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COHERENT INTERACTION OF MOLECULAR VIBRATIONS WITH STRONG MONOCHROMATIC LASER LIGHT — CLASSICAL APPROACH*

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We study molecular vibrations in strong monochromatic laser light. The rotating wave approximation if formulated, which allows for analytical discussion of vibrations for moderately strong resonant field. A numerical study of vibrations in very strong fields is also given.

1. Introduction

The importance of the interaction of molecular vibrations with strong laser light has been recognized in the study of isotope separation by strong infrared radiation [1]. It turns out, that SF_6 molecules irradiated by resonant laser pulse dissociate very rapidly, absorbing about 30 photons. The process is isotopically selective if the laser light is in resonance with vibrations of one isotopic component. However, the physics of the dissociation process is not well understood.

It has been argued, that the process of excitation and dissociation by multiphoton absorption can be adequately described in terms of classical mechanics, quantum theory will introduce only small corrections. We will not repeat the arguments, but refer to the beautiful original papers by Lamb [2, 3].

The classical approach to the molecular excitation is much simpler than the quantum one. Although one cannot suppose to obtain excellent quantitative agreement with the experimental data, one can gain insight in the physical process taking place in the molecule. Moreover in the classical approach one is not faced with difficult problems, like spreading of the wave packet, tunneling effects and so on. One can simply discuss the classical trajec-

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tory, which is the solution of Newton's equation of motion. Knowing the trajectory one can easily find all the interesting physical quantities without any other approximations.

The quantum approach to the coherent interaction of the molecules with the resonant radiation has been studied rather extensively in the last few years. The most common approach was to represent the molecule as a many-level system [4]. The laser beam causes transitions between levels, and the dipole moments, or the Rabi frequencies are taken as phenomenological parameters. The Schrödinger equation for such systems can be solved numerically or, in some cases, analytically, and the time dependence of physically interesting quantities can be discussed.

Our classical approach to the problem is closely related to these works. However, all the parameters of the problem are fixed by the choice of the potential rather than being only ad-hoc introduced to the model. Since the potential has a realistic shape there is no possibility of finding non-physical results.

A lot of work on the forced non-linear oscillator used the so-called Duffing equation [5]:

$$\ddot{x} = -\omega_0^2 x + \beta x^2 + F \cos \omega_L t,$$

where ω_0, $\beta > 0$, F, ω_L are parameters, as an example. This is often considered to be the simplest generalization of the linear forced oscillator equation. We will not be specially interested in this equation, it does not represent a realistic molecular force due to the repulsive part βx^2, dominant for large x. We will however, comment rather frequently on the corresponding results known for the Duffing equation.

It has been argued in the quantum approach to multiphoton processes that the coherent interaction of vibrations with laser light cannot lead to dissociation. One has to add various assumptions about the interaction of vibrations with other degrees of freedom of the molecule. A similar result will be found in the classical approach — coherent interaction with the laser field does not lead to dissociation, unless for an extremely strong field.

In the present work we study in some detail molecular vibrations in the presence of a driving monochromatic force. We shall not restrict ourselves to the case of weak fields and discuss the trajectory in strong fields as well. For realistic fields we will give an analytical treatment of the motion. The use of action-angle variables, together with the assumption of resonance, allow one to formulate the rotating wave approximation (RWA) [6]. The general features of the trajectory can be found in this approximation, and in some special cases, equations of motion in RWA can be solved exactly. It will be shown that in RWA the trajectory is bounded, hence this approximation does not allow for dissociation. The influence of other terms (non RWA) in the equations of motion is studied in perturbation theory up to second order. It is shown that these terms give rise to a frequency shift (the Stark shift) and to high frequency corrections to the trajectory. However, the trajectory remains bounded $|x(t)| < L$ for some L for all t, hence there is no dissociation. These features are confirmed by numerical calculations.

The above results are valid for relatively small values of the applied driving field. In the case of strong driving fields we failed to find a suitable approximation method and our results are based on numerical calculations only. We find that for field strength below some critical value the weak field approximation holds and the trajectory is bounded. For field strength above the critical value the trajectory is unbounded — dissociation takes place very rapidly, the time needed for dissociation is of the order of one optical cycle. In other words our numerical calculations predict a sharp dissociation threshold — dissociation does not occur for fields below the threshold, and is very rapid above the threshold.

