hat{\rho}_{22}^0(\tau)/\chi(\tau) - X_1$. Let us represent $\hat{\rho}_{22}^0$ as follows:

$$\hat{\rho}_{22}^0(\tau) = U_2(\tau) U_1(\tau) \hat{\rho}_{11}^T U_1(\tau) U_2(\tau),$$

where U_1 , U_2 , $\hat{\rho}_{11}^T$ are the Gaussian operator forms. Using the above commutation rule we deduce the middle-stage equation with appropriate quadratic form matrices Q_1 , Q_2 corresponding to electronic terms |1), |2):

$$\Delta X(\tau) = (e^{2CQ_2} e^{2CQ_1} e^{2CQ_2} - 1)^{-1} (e^{2CQ_2} e^{2CQ_1} + 1) (e^{2CQ_2} - 1) (X_2 - X_1).$$

After some proper transformations we obtain Eqs. (6), (7) and get the expression

$$K(\tau) = \frac{1}{2} (e^{CQ_1} e^{2CQ_2} - e^{-CQ_1} e^{-2CQ_2})^{-1} (e^{CQ_1} e^{2CQ_2} + e^{-CQ_1} e^{-2CQ_2}) C.$$

To calculate the absorption probability we can use the following expression:

$$\chi(\tau) = \text{Tr} e^{-(\hat{X}-a)^T Q_2 (\hat{X}-a)} e^{-\hat{X}^T Q_1 \hat{X}},$$

with corresponding a , Q_1 , Q_2 . Using also characteristic function technique⁶ we obtain Eq. (5) if in addition to the above we take into account the impossibility to represent the normalization constants as a modula. Using also the technique of Wigner representation we can also get the analytical or computer usable representation of density matrix $\hat{\rho}_{22}^0$ itself. However, it needs using a good number of rather complicated but routine-like transformations of quadratic forms. At the same time many real calculations may be performed without using this representation.

