Effective potential method for calculation of wave-packet propagation and atomic collision dynamics

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(Received 2 April 1990; revised manuscript received 13 December 1990)

With the advent of laser pulses of ultrashort duration, the possibility of exploring the details of atomic collision phenomena has become a reality. However, the estimate of the duration of pulse that is expected to produce new effects is made difficult as it crucially depends on the details of the interatomic potential, the collision time, as well as the characteristics of the wave packets describing the atoms. Following the effective potential approach developed by Basu and Sengupta (unpublished) to study the wave-packet propagation in a potential field, we have evaluated the trajectories and the pulse duration necessary for different wave packets. The method has been applied to the investigation of two atomic systems, one of which has also been studied by others. The results obtained for the Na-Ar system are found to compare favorably with those calculated by the split operator method. Also, the present method has the advantage of being direct and simple, and the error may easily be estimated. A comparison of the two methods is also given in the Appendix. Finally, the present study also predicts for the Ne-Ar system that the expected new effects may be observed with the available experimental facility.

I. INTRODUCTION

The recent advances in the study of atomic collision dynamics [1] have been stimulated by the development of laser pulses of very short duration in the femtosecond time domains [2]. In contrast to a long nanosecond pulse, these short pulses offer the possibility of probing the collision dynamics in greater detail and altering the same, as the pulse irradiates only a portion of the collision event since its duration is much smaller than the normal collision time. It seems to affect the dynamics in novel ways. The explanation of the pulse duration effect is quite transparent. It may be understood as follows. Let us consider the collision of two atoms in presence of a radiation field, and R_c, the internuclear separation, is defined at which the potential energy difference between the ground state and an excited state equals the applied radiation energy $\hbar\omega$. During the process of collision the atoms cross R_c twice, once on the inward journey and again on the outward. If the pulse duration is smaller than the time between these crossings ΔT_c, an excitation of the system may be induced at the first crossing, and while it will be absent during the second crossing, with a pulse time larger than ΔT_c this cannot be achieved as the presence of the pulse at the second crossing may produce deexcitation. In the previous case the exclusion of the latter deexcitation is expected to produce new and interesting effects. However, in actual experiments other complexities will be present. Still the duration of pulse is a very crucial and important parameter for a specific pair of atoms or molecules participating in a collision.

Although the ultrashort laser pulses at present are available with facility, the theoretical estimates for ΔT_c are neither readily available nor precise enough to guide and suggest suitable experiments of where to look for the desired effect. The difficulties mainly stem from the absence of any standard, easily tractable method of computing explicit time dependence of wave-packet propagation in a potential field. Although the time-dependent Schrödinger equation in principle provides the exact theoretical framework for the wave-packet propagation, few calculations involving various situations have been reported so far. The previous theoretical investigation by Lee and George [3,4] and Sizer and Raymer [5], using constant velocity classical trajectories, has been shown to be inadequate by DeVries [6] who has employed the split-operator method due to Fleck, Morris, and Feit [7] to compute the trajectory of the wave packet for an estimate of ΔT_c. The split-operator method envisages the evolution of the wave packet in time by taking a series of Fourier transforms, followed by the multiplication of inverse transforms and others. As the wave packet propagates in time the expectation value of the mean position of the packet has to be evaluated at each step which ultimately leads to the desired trajectory. The approximation involved in splitting the operator has an error $O(t^3)$. (See the Appendix for further discussion of this point.)

Even though it is feasible to implement the above program, it is still very difficult to apply and manipulate in particular for an arbitrary potential. It seems worth looking for a simple yet accurate method for such estimates, which is one of the main objectives of the present work. Recently Basu and Sengupta [8] studied in detail the dependence of scattering cross section on the nature of the incident wave packet in the case of scattering by an arbitrary potential. The various wave packets considered in the investigation show quite rich structure in the scattering phenomena. The result obtained for the case of a narrow wave packet localized both in configuration as well as momentum spaces propagating in a potential field has particular relevance to the present problem. It is found that the method, which may be termed an

effective potential approach, leads to an exact result for an oscillator potential (see the Appendix for details). In the present investigation we shall employ this method for an estimate of trajectories and ΔT_c's for two specific systems. In Sec. II we briefly discuss the method and its advantages over existing ones. In Sec. III we consider an application of the method to the collision dynamics of the Na-Ar system that compares favorably with the results obtained by DeVries and also predicts the possibility of observing the desired novel effect for another new system, namely, the Ne-Ar system under the presently available experimental facilities. In the last section we discuss the results of the present investigation and also some of the limitations of the present approach.