The problem whether the trajectory is bounded or not is closely related to the similar one for the case of the Duffing equation. The latter one has been studied extensively in the literature (see Ref. [5]) both from the mathematical and physical point of view. Although the potentials in our case and in the Duffing case differ significantly for large x, our results about the existence of a threshold are in qualitative agreement with the Duffing case.

Montroll et al. (Ref. [5]) predict that in the Duffing case, if the driving force is in exact resonance the trajectory is unbounded for any nonzero amplitude of the force. It turns out that in our case the trajectory seems to be bounded for sufficiently small values of the resonant driving force, or at least is bounded for a rather long time. Because of the anharmonic frequency shift and fieldinduced shift it seems rather unlikely, that the exact resonance of the driving force with the bare frequency should be distinguished.

Of course, these results do not apply to complex molecules, like SF_6, where the interaction of vibrations with other degrees of freedom seems to be strong and is, in fact, responsible for the dissociation. Our approach is suitable rather for simpler molecules, like diatomic ones, where there is only one mode of vibrations. It has been shown experimentally [5] that diatomic molecules do not dissociate in a strong laser pulse, contrary to the case of SF_6. This fact is in qualitative agreement with our results.

2. *Action-angle variables and equations of motion*

Let us consider the motion of a particle subject to a driving oscillating force and a time independent potential. Although we will not assume any particular form of the potential, we will have in mind the general features of a molecular potential. It has a minimum around which it can be approximated by a harmonic potential $-\frac{1}{2}m\omega_0^2(x-x_0)$; for $x \to \infty$ it goes to 0; and for $x \to 0$ it tends to ∞. A specific example, the Morse potential, is discussed in detail in Section 5.

Our discussion of the motion will be based on the Hamilton equations in action-angle variables. These variables are well known in classical mechanics. We refer to standard textbooks for their detailed discussion [7]. Here we shall give main definitions only and restrict ourselves to one dimensional systems.

Let x and p describe the trajectory of a bound system in the phase space. Define the action variable as:

$$I = \frac{1}{2\pi} \int p dx,$$

where the integration is taken over the closed trajectory. The angle variable φ is, by definition, the canonically conjugate coordinate to I.

The total energy of the system is a function of I only. The Hamilton equations of motion are:

$$\dot{\varphi} = \frac{\partial E}{\partial I} \equiv \omega(I),$$

$$\dot{I} = -\frac{\partial E}{\partial \varphi} = 0.$$

The trajectory $x(t)$ can be expressed as a function of I and φ:

$$x = x(I, \varphi).$$

Since x is periodic, one can expand it into Fourier series:

$$x(I, \varphi) = \sum_{n=-\infty}^{\infty} c_n(I) \exp(in\varphi). \tag{1}$$

This formula will be extensively used later.

Let us include now the interaction with the laser field. We will use the dipole approximation; therefore the interaction Hamiltonian is

$$H_1 = -e\mathscr{E} \cos(\omega_{\mathrm{L}} t) x(I, \varphi),$$

where e is the electric charge, $\mathscr{E}$ the field amplitude, ω_{L} the laser frequency and x the position of the particle. If we make use of the Fourier expansion we may write

$$H_1 = -e\mathscr{E} \cos \omega_{\mathrm{L}} t \sum_{n=-\infty}^{\infty} c_n(I) \exp(in\varphi). \tag{2}$$

From the total Hamiltonian $H = H_0 + H_1$ the canonical equations follow:

$$\dot{\varphi} = \omega(I) - e\mathscr{E} \cos \omega_{\mathrm{L}} t \sum_{n=-\infty}^{\infty} \frac{dc_n}{dI} \exp in\varphi, \tag{3a}$$

$$I = e\mathscr{E} \cos \omega_{\mathrm{L}} t \sum_{n=-\infty}^{\infty} c_n(I) in \exp in\varphi. \tag{3b}$$

These equations form the basis of our discussion. If we solve (3) for I and φ we may find the particle trajectory from the formula (1).