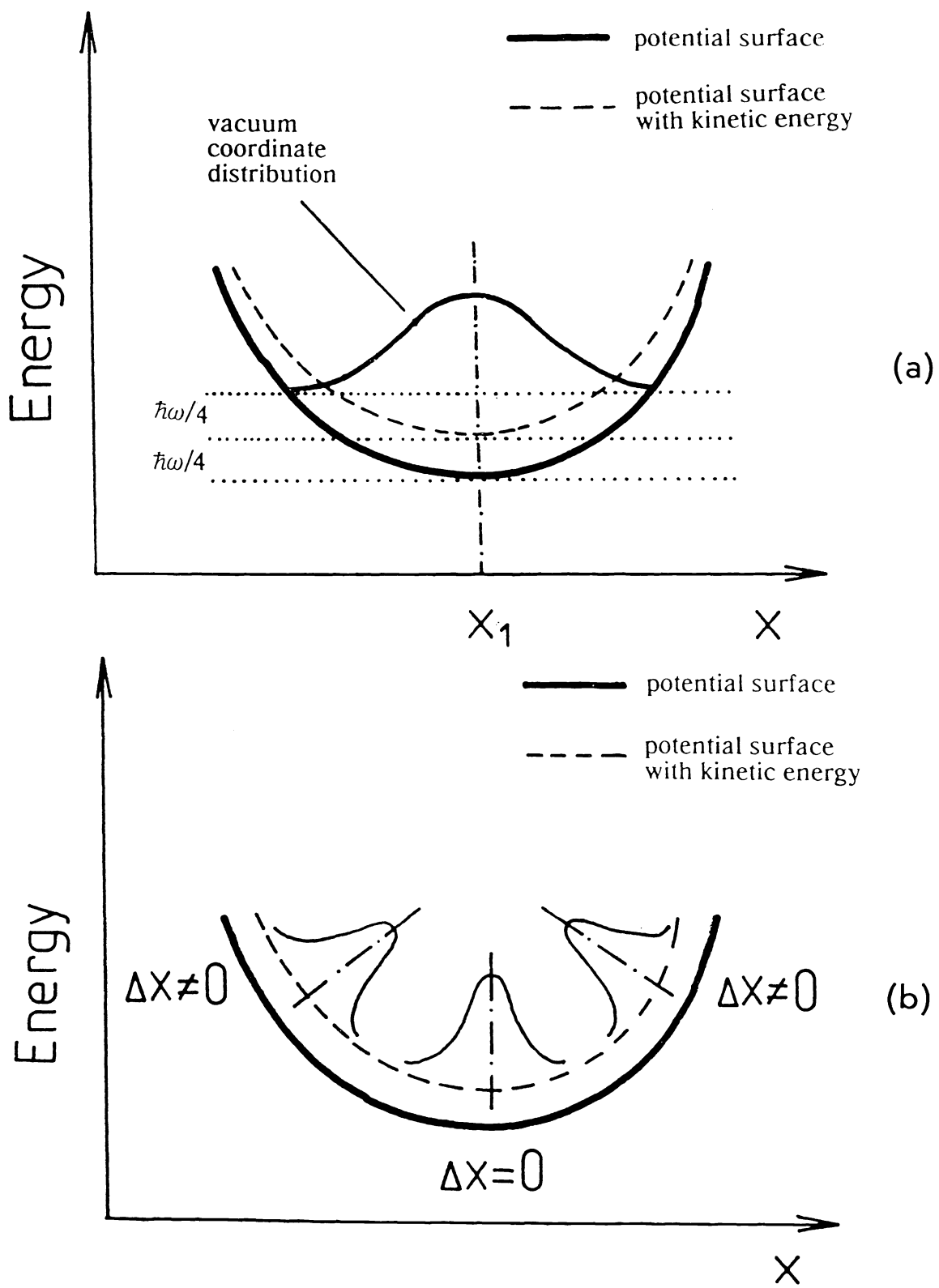


Fig. 2. The structure of the vibronic distribution of ground state: (a) — vacuum state ($T = 0$), (b) — temperature equilibrium state ($T \neq 0$).

4. COMPUTER SIMULATION AND DISCUSSION

In this work we have analyzed the excitation of a one-dimensional harmonic system with two different harmonic terms as a simple model of a real molecule. Calculations for real multi-atomic molecules do not require any special methods and are in progress now. Figures 3–6 show typical spectra of absorption probability in comparison with the same ones for the electronically equal two-level atom and the spectra of x -coordinate displacement for the Gaussian pulse with $\tau_p = 0.5$ ps; electronic transition frequency $\omega_{12} = 10^{15} \text{ s}^{-1}$; mass parameter $m = 1.4 \times 10^{-23} \text{ g}$; vibronic frequency for the ground state $\omega_1 = 10^{13} \text{ s}^{-1}$ and for the excited state $\omega_2 = 10^{13}, 3 \times 10^{13}, 5 \times 10^{13} \text{ s}^{-1}$; temperatures $T = 0, 300 \text{ K}$; terms displacements $x_2 - x_1 = 0, 0.3 \text{ \AA}$.

We can see the following properties of spectra on Figs. 3–6:

- the partially resolved satellite structure of spectra; quantum vacuum shift $(\omega_2 - \omega_1)/2$ ($\omega_2 = 5 \times 10^{13} \text{ s}^{-1}$) and vibronic resonances on additional frequencies $\pm n\omega_2$ for $x_2 - x_1 = 0$ at $T = 0 \text{ K}$ (Fig. 3);
- the Condon frequency shift for $x_2 - x_1 = 0.3 \text{ \AA}$ (Figs. 4, 5, 6);
- the vanishing of resonances at the frequencies below the electronic resonance for the value of $n\omega_1$ at $\omega_1 = \omega_2$ and $T = 0$ (Fig. 4);
- symmetrization of spectral lines at the above frequencies at temperature $T = 300 \text{ K}$ (Fig. 6).