II. EFFECTIVE POTENTIAL APPROACH FOR THE COLLISION DYNAMICS

Following the method suggested by Basu and Sengupta [8] we consider a normalized wave packet in the three-dimensional space given by

$$\psi_k(\mathbf{r},t)=\frac{1}{(2\pi)^{3/2}}\frac{1}{\left[\sigma+\frac{i\hbar t}{2\pi\sigma}\right]^{3/2}}e^{i[kz-(\hbar k^2 t/2m)]} \times\exp\left[-\frac{\xi_1^2+\xi_2^2+(z+z_0-hkt/m)^2}{4\sigma^2+2ikt/m}\right], \quad (1)$$

where

$$\xi_1=x-x_0,\quad \xi_2=y-y_0,\ \text{etc.},$$

which represent a quantum-mechanical dynamical state of a free atom with mean position $\langle\mathbf{r}\rangle=\mathbf{r}_0+\hbar\mathbf{k}t/m$; $\mathbf{r}_0=(x_0,y_0,-z_0)$, mean momentum $\langle\mathbf{p}\rangle=\hbar\mathbf{k}$; $\mathbf{k}=(0,0,k)$, spatial width

$$\Delta x=\Delta y=\Delta z=\left[\sigma^2+\frac{\hbar^2t^2}{4\sigma^2m^2}\right]^{1/2},$$

and momentum width $\Delta p_x=\Delta p_y=\Delta p_z=\hbar/2\sigma$.

At $t=0$, the maximum of $|\psi_k|^2$ is located at $\mathbf{r}_0$, which moves along the z axis with a momentum $\hbar k$. If the time interval t is such that

$$\frac{\hbar^2t^2}{4\sigma^2m^2}\ll\sigma^2, \quad (1a)$$

the spatial width of the packet remains constant within this interval. Now if the scatterer is at the origin, which generates a potential $V(\mathbf{r})$, the mean position vector satisfies the following equation.

$$m\frac{d^2}{dt^2}\langle r_\alpha\rangle=-\left\langle\frac{\partial V}{\partial r_\alpha}\right\rangle, \quad (2)$$

where the expectation values are taken with respect to the packet $\Phi(\mathbf{r},t)$, which is a solution of the time-dependent Schrödinger equation

$$-\frac{h^2}{2m}\nabla^2\Phi+v\Phi=i\hbar\frac{\partial}{\partial t}\Phi \quad (3)$$

with $\Phi(\mathbf{r},0)=\psi k(\mathbf{r},0)$.

Next, expanding $V(\mathbf{r})$ about $\langle\mathbf{r}\rangle$ we get

$$\left\langle\frac{\partial V}{\partial r_\alpha}\right\rangle=V_\alpha^{\rm cl}+\tfrac{1}{2}\sum_\beta(\langle r_\beta^2\rangle-\langle r_\beta\rangle^2)V_{\beta\beta\alpha}^{\rm cl} +\sum_{\beta\,(>\gamma)}(\langle r_\beta r_\gamma\rangle-\langle r_\beta\rangle\langle r_\gamma\rangle)v_{\beta\gamma\alpha}^{\rm cl}+\cdots \quad (4)$$

with $V^{\rm cl}=V(\langle\mathbf{r}\rangle)$ and $V_\alpha^{\rm cl}=\partial/\partial\langle r_\alpha\rangle V(\langle\mathbf{r}\rangle)$.