Of course Eqs (3) cannot be solved exactly (except in the case of the harmonic oscillator). We will therefore study various approximations and also give a numerical example.

3. *The rotating wave approximation*

Our main approximation will be based on the fact that the laser frequency is very close to the fundamental frequency of the motion. To be more precise, let $\omega(I) \to \omega_0$ for $I \to 0$. For very small I (small excitation) the motion is nearly harmonic, with frequency

ω_0. We assume that $\omega_L \approx \omega_0$. Under this assumption on the right-hand side of Eqs (3) we may find slowly varying terms and rapidly oscillating terms. Dropping the rapidly varying terms and retaining slowly varying ones is known as the rotating wave approximation (RWA). In this approximation we find:

$$\dot{\varphi} = \omega(I) - \tfrac{1}{2}\, e\mathscr{E}\left[\frac{dc_1}{dI} \exp i(\varphi - \omega_L t) + \text{c.c.}\right], \tag{4a}$$

$$\dot{I} = \tfrac{1}{2}\, e\mathscr{E}[ic_1 \exp i(\varphi - \omega_L t) + \text{c.c.}]. \tag{4b}$$

We will now discuss these equations. Let us first introduce a new variable $\chi = \varphi - \omega_L t$, Eqs 4 take form

$$\dot{\chi} = \omega(I) - \omega_L - \tfrac{1}{2}\, e\mathscr{E}\left[\frac{dc_1}{dI} \exp i\chi + \text{c.c.}\right], \tag{5a}$$

$$\dot{I} = \tfrac{1}{2}\, e\mathscr{E}[ic_1 \exp i\chi + \text{c.c.}]. \tag{5b}$$

Note, that we do not have explicit time dependence on the right-hand side of (5a) and (5b).

Equations (5) are of Hamiltonian form for I and χ. Therefore the "Hamiltonian". is a constant of motion. One can easily find that the "Hamiltonian" is given by

$$H = E(I) - \omega_L I - \tfrac{1}{2}\,[c_1(I) \exp i\chi + \text{c.c.}], \tag{6}$$

where $E(I)$ is the energy of the initial problem, expressed as a function of I.

With the help of this constant one can eliminate χ and obtain an equation for I alone. We have

$$\dot{I} = \{(\tfrac{1}{2}\, e\mathscr{E})^2 c_1(I) c_{-1}(I) - (H - E(I) + \omega_L I)^2\}^{1/2}. \tag{7}$$

This first order equation gives the time dependence of I in the rotating wave approximation.

We will solve this equation for the particular case of the Morse potential in Section 5. Here we will give some qualitative discussion only. Let $\mathscr{E} = 0$; then (7) reads:

$$\dot{I} = \{-(H - E(I) + \omega_L I)^2\}^{1/2}.$$

It may seem that this is a contradictory result, because of the negative quantity under the square root sign. However, from (6) we find (for $\mathscr{E} = 0$)

$$H = E(I) - \omega_L I,$$

hence $\dot{I} = 0$ in this case.

For $\mathscr{E} > 0$ the right-hand side of Eq. (7) depends strongly on the shape of the functions $c_1(I)$ and $E(I)$. In the case we are interested in, namely that of molecular vibrations, these functions do not depend critically on the details of the potential, and their typical form is plotted in Figs. 1, 2. Hence the right-hand side of equation has a typical form shown in Fig. 3.