The formation of the probability of the electronic transition is reversible because of the absence of statistical averaging (the entropy of vacuum state is equal to zero). So, we can see the vibronic resonances not only above the electronic one. This is connected with the finite duration of laser pulse. The coordinate displacement x_q which is proportional to $x_2 - x_1$ shows the large maxima at the points of minimum absorption.

The above mentioned rule of zero displacement (see Eq. (11) and the text below) is confirmed by Figs. 4–6. For the laser frequencies below the resonance relation $x_q > 0$ is more typical and at the laser frequencies above the resonance we have $x_q < 0$ (Fig. 4). It is correlated with the main direction of coordinate shift on the potential surface due to the excess of the photon energy (see Fig. 1). In the region of meaningful absorption (Figs. 4, 6). the typical value of the displacement $\Delta x(\tau)$ is about $|x_2 - x_1|$. But it can be infinitely large in the regions of weak absorption (Fig. 5).

For one-dimensional system the computation of one spectral curve on the personal computer IBM PS/2-50 takes about 1 minute. In many-dimensional systems there are two extremely different cases: commuting ($\omega_1\omega_2 - \omega_2\omega_1 = 0$) and non-commuting frequency matrices. For the first one, the calculations based on Eq. (5) do not require independent spectral analyses for different τ because of simultaneous diagonalization of the both matrices ω_1, ω_2 . So, the number of operations increases in $3N$ times for the first case and in $3N \times 3N$ times for the second one.

Therefore, for multi-atomic molecules with terms differing only in displacement $x_2 - x_1$, the calculations described above are really realized by modern computers. There exist a general class of molecules with the commuting frequency matrices of electronic terms. It is represented by molecules with terms differing not only in displacement but in additional scaling transformation $x' - x_2 = \alpha(x - x_1)$ as well. It means that the values of force constants for the both terms are proportional. Sometimes it can be accepted as a good approximation.

5. CONCLUSION

The methods presented in this article based on analytical and classical approach and further computer simulation are applicable for MD analyses of laser excited multi-atomic molecules.

6. ACKNOWLEDGEMENT

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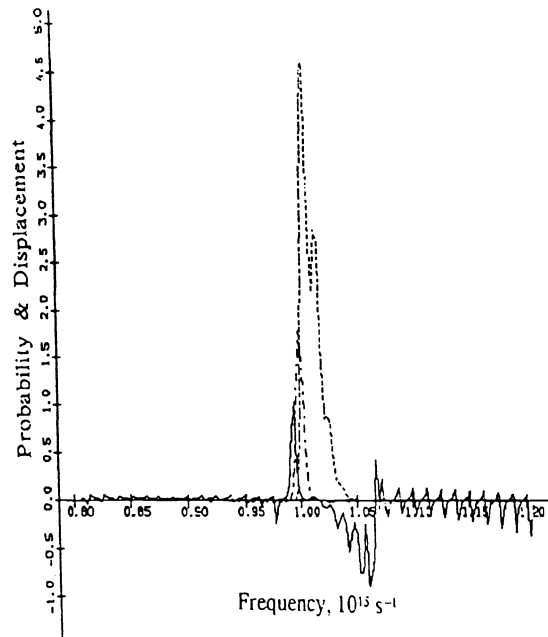
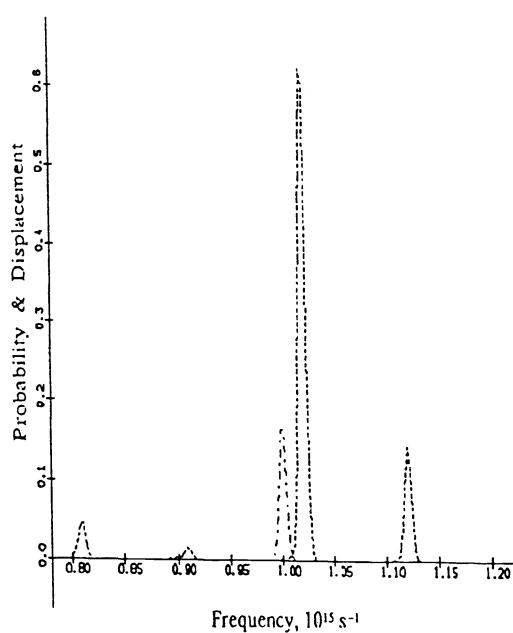