If we now assume that the packet is narrow so that the higher-order terms in Eq. (4) may be neglected, that the potential field does not change the spatial width of the packet, and that the spreading effect is small over the relevant time interval, we can rewrite Eq. (4) as

$$\left\langle\frac{\partial V}{\partial r_\alpha}\right\rangle=V_\alpha^{\rm cl}+\sigma^2\frac{\partial}{\partial\langle r_\alpha\rangle}\nabla^2V^{\rm cl}. \quad (5)$$

It is to be noted that the wave packet has the characteristic $\langle r_\beta r_\gamma\rangle=\langle r_\beta\rangle\langle r_\gamma\rangle$, for $\beta\neq\gamma$, etc. By substituting Eq. (5) in Eq. (2), we find that the mean position vector of the packet traces out a track which is the same as that of a classical particle moving under a potential field given by

$$V_{\rm eff}(\mathbf{r})=V(\mathbf{r})+(\sigma^2/2)\nabla^2V(\mathbf{r}), \quad (6)$$

having the initial position $\mathbf{r}_0$ and momentum $\hbar\mathbf{k}$. In the present case under investigation for the atomic collision, the isotropic interatomic potential $V(r)$ is given by

$$V(r)=V_{\rm at}(r)+\hbar^2l(l+1)/2\mu r^2, \quad (7)$$

where the second term represents the centrifugal barrier for the atomic motion having angular momentum l, and the first term is the atom-atom potential.

In the following we carefully discuss the real restrictions on the time interval over which the present approach is valid. Equation (1a) indicates that the time interval should be sufficiently short while Eq. (4) stresses the fact that the wave packet has to be narrow. In order to check whether these two conditions are simultaneously satisfied in the real systems that we consider in our present work, we explicitly introduce the time dependence of the wave packet,

$$V_{\rm eff}(\mathbf{r},t)=V(\mathbf{r})+[\sigma^2(t)/2]\nabla^2V(\mathbf{r}), \quad (6')$$

where

$$\sigma^2(t)=\sigma_0^2+(\Delta p_0t/m)^2$$

which is really the spreading law for a free wave packet [9]. There is another contribution to this spreading effect due to the potential field on the width of the packet which has been found to be insignificant in the cases discussed here. Inclusion of this time dependence in the effective potential will clearly indicate the range of validity of the present approach.

The atomic potential $V_{\rm at}$ in Eq. (7) has been extracted from the molecular-beam scattering experiments for a number of atom pairs. The present study employs the potential energy curve of Saxon, Olson, and Liu [10] for the Na-Ar pair which has also been used by DeVries [6]. The curve is fitted with high accuracy to the Simons-Parr-Finland modification of Dunham (SPF-Dunham)

parametrized form [10], given by

$$V(r)=\epsilon f(x)\ ,$$
$$f(x)=b_0\lambda^2\left[1+\sum_{n=1}^{6} b_n\lambda^n\right]-1\ , \tag{8}$$
$$x=r/r_m\ ,\quad \lambda=1-1/x$$

in the desired region.

The same form (8) was earlier fitted to the potential for the Ne-Ar system given by Candori, Pirani, and Vecchiocattivi [11], which is favored over others in the analysis of high-resolution differential cross-section data by Beneventi, Casavecchia, and Volpi [12] and is used in the present study of the Ne-Ar system. The potential parameters are given in Table I. The equation of motion is then solved numerically using Rungge-Kutta method for V_{eff} with the initial conditions obtained from the corresponding experimental situation.

Before we present our calculation it may be pointed out how the above method compares with the standard quantum-mechanical calculations. In the Appendix we consider the case of an oscillator potential and demonstrate that the above method gives the exact result, whereas the operator method of Fleck, Morris, and Feit used by DeVries is only approximate. However, since both are approximate for an arbitrary potential we shall compare them in the next section.

III. RESULTS AND DISCUSSIONS

The results of the present calculations are shown in Figs. 1–4. For the Na-Ar system the present results compare broadly with that of DeVries. In both methods the wave packet never reaches the classical turning point and rebounds earlier (both in space and time), the nearest approach (for $l=0$) being 6.70 a.u. in the present calculation and 6.66 a.u. according to DeVries. However, there exist important differences between the two results. It seems the $\langle r\rangle - t$ curves for the two wave packets, having different widths given by DeVries, follow the same path in the asymptotic region; whereas it is quite definite from Figs. 1(a) and 1(b) that the wave packets with different widths follow different paths in the asymptotic region. This may be understood as follows. From Eqs. (6) it is clear that the effective potential depends upon the width of the wave packet and the effective potential is different for different wave packets. Moreover as we have included the time dependence of the width of the packet, this effective potential will also vary with time. Naturally if we consider a point particle moving in different potential fields it will describe different paths. However, it should be noted that the change of width as given by Eq. (6′) does not invalidate the restrictions imposed by Eqs. (1a) and (4) for the wave packets considered.