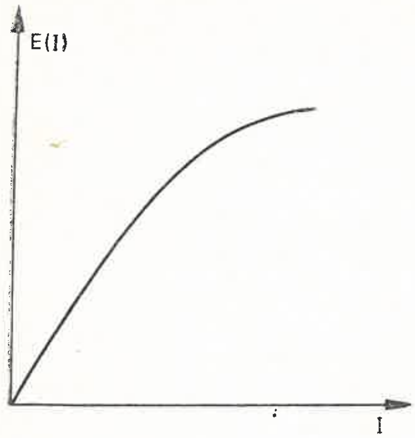

Fig. 1

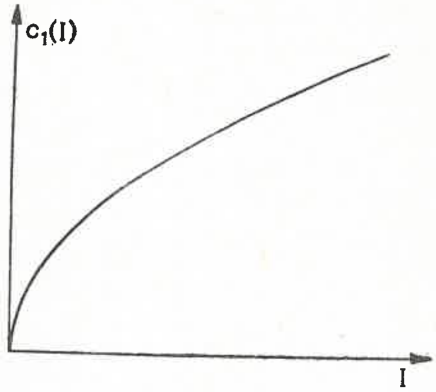

Fig. 2

Fig. 1. Typical form of $E(I)$
Fig. 2. Typical form ot $c_1(I)$

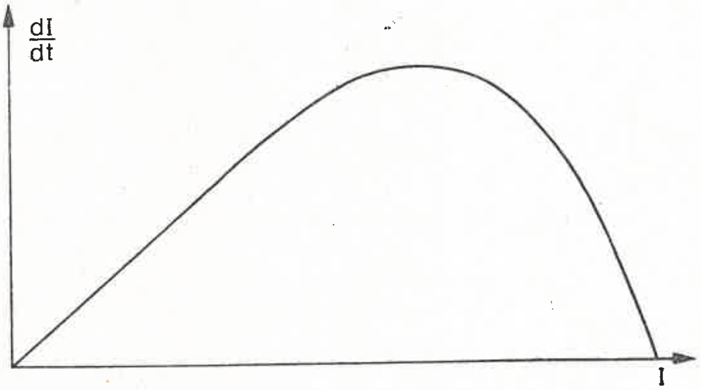

Fig. 3. Typical form of $\frac{dI}{dt}$

From this typical shape it can be seen that I performs oscillations between two roots of the equation

$$\left[\tfrac{1}{2}\, e\mathscr{E} c_1(I)c_{-1}(I)\right]^2-(H-E(I)+\omega_L y)^2 = 0.$$

We will solve Eq. (7) explicitly for the case of the Morse potential.

4. *First and second order corrections to the RWA — the frequency shift*

Let us now study corrections to the rotating wave approximation. We will show, that there are two kinds of corrections. The first kind are the rapidly oscillating terms which should be added to I and φ calculated from the approximate Eqs (4a) and (4b). The other term is the frequency shift. This may be called "AC classical Stark shift", and will be calculated below.

Let

$$\varphi = \varphi^{(0)}+\varphi^{(1)}+ \dots, \tag{8a}$$

$$I = I^{(0)}+I^{(1)}+ \dots, \tag{8b}$$

where $\varphi^{(0)}$, $I^{(0)}$ satisfy Eqs (4a) and (4b) and φ, I are solutions of full Eqs (3a) and (3b). The first order corrections $\varphi^{(1)}$ and are $I^{(1)}$ given by:

$$\varphi^{(1)} = \int^{t} dt' \left[\frac{d\omega}{dI} I^{(1)} - e\mathscr{E} \sum_{n}{}' \cos \omega_{\mathrm{L}} t' \frac{dc_n}{dI} \exp in\varphi^{(0)} \right], \tag{9a}$$

$$I^{(1)} = -e\mathscr{E} \int^{t} dt' \sum_{n}{}' \cos \omega_{\mathrm{L}} t' c_n in \exp in\varphi^{(0)}, \tag{9b}$$

where $\sum'$ means that the resonant terms are excluded. These integrals cannot be worked out exactly. The reason is that $I^{(0)}$ and $\varphi^{(0)}$ are time dependent. We may, however, make use of the fact, that the time dependence of $I^{(0)}$ and $\varphi^{(0)}-\omega_{\mathrm{L}}t$ is slow compared to ω_{L}. This is true, of course, for fields not too strong. In this case we may calculate the integrals adiabatically, approximating $I^{(0)}(t')$ by $I^{(0)}(t)$ and $\varphi^{(0)}(t')$ by $\omega(I^{(0)}(t))t'+\chi^{(0)}(t)$. Such a procedure leads to:

$$\begin{aligned} \varphi^{(1)} = -e\mathscr{E} \sum{}' \Bigg\{ & \frac{d\omega}{dI} c_n in \tfrac{1}{2} \left[\frac{\exp(in\omega+i\omega_{\mathrm{L}})t}{(in\omega+i\omega_{\mathrm{L}})^2} + \frac{\exp(in\omega-i\omega_{\mathrm{L}})t}{(in\omega-i\omega_{\mathrm{L}})^2} \right] \\ & + \tfrac{1}{2} \frac{dc_n}{dI} \left[\frac{\exp(in\omega+i\omega_{\mathrm{L}})t}{in\omega+i\omega_{\mathrm{L}}} + \frac{\exp(in\omega-i\omega_{\mathrm{L}})t}{in\omega-i\omega_{\mathrm{L}}} \right] \Bigg\}, \end{aligned} \tag{10a}$$

$$I^{(1)} = e\mathscr{E} \sum{}' c_n in \tfrac{1}{2} \left[\frac{\exp(in\omega+i\omega_{\mathrm{L}})t}{in\omega+i\omega_{\mathrm{L}}} + \frac{\exp(in\omega-i\omega_{\mathrm{L}})t}{in\omega-i\omega_{\mathrm{L}}} \right]. \tag{10b}$$

Note that $\varphi^{(1)}$ and $I^{(1)}$ are oscillatory, i.e. their time average is zero.

We will not reproduce formulas for the seond order corrections here. We will state only, that the second order correction to I, i.e. $I^{(2)}$ has no d.c. term, in other words its time average is zero.

On the other hand, the second order correction to $\varphi^{(2)}$ contains a d.c. term. It is given by

$$\begin{aligned} \dot{\varphi}^{(2)} = \tfrac{1}{2}(e\mathscr{E})^2 \sum_{n=0}^{\infty}{}' \Bigg\{ & n^2 c_n c_{-n} \frac{d^2\omega}{dI^2} \left[\frac{1}{(n\omega+\omega_{\mathrm{L}})^2} + \frac{1}{(n\omega-\omega_{\mathrm{L}})^2} \right] \\ & - n^2 c_{-n} \frac{dc_n}{dI} \frac{d\omega}{dI} \left[\frac{1}{(n\omega+\omega_{\mathrm{L}})^2} + \frac{1}{(n\omega-\omega_{\mathrm{L}})^2} \right] \\ & + n^2 c_{-n} \frac{d^2 c_n}{dI^2} \left[\frac{1}{n\omega+\omega_{\mathrm{L}}} + \frac{1}{n\omega-\omega_{\mathrm{L}}} \right] \Bigg\} + \text{a.c. terms}. \end{aligned} \tag{11}$$

The d.c. term given above represents a frequency shift due to the interaction with the oscillating field. Contrary to the a.c. terms, the d.c. term causes systematic deviations of the solutions of the Eqs (3a, b) from the corresponding solutions found in the rotating wave approximation. However, if one takes the corrected value of the frequency in the Eqs (4 a, b) one finds that the RWA solutions follow the exact solutions for all times.

It is interesting that there is no d.c. contribution, at least in the second order, to $I^{(2)}$. Therefore, the solution of the full Eqs (3a, b) should be qualitatively the same, as the solutions of Eqs (4a, b), i.e. the action variable, or the energy, should be oscillatory. In other words there is no net energy uptake from the oscillating field by a nonlinear oscillator.

There is an attempt to use the above model (possibly with quantum corrections) to describe the multiphoton dissociation of molecules, particularly the widely discussed SF_6 molecule. It follows from our results, however, that a purely coherent interaction of radiation with an anharmonic oscillator cannot lead to a rapid energy growth, hence dissociation. What seems to be responsible for the rapid energy uptake from the laser field by the molecule is a strong coupling between the resonant vibrational mode of the molecule with other degrees of freedom [1, 2]. Our model does not take into account those effects, hence is applicable to such molecules, where coupling of an oscillatory mode to other modes is much weaker, e.g. diatomic molecules. Experimentally, the multiphoton dissociation of diatomic molecules has not been observed, although attemps were made (see Ref. [1]), that confirms, at least qualitatively our results.

