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UNCERTAINTY PRINCIPLE IN CLASSICAL MECHANICS: APPLICATION TO COLLINEAR COLLISIONS

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Classical theory of collisions is formulated which also includes uncertainty principle. The theory is used for the calculation of transition probabilities in the collinear He-H_2 collision, and the results are compared with quantum calculations. Very good agreement is found.

1. Introduction

Investigation of the relationship between quantum and classical theory is of great interest and importance. Quantum theory is more fundamental than classical theory, however latter often gives physical insight into the processes governing the dynamics of a system. This is clearly manifested in the application of classical theory in the analysis of atom-molecule collissions [1,2], where it helps understanding of the scattering cross sections [3-5]. Furthermore, classical theory is an initial value problem, while the problems in quantum mechanics are both boundary and initial value problems. Therefore, classical theory is usually easier to implement.

By putting the uncertainty principle into classical mechanics one can improve its results for the problems where there was a substantial discrepancy between quantum and classical theory. Various tests have been made, ranging from nonrelativistic [6-8] to relativistic [9,10] systems, and in all the cases classical theory gave virtually the same answers as quantum theory. The dynamics of unbound particles was described in an almost total accord with quantum theory [6,9,10]. However, the problems where encountered in describing the excited states of bound particles [7,8]. Here, we present a sligthly more general approach that can overcome those difficulties.

2. *Classical theory of bound states*

One of the major problems is finding the stationary states of bound particle, and if properly solved – in the frames of classical theory – a number of classical studies could be carried out, including the atom-molecule collision problem of this paper. The new approach to classical theory is based on two assumptions: the coordinate and the momentum of a particle are uncertanity, i.e., they are represented by the probability distribution and those distributions are mutually related. The precise form of the relationship between the probability distribution in the coordinate $P(x)$ and the probability distribution in its momentum $Q(p)$ is difficult to guess without making reference to the basic principles of quantum theory, but in principle one could think of various ways of doing it. We will take this relationship from quantum theory, in which case the distributions are related by (for simplicity we work in one dimension):

$$P(x) = |\psi(x)|^2; \qquad Q(p) = |\phi(p)|^2 \tag{1}$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \mathrm{d}p \phi(p) e^{ipx/\hbar}. \tag{2}$$

Here, $\psi(x)$ and $\phi(p)$ are just auxiliary functions; the physics is in $P(x)$ and $Q(p)$.

Discussion of the time dependence of the probability distributions is made more general by working in the phase space, where one defines the density $\rho(x, p, t)$ with the following properties: The total amount of probability in a volume element should be conserved, hence

$$\rho(x, p, t)\mathrm{d}x\mathrm{d}p = \rho_0(x_0, p_0, t_0)\mathrm{d}x_0\mathrm{d}p_0 \tag{3}$$

where p and x are related to x_0 and p_0 by the classical equations of motion. It follows then that the density ρ obeys the Liouville's equation

$$\frac{\partial\rho}{\partial t} + \frac{p}{m}\frac{\partial\rho}{\partial x} + F\frac{\partial\rho}{\partial p} = 0 \tag{4}$$

where F is force which acts on the particle and m is mass of the particle. The probability densities P and Q are obtained from ρ by

$$P(x,t) = \int \mathrm{d}p\rho(x,p,t) \qquad Q(x,t) = \int \mathrm{d}x\rho(x,p,t). \tag{5}$$

If analysis in the phase space gives more general overview of the properties of P and Q, and they are related by (1) and (2), the question obvious to ask is: can $\rho(x,p,t)$ be related to the function $\psi(x,t)$? The answer is not simple, but various approximate forms can be readily found. Among them is the Wigner's function [11,12]

$$\rho(x,p,t) = \frac{1}{2\pi\hbar} \int \mathrm{d}y\psi(x+y/2)\psi(x-y/2)e^{-ipy/\hbar} \tag{6}$$

which has been used for various purposes [13-15], but basically to define the phase space quantum theory. We discuss entirely classical theory, the only reference to quantum theory being the relationships (1) and (2). In this respect the discussion is different from Wigner's, because his starting point is quantum theory and the classical phase density is obtained as the limit $\hbar \to 0$ of the function ρ [11,15,16,17]. This is not the correct assumption because classical theory cannot be regarded as the limiting case of the quantum theory, when the Planck constant goes to zero. Our analysis will confirm this, showing that the classical results are virtually the same as quantum, even when the ground state of particle is involved (hence the state for which this limit is not valid).