It may be mentioned that the different trajectories for wave packets differing in width have also been obtained by DeVries who has used a totally different formulation for the evaluation of the wave-packet trajectory. In Fig. 1 of Ref. 6 the difference between the two trajectories corresponding to wave packets having widths of 0.5 a.u. and 2 a.u. is found to be quite pronounced near the turning point, the narrower packet describing a path that reaches closer to the classical turning point than that of the wider one. This is both qualitatively and quantitatively similar to the results obtained in the present investigation. While existing formulations of the wave-packet

TABLE I. Potential parameters.

	Na-Ar	Ne-Ar[a]
ϵ (meV)	6.806	5.74
r_m (a.u.)	9.50	6.65
b_0	17.028	41.50
b_1	−1.932	−3.9673
b_2	2.291	5.0580
b_3	2.238	−3.7908
b_4	−20.552	11.5590
b_5	−38.935	−8.4038
b_6	−18.927	−11.9501

[a]Reference [12].

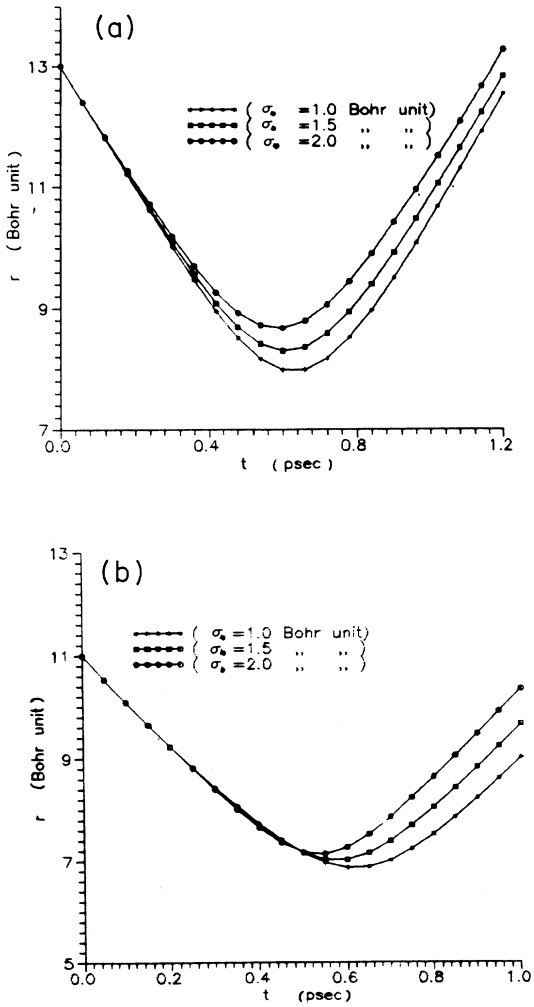

FIG. 1. Wave-packet position $\langle r\rangle$ plotted as a function of time for angular momentum $L=50\hbar$ for three different spatial widths (σ) for (a) Na-Ar and (b) Ne-Ar systems.