5. *Example-motion of a charged particle in the Morse potential*

We will illustrate our results in one example-motion of a charged particle in the Morse potential with a harmonic driving force. The Morse potential is used very often as a suitable analytical model for molecular vibration. It allows for the analytical solution for the anharmonic vibrations.

The Morse potential is given by:

$$U(x) = U_0[2\exp(-2x/a)-\exp(-x/a)].$$

Let us find first the free motion (without external force) in this potential. The Newton equation:

$$m\ddot{x} = -\frac{dU(x)}{dx}$$

can be easily solved:

$$x(t) = -a\left\{\ln\frac{\omega^2(E)}{4\omega_0^2}-\ln\left[1-\left(1-\frac{\omega^2(E)}{\omega_0^2}\right)^{1/2}\cos\omega(E)(t-t_0)\right]\right\},$$

where $\omega_0^2 = \frac{U_0}{4ma^2}$ is the frequency near the potential minimum, $E < 0$ is the total energy, $\omega^2(E) = -\frac{2E}{ma^2}$ and t_0 is the initial time. Positive values of E correspond to unbounded motion. We will not discuss it here. The simplicity of the above solution allows one to find explicitly action-angle variables. One finds

$$\varphi = \left(\frac{-2E}{ma^2}\right)^{1/2} (t-t_0) = \omega(E)\,(t-t_0), \qquad (12a)$$

$$I = (-2ma^2E)^{1/2} - (\tfrac{1}{4}\, ma^2U_0)^{1/2} = (-2ma^2E)^{1/2} - I_0. \qquad (12b)$$

Note, that I is a constant, and is a function of energy only.

One can find the trajectory $x(E, t, t_0)$ as a function of I and φ:

$$x(I, \varphi) = -a\left\{\ln\frac{(I_0-I)^2}{4I_0^2} - \ln\left[1 - \left(\frac{I(I-2I_0)}{I_0^2}\right)^{1/2}\cos\varphi\right]\right\}. \qquad (13)$$

The Fourier coefficient for $x(I, \varphi)$ can also be found:

$$c_n = \frac{a}{n}\left[\frac{I}{2I_0-I}\right]^{n/2}, \quad n > 0 \qquad (14)$$

$$c_{-n} = c_n.$$

In particular

$$c_1(I) = a\left[\frac{I}{2I_0-I}\right]^{1/2}.$$

Let us introduce dimensionless variable $\beta = I/I_0$. We have

$$c_1(\beta) = a\left(\frac{\beta}{2-\beta}\right)^{1/2}, \qquad (15)$$

$$\omega(\beta) = \omega_0(1-\beta). \qquad (16)$$

Let us discuss now the influence of the external driving harmonic force. Eqs (5 a, b) now read:

$$\dot{\chi} = \omega_0(1-\beta) - \omega_L - e\mathscr{E}a/I_0\,\frac{d}{d\beta}\left[\frac{\beta}{2-\beta}\right]^{1/2}\cos\chi, \qquad (17a)$$

$$\dot{\beta} = -e\mathscr{E}a/I_0\left[\frac{\beta}{2-\beta}\right]^{1/2}\sin\chi. \qquad (17b$$

Let us now find the explicit form of the Eq (7) for the Morse potential. We find

$$\dot{\beta} = 1/I_0\left[(e\mathscr{E}a)^2\,\frac{\beta}{2-\beta} - (H - \tfrac{1}{2}\,\omega_0 I_0\beta^2)^2\right]^{1/2}, \qquad (18)$$

or, in dimensionless units ($\tau = \omega_0 t$, $F = 4e\mathscr{E}a/U_0$):

$$\frac{d\beta}{\tau} = \tfrac{1}{2}\left[F^2\,\frac{\beta}{2-\beta} - \left(\frac{8H}{U_0}\right)^2 + 2\,\frac{8H}{U_0}\,\beta^2 - \beta^4\right]^{1/2}. \qquad (19)$$