The function (6) is not positive definite but there is nothing to prevent us from using it as the phase space density in a more general sense, i.e. by defining negative phase space densities. Still, if ρ is to be regarded as the phase space density it has to satisfy the Liouville's equation (4), and this requirement will provide the condition that ψ should satisfy in order this to be true.

The force F in (4) can be replaced by $-\delta V/\delta x$, and providing that the second and higher derivatives of $V(x)$ go to zero it can be shown that ρ satisfies the Liouville's equation if ψ satisfies the equation

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x,t)\psi. \tag{7}$$

We have solved in this way the problem of time evolution of $P(x,t)$ which was defined in (1) and (2), and which satisfies Eq. (7). This equation is exact for harmonic potential and approximate for any other potential. The stationary states of bound particle are characterized by the time independence of the distributions $P(x,t)$ and $Q(p,t)$. This criterion has its physical significance since the time dependent probability distribution of a charged particle radiates. Therefore, for the stationary states $\psi(x,t)$ satisfies

$$\frac{\mathrm{d}P(x,t)}{\mathrm{d}t} = \frac{\mathrm{d}\psi}{\mathrm{d}t}\psi^* + \psi\frac{\mathrm{d}\psi^*}{\mathrm{d}t} = 0. \tag{8}$$

The equation (8) suggests that we should seek the solution for the stationary states in the form

$$\psi(x,t) = \psi_0(x)e^{-iEt/\hbar}. \tag{9}$$

Then Eq. (7) reduces to

$$E\psi_0 = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0 x^2\right]\psi_0 \tag{10}$$

where we have assumed that particle is bound by a harmonic potential, ω_0 being its characteristic angular frequency. As it is well known, the equation has solutions only for discrete values of E if ψ_0 is to be physically acceptable. E is the average total energy because using Eqs. (1) and (2) from the definition of average total energy of the particle

$$\overline{E} = \int \mathrm{d}p\frac{p^2}{2m}Q(p) + \int \mathrm{d}xV(x)P(x) \tag{11}$$

one can reproduce Eq. (10) for the ψ_0. The discrete values for the energy are

$$E = \omega_0\hbar(n+1/2) \tag{12}$$

where $n = 0, 1, 2, \ldots$ The appropriate functions $\psi_0(x)$ are

$$\psi_0(x) = NH_n\left(x\sqrt{\lambda}\right)\exp\left(-\lambda x^2\right) \tag{13}$$

where N is a constant that ensures that $P(x,t)$ is normalized to unity, H_n is Hermite polynomial, and $\lambda = m\omega_0/\hbar$. Therefore, the classical theory predicts infinite number of discrete probability distributions that are stationary. The first few phase space densities ρ are

$$\begin{aligned}\rho_0 &= \frac{1}{\pi\hbar}e^{-u/\hbar} \\ \rho_1 &= \frac{1}{\pi\hbar}(2u/\hbar - 1)e^{-u/\hbar} \\ \rho_2 &= \frac{1}{\pi\hbar}(2u^2/\hbar^2 - 4u/\hbar + 1)e^{-u/\hbar}\end{aligned} \tag{14}$$

where $u = p^2/m\omega_0 + m\omega_0 x^2$.

These densities will be used in the study of atom – molecule collisions.

3. *Atom – molecule collinear collision*

In this section we develop classical theory for calculating transition probabilities in a collinear collisions problem, in which atom approaches diatomic molecule along the molecular axis. The internal coordinate of the molecule is designated by x, while the relative separation of the incoming atom and the centre of mass of the molecule is y. The molecule is approximated by harmonic oscillator. Initially, say at $t = 0$, the atom and the molecule are well separated, the molecule being in the bound state n_0 described by the phase space density $\rho_{n_0}(x, p)$ and the atom is localized around some initial position, its probability density given by $P_a(y)$. The overall probability density is $P_0(x, y)$ and it is interpreted as the probability of finding atom at the distance y and molecule being streched by x.