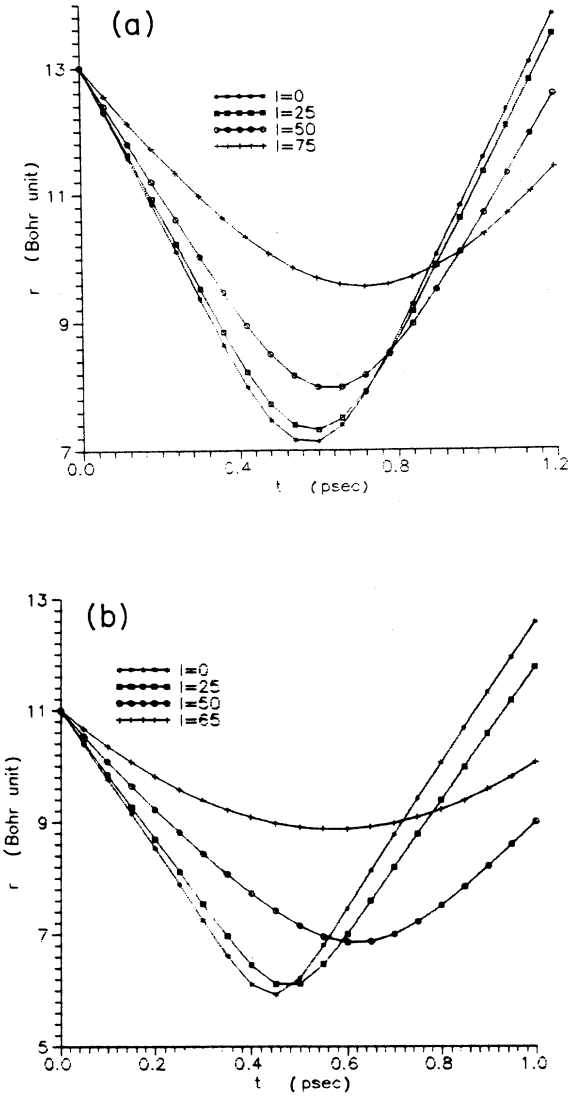

FIG. 2. Wave-packet position $\langle r \rangle$ plotted as a function of time for $\sigma = 1.0$ a.u. for three different l values for (a) Na-Ar and (b) Ne-Ar systems.

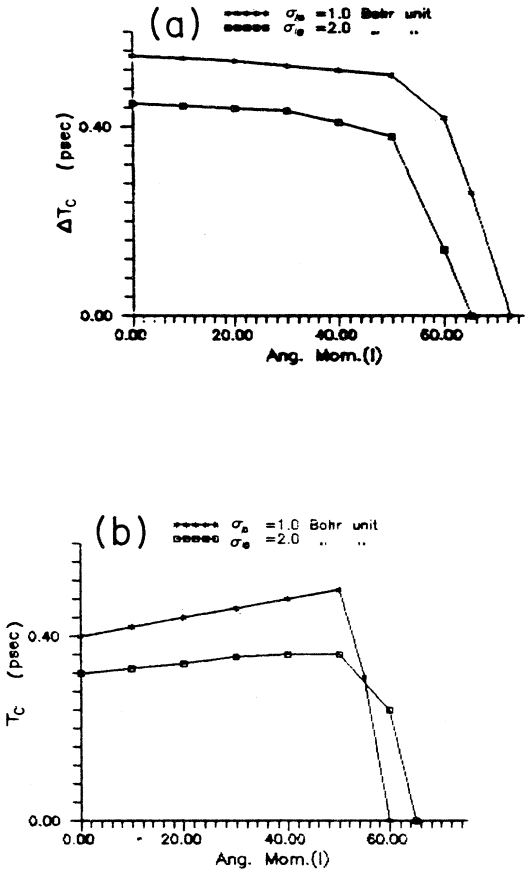

FIG. 3. Time between curve crossings plotted as a function of incident angular momentum for two different σ values for (a) Na-Ar and (b) Ne-Ar systems.

propagation imply separate trajectories for different widths of wave packets in the same potential, it remains to be verified experimentally.

In order to have a quantitative estimate of the spreading of the wave packets considered over the time of collision we have calculated the same and found that it is at most 12% and 10% for Na-Ar and Ne-Ar systems, respectively. Both the cases are consistent with Eqs. (6'), (4), and (1a). The effect of spreading of the wave packet on its trajectory is shown in Fig. 4. Moreover, it is also clear that the width attained by each packet at the nearest separation is smaller than the distance of the closest approach which is also essential for the validity of the present method of calculation.

However, a similar conclusion is reached regarding the wave-packet-width dependence of the time interval ΔT_c between curve crossing—the more delocalized the wave packet, the smaller is ΔT_c (Figs. 3). Also ΔT_c is maximum for a head on ($l=0$) collision and is less than 0.6 ps (0.75 ps according to DeVries) for Na-Ar with $\sigma = 0.5$ a.u., providing an upper limit on pulse duration capable of altering the collision dynamics. Beyond a certain value of l, $\Delta T_c = 0$, i.e., no radiative transition is possible. Also the difference between the narrow and broad