Fig. 3. Probability of absorption and coordinate displacement spectra for one-dimensional case: $x_2 - x_1 = 0$, $T = 0$, $\omega_2 = 5 \times 10^{13} \text{ s}^{-1}$. Solid line: results for coordinate displacement. Dashed line: results for probability of absorption of molecule. Dash-dott line: results for probability of absorption of two-level atom.

Fig. 4. Probability of absorption and coordinate displacement spectra for one-dimensional case: $x_2 - x_1 = 0.3$, $T = 0$, $\omega_2 = 1 \times 10^{13} \text{ s}^{-1}$. Solid line: results for coordinate displacement. Dashed line: results for probability of absorption of molecule. Dash-dott line: results for probability of absorption of two-level atom.

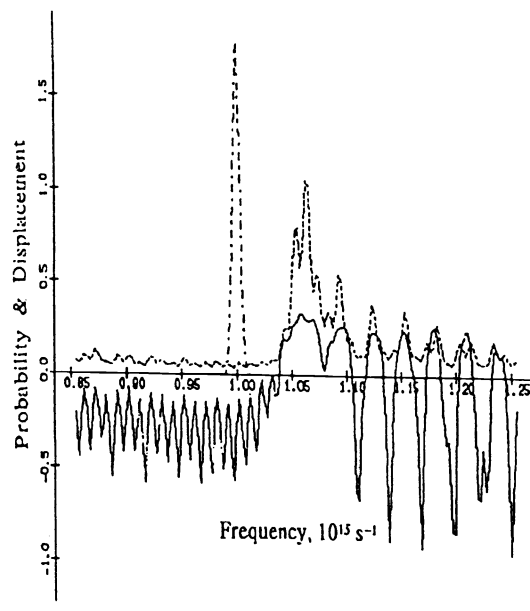
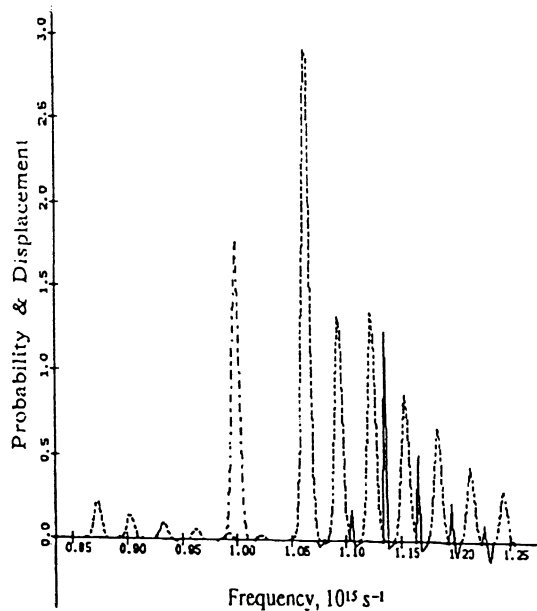


Fig. 5. Probability of absorption and coordinate displacement spectra for one-dimensional case: $x_2 - x_1 = 0.3$, $T = 0$, $\omega_2 = 3 \times 10^{13} \text{ s}^{-1}$. Solid line: results for coordinate displacement. Dashed line: results for probability of absorption of molecule. Dash-dott line: results for probability of absorption of two-level atom.

Fig. 6. Probability of absorption and coordinate displacement spectra for one-dimensional case: $x_2 - x_1 = 0.3$, $T = 300$, $\omega = 3 \times 10^{13} \text{ s}^{-1}$. Solid line: results for coordinate displacement. Dashed line: results for probability of absorption of molecule. Dash-dott line: results for probability of absorption of two-level atom.

7. REFERENCES

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