Classical equations of motion for the system we consider, in the centre of mass of three atoms, for the case of homonuclear diatomic molecule, are

$$\frac{2mM}{2mM + M}\ddot{y} = \frac{\partial V(y - x/2)}{\partial y} \tag{15}$$

$$\frac{m}{2}\ddot{x} = -\kappa x + \frac{1}{2}\frac{\partial V(y - x/2)}{\partial y} \tag{16}$$

where M is mass of the incoming atom and m is mass of one of the atoms in the homonuclear diatomic molecule. The potential of the diatomic molecule is assumed to be the one of harmonic oscillator, of the form $\kappa x^2/2$, and the potential between the incoming atom and the molecule is assumed to be a function of the distance $y - x/2$. In the calculations we will assume that the potential V is repulsive, of the form $V_0 \exp\left[-\alpha\sqrt{\lambda}(2y - x)\right]$, where α and V_0 are constants and $\lambda = m\omega/(2\hbar)$. This form is assumed in order to compare our classical results with the quantum calculations of Secrest and Johnson [19].

The aim of classical theory is now to calculate the probability distribution $P(x, y, t)$ at any later time, from the knowledge of the initial distributions just described. There are various ways of doing this, but the simplest is the following: a set of pairs of random numbers $[x_i, p_i]$ and $[y_i, q_i]$ is generated, with the property that $[x_i, p_i]$ are distributed according to phase space density $\rho_{n_0}(x, p)$, whilst y_i is distributed according to $P_a(y)$ and q_i is distributed according to $Q_a(q)$. $P_a(y)$ is determined from the assumption that the incoming atom is uniformly delocalized in a large interval for $y < y_0$, where y_0 is sufficiently far from the molecule so that the potential V is negligible. If the interval within which the incoming atom is delocalized is sufficiently large we can assume that the relative momentum q has a fixed value given from the energy conservation. These numbers determine the initial conditions for a classical trajectory which is calculated from the classical equations of motion, (15) and (16). After time t the value of the coordinates is x and y, and if N sets of initial conditions are generated, out of which n_{xy} trajectories end in a small interval around the coordinates x and y, then the classical probability density at the time t is

$$P(x, y, t,) \approx \frac{n_{xy}}{N\delta_x\delta_y} \tag{17}$$

where δ_x and δ_y are intervals within which trajectories are sampled. At this point an important assumption is made. The phase space density $\rho(x, p)$ is not positive definite, and therefore it cannot be taken as the distribution from which the random numbers $[x_i, p_i]$ are generated. However, our assumption is that these random numbers are generated from $|\rho(x,p)|$, and if the pair $[x_i, p_i]$ is such that $\rho(x_i, p_i) > 0$ then we associate $+1$ with the trajectory, and if $\rho(x_i, p_i) < 0$ then we associate -1. Therefore the number n_{xy} in (17) represents the difference between all the trajectories with $+1$ and all those with -1 associated with them, and end in interval around x, y. This assumption is only a more general use of the probability density. The important thing is that the final result must have physical significance, meaning that $P(x, y, t)$ must always be positive.

In our study we are interested in obtaining results in the limit of the stationary scattering, which is achieved by calculating the probability distribution $P(x, y, t)$ for $t \gg t_0$, where t_0 is the period of oscillations of the molecule. The knowledge of the final coordinate of the scattered atom is not necessary, so that we calculate the average probability

$$\underline{P(x,t)} = \int \mathrm{d}y P(x, y, t). \tag{18}$$

The practical procedure for calculating $\underline{P(x,t)}$ is simple: one counts final trajectories in a certain interval around x irrespective of what the value of y is. The question is now how to obtain the probability of finding molecule in the state n if it was initially in the state n_0 from the quantity given by relationship (18). The same quantity, $\underline{P(x,t)}$, averaged over time, can be calculated from the quantum theory and the result is given by [7,18]

$$\underline{P(x,t)} = \sum_n w_n^2(x) P_{n,n_0} \tag{19}$$

where P_{n,n_0} is the transition probability of finding molecule in the state n if it was initially in the state n_0, and the $w_n(x)$ is the eigenfunction of the harmonic oscillator. Therefore, getting P_{n,n_0} is possible by making the least square fit of the classical $\underline{P(x,t)}$, given by the time average of Eq. (18).

4. *Results and discussion*

The example which we analyze is collision of He atom with H_2 molecule, and compare our classical transition probabilities with those calculated from quantum theory by Secrest and Johnson [19]. This particular example showns that classical theory is unable to predict correctly the transition probabilities in vibration energy transfer. The same is true for the semiclassical theory, based on the path integral method [21], and it is only the uniform semiclassical theory [20] which gives the correct transition probabilities.