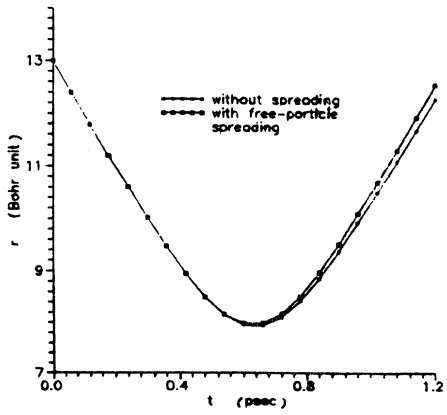

FIG. 4. $\langle r \rangle - t$ curves with and without spreading with a packet of initial width $\sigma_0 = 1.0$ Bohr unit and $l = 50$.

packets increases with increasing angular momentum. We also present the calculation for the Ne-Ar system for which V_{at} is also available, and an experimental search for the desired effect may be undertaken. Nonavailability of any estimation of R_c, of course, precludes any precise definition of ΔT_c in this case. However, for $R_c=8$ a.u., ΔT_c is maximum for $l=0$ and for a wave packet maximum value of ΔT_c varies between 0.35 ps and 0.5 ps for σ_0 in the range 1–2 a.u. With a laser pulse spanning this region, it is likely that the effect may be observed.

In conclusion it may be stated that the present approach using the effective potential provides a simple method for estimating the different parameters characterizing the collision dynamics and gives accurate results comparable to more elaborate and difficult programs.

APPENDIX

Following is the propagation of a wave packet in an oscillator potential by the split-operator method. Let $\psi_0=\bar{\psi}_0(x-x_0)e^{ik_0x}$ be the initial wave packet localized with a peak at $x=x_0$ and $\langle p\rangle=\hbar k_0$, and $\bar{\psi}_0(x-x_0)$ is an even function of $x-x_0$. Consider the Fourier expression of $\bar{\psi}_0(x-x_0)$,

$$\bar{\psi}_0=\int g(k)e^{ik\xi}dk \ .$$

Now if $\bar{\psi}_0(\xi)$ is an even function of ξ, $g(k)$ is also even in k and vice versa.

Following Fleck, Morris, and Feit [7] we can write

$$\psi_t\simeq e^{-i(t/2h)T}e^{-iVt/h}e^{-i(t/2h)T}\psi_0 \ .$$

Then, with the kinetic energy operator $T=-(\hbar^2/2m)d^2dx^2$, the successive operators are given below:

$$e^{-itT/2h}\psi_0=e^{ik_0x_0}\int e^{-i\beta(k+k_0)^2}g(k)\times e^{i(k+k_0)\xi}dk$$

$$\beta=\hbar t/4m \ , \quad \xi=x-x_0$$

$$=\psi_1(\xi-2\beta k_0)e^{ik_0\xi}P$$

where P represents the phase factor and $\psi_1(z)$ is an even function of z. In the following we ignore the phase factor as it does not affect the calculation of $\langle x\rangle$. Again, we set

$$\psi_2=e^{-iVt/\hbar}e^{ik_0\xi}\psi_1(\xi-2\beta k_0)$$

and expanding $V(x)$ about x_0 in powers of ξ, we may write, ignoring the phase factor,

$$\psi_2\approx e^{ik_0\xi-it\xi/\hbar(V'+V''\xi/2)}\psi_1(\xi-2\beta k_0)$$

$$=e^{i(k_0-tV'/\hbar)(z+2\beta k_0)}e^{-(itV''/2\hbar)(z+2\beta k_0)^2}\psi_1(z) \ ,$$

where

$$z=\xi-2\beta k_0=e^{i\gamma z}e^{-(itV''/2\hbar)z^2}\psi_1(z)$$

$$\gamma=k_0-tV'/\hbar-2\beta tk_0V''/\hbar$$

$$=e^{i\gamma z}\int g_2(k)e^{ikz}dk \ ,$$

where $g_2(k)$ is the Fourier transform of $\psi_1(z)e^{-(itV''/2\hbar)z^2}$ and is even in k.