Denote $\frac{8H}{U_0}$ (the ratio of the initial energy to the binding energy) by b. Note also, that one can neglect β as compared to 2 (the excitation cannot be large), we find

$$\frac{d\beta}{d\tau} = \tfrac{1}{2}\left[\frac{F^2}{2}\beta - b^2 + 2b\beta^2 - \beta^4\right]^{1/2}. \tag{20}$$

This equation can be solved in terms of elliptic functions. In the case $b = 0$ (initially there was no excitation) one finds

$$\beta(t) = \left(\frac{F}{2}\right)^{1/3}\left\{1 + \left[m - n\,\mathrm{tg}\left[\alpha + \mathrm{sn}_{\frac{2\sqrt{p_1 p}}{p_1+p}}\left(\frac{p+p_1}{8}\left(\frac{F}{2}\right)^{1/3}(t-t_0)\right)\right]\right]^2\right\}^{-1}, \tag{21}$$

where

$$m = [\tfrac{1}{2}(\sqrt{3}-\tfrac{3}{2})]^{1/2}, \quad n = [\tfrac{1}{2}(\sqrt{3}+\tfrac{3}{2})]^{1/2}, \quad p = 2\cdot 3^{1/4}, \quad p_1 = (2\sqrt{3}-3)^{1/2},$$

$$\mathrm{ctg}\,\alpha = \left[\frac{(p+p_1)^2 - 4n^2}{4n^2 - (p-p_1)^2}\right]^{1/2},$$

sn is the elliptic sine and t_0 is determined from the condition $\beta(t = 0) = 0$. We will not quote the result for $b \neq 0$ because it does not introduce new features.

Numerical calculations have been done to visualize the trajectory of a charged particle in Morse potential under the influence of driving harmonic force. Similar calculations can be found in Ref. [3]. The following conventions have been used.

We have assumed that the driving force is in resonance ($\omega_L = \omega_0$). The dimensionless distance and time have been defined