First, we analyzed the transition probabilities from the initially ground state ($n = 0$) of the molecule. Before collision the incoming atom (He) was located far away from the molecule (H_2), and it was delocalized within the distance $2\pi v_0/\omega$

where v_0 is initial relative velocity between the atom and the molecule. The averaged probability distribution (18) was calculated for the time $t \gg t_0$. It was obtained by sampling the coordinates x regardless of the position y of the scattered atom. The calculations were made for several time moments t, that showed that the averaged probability distribution is independent of the time when the sampling is done. Two examples of these probability distributions are shown in Fig. 1, one for low and the other for high collision energy (collision energy is measured in the units of $\hbar\omega/2$, i.e. the zero point energy of harmonic oscillator). The circles represent our classical calculation based on 100 000 sets of initial conditions, whilst the solid line is the probability distribution calculated from the transition probabilities of Secrest and Johnson [19] via Eq. (19). It is interesting to note that no large numerical instabilities are encountered in the least square fit procedure, despite the fact the basis functions are all positive definite. The transition probabilities were calculated for 4 different collision energies, and the numerical values of the classical and the quantum calculations are given in Table 1. The agreement between the results from "classical" classical calculation [20] and quantum results is very bad, especially at lower energies. The semiclassical results do not show great improvement over the "classical" classical results and just the uniform semiclassical calculations give comparable accuracy with the quantum results [20]. The agreement between

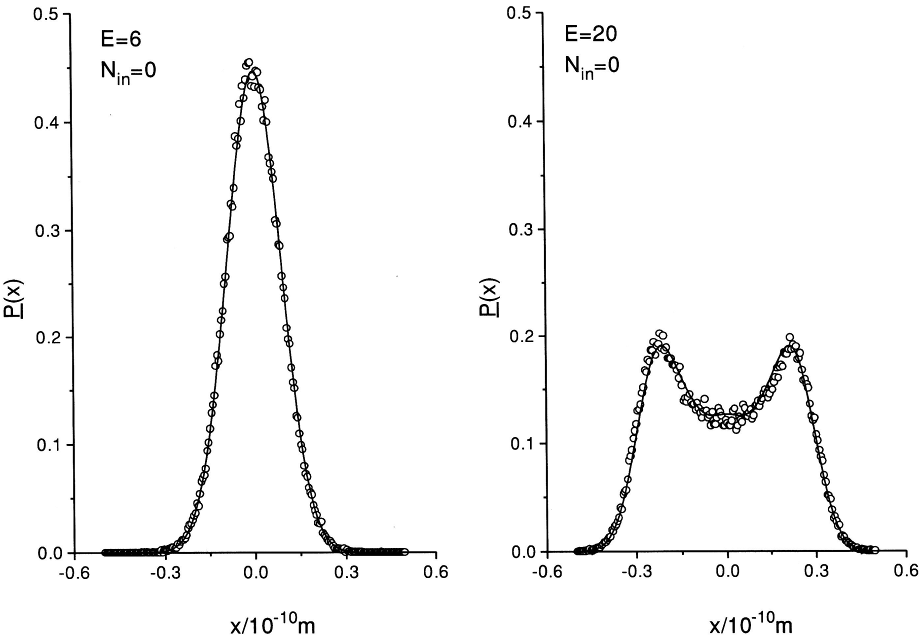

Fig. 1. Quantum time-averaged probability distribution (solid line) and classical time-averaged probability distribution (circles) when the molecule is initially in its ground state.

Table 1. Transition probabilities for transitions from the initial ground state of H_2 molecule for various collision energies. Comparison is made with the quantum results of Secrest and Johnson. Energy is measured in the units of $\hbar\omega/2$.

	$E = 6$		$E = 10$		$E = 16$		$E = 20$	
N_f	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}
0	0.984	0.978	0.740	0.733	0.192	0.204	0.054	0.060
1	0.016	0.022	0.247	0.252	0.433	0.434	0.202	0.218
2			0.015	0.015	0.305	0.291	0.352	0.366
3					0.071	0.071	0.294	0.267
4							0.107	0.092

our classical and quantum calculations is very good, becoming progressively worse as the collision energy increases.