Finally,

$$e^{-itT/2\hbar}\psi_2=\int e^{-i\beta(k+\gamma)^2}g_2(k)e^{iz(k+\gamma)}dk$$

$$=\int e^{-i\beta k^2}g_2(k)e^{ik(z-2\beta\gamma)}e^{i\gamma z}dk$$

$$=e^{i\gamma z}\psi_t(z-2\beta\gamma) \ ,$$

But $\psi_t(z-2\beta\gamma)$ is an even function of the argument. Hence

$$\langle x\rangle=x_0+\langle x-x_0\rangle=x_0+\int\xi|\psi_t|^2d\xi=x_0+2\beta(k_0+\gamma)$$

$$=x_0+\frac{\hbar t}{2m}(2k_0-tV'/\hbar-t^2k_0V''/2m)$$

$$=x_0+t(\hbar k_0-V't/2-\hbar k_0V''t^2/4m)/m \ . \tag{A1}$$

If $V=\alpha x^2/2$, $V_0'=-\alpha x_0/m=\omega^2x_0$, and $V_0''=\alpha$, then

$$\langle x\rangle=x_0-\frac{\omega^2x_0}{2}t^2+p_0t(1-\omega^2t^2/4)/m \ . \tag{A2}$$

In the present effective potential method, the bare harmonic oscillator potential $V(x)=\alpha x^2/2$ for a wave packet with a spatial width σ will be modified according to Eq. (6) as follows:

$$V_{\text{eff}}(x)=V(x)+\sigma^2\nabla^2(\alpha x^2/2)$$

$$=V(x)+\sigma^2\alpha=V(x)+v^* \ . \tag{A3}$$

This dressed potential yields the exact solution for the trajectory given by

$$\langle x\rangle=x_0\cos\omega t+(p_0/m\omega)\sin\omega t$$

$$=x_0(1-\omega^2t^2/2+\omega^4t^4/24+\cdots)$$

$$+(p_0/m)(t-\omega^2t^3/6+\cdots) \ . \tag{A4}$$

It should be noted here that the spreading effect of the wave packet has been assumed to be small in Eq. (A3) so the time of measurement has to be small. Even this assumption can be lifted for a coherent state of the oscillator which gives a nonspreading wave packet [13],

$$\psi(x,0)=Ne^{-[(x-a)/2\sigma]^2}$$

$$\sigma^2=\hbar/2m\omega \ , \quad a=\text{ classical amplitude}$$

from which it follows that

$$\langle E \rangle_{qm} = ma^2\omega^2/2 + \hbar\omega/2 = E_{\rm cl} + \hbar\omega/2 \ .$$

According to our analysis the additional potential $V^* = \sigma^2\alpha$ given by (A3) becomes

$$V^* = \sigma^2\alpha = \hbar\omega/2 \ .$$

Thus according to the present approach the coherent packet will execute a classical motion, but will have an additional energy of $\hbar\omega/2$. Additionally, comparing Eqs. (A2) and (A4) we find that the split-operator method agrees with the exact result only up to an order of t^2.

[1] For a recent review see H. F. Arnoldus, T. F. George, K. S. Lam, J. P. Scipione, P. L. DeVries, and J. M. Yuan, in *Laser Applications in Physical Chemistry,* edited by D. K. Evans (Dekker, New York, in press).
[2] *Ultrashort Laser Pulses,* edited by W. Kaiser (Springer-Verlag, New York, 1988).
[3] H. W. Lee and T. F. George, J. Phys. Chem. **83**, 928 (1979).
[4] H. W. Lee and T. F. George, Phys. Rev. A **35**, 4977 (1987).
[5] T. Sizer and M. G. Raymer, Phys. Rev. Lett. **56**, 123 (1986).
[6] P. L. DeVries, Phys. Rev. A **37**, 981 (1988).
[7] J. A. Fleck, Jr., J. R. Morris, and M. D. Feit, Appl. Phys. **10**, 129 (1976).
[8] A. N. Basu and S. Sengupta (unpublished).
[9] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1974), Vol. 1, p. 222.
[10] R. P. Saxon, R. E. Olson, and B. Liu, J. Chem. Phys. **67**, 2692 (1977).
[11] R. Candori, F. Pirani, and F. Vecchiocattivi, Chem. Phys. Lett. **90**, 202 (1982).
[12] L. Beneventi, P. Casavecchia, and G. G. Volpi, J. Chem. Phys. **84**, 4828 (1986).
[13] S. M. Roy and V. Sing, Phys. Rev. D **35**, 3413 (1982).