$$y = x/a, \quad \tau = \omega_0\tau.$$

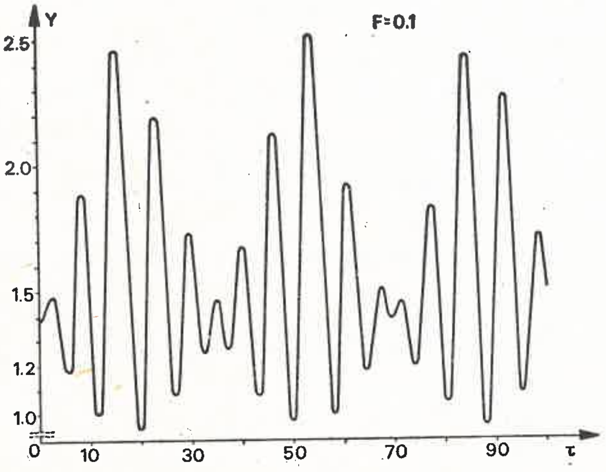

Fig. 4

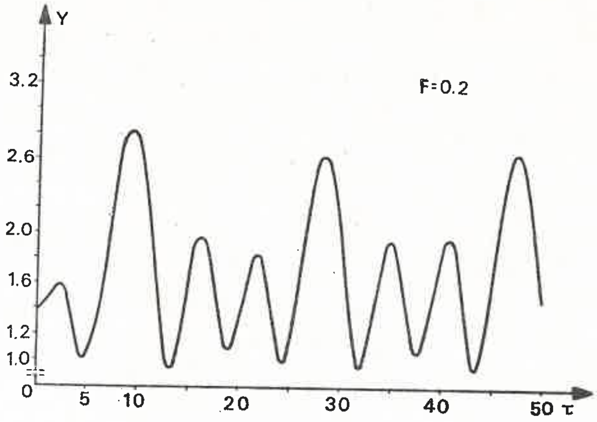

Fig. 5

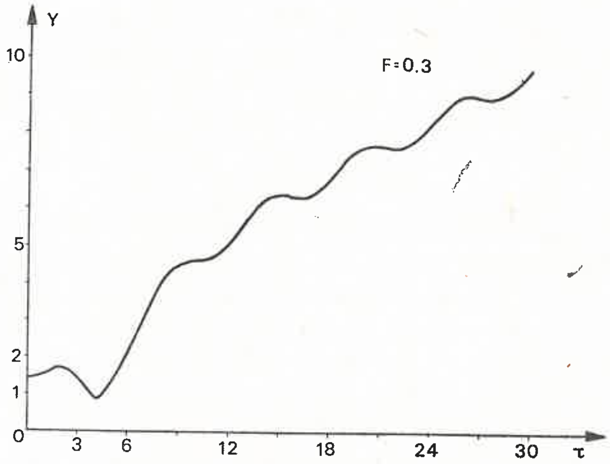

Fig. 6

Fig. 4–6. Trajectories in Morse potential and oscillating field for various field strengths

Newton equations are now

$$\frac{d^2y}{d\tau^2} = 4[4\exp(-2y)-\exp(-y)]+F\cos\tau,$$

where $F = 4e\mathscr{E}a/U_0$.

Note, that F is the ratio of the interaction energy with the field $e\mathscr{E}a$ to 2 times the binding energy.

In the case of weak fields ($F < 0.3$) the trajectory is bounded. One can see that the particle oscillates with the frequency of the driving field, the amplitude of these oscillations is modulated with a smaller frequency λ. One can check, that formula (21) gives the correct value of this frequency. Higher frequency components are not seen on the plots. Notice, that the amplitude does not show any tendency to systematic growth. Although this statement cannot be treated as a proof that the trajectory is bounded for all values of time, it provides nevertheless, together with the perturbative analysis of Section 4, a very strong indication, that the trajectory remains bounded for very large times.

The case of strong fields $F > 0.3$ has also been studied numerically. Notice the dramatic change in qualitative behavior of the trajectory for $F < 0.3$ and $F > 0.3$. In the latter case the trajectory is open, contrary to the previous one. The disintegration of the system is very rapid, in fact the particle remains "bounded" for time of the order of one optical cycle. Similar problem was studied extensively for the case of Duffing equation (see Ref. [4] and references quoted therein). Similar thresholds exist in this case too. It is, however, rather hard to compare these two cases due to the repelling part of the potential in the Duffing case.

It is doubtful, whether these results have any physical significance. In fact values of F larger than 0.3 correspond to light intensities $I \gtrsim 10^{16}\,\mathrm{W/cm^2}$. Such high intensities are not accessible, and will not be accessible soon.

Nevertheless, we think that it is interesting from the mathematical point of view to realize the dramatic difference in solutions of Newton equations for different values of the driving force.

6. Conclusions

We have studied motion of a particle bounded in a potential subject to a driving harmonic force. The driving field was assumed to be close to the resonance with the fundamental frequency in the potential. Particular attention was paid to the case of relatively weak driving forces, since only such are experimentally accessible. Under these conditions the rotating wave approximation can be used to find the motion. We have shown, that the trajectory in this case is relatively simple: the action-angle variables oscillate around their steady state values. These oscillations have been discussed thoroughly.

Experimental verification of our results can be provided by the study of the fluorescence spectrum of a molecule illuminated by a strong resonant laser light. The trajectory $x(t)$ in this case has (in the rotating wave approximation) many Fourier components, hence the spectrum should have a multi-peak structure. Similar three peak structure of the fluorescence spectrum has been recently found in two level systems [8]. It must be noted, however, that in the two-level systems the separation between the central peak and the side-bands is equal to the Rabi frequency, hence is a linear function of the driving force. In our case the seperation is given by a much more complicated formula. Therefore the analogy with the two-level systems is not very close.

It is evident from our results that coherent interactions of vibrations with monochromatic driving field cannot lead to dissociation. As we mentioned in Section 4, in a complex molecule, like SF_6, interaction of vibrations with other degrees of freedom cannot be neglected. This effect is responsible for the energy uptake by complex molecules and for the dissociation.

The strong field limit of Newtons equation is studied in this paper numerically only. This point of the work is of less physical importance, because lasers of such power do not exist. Nevertheless one can gain some insight into the limits of applicability of the weak field approximation.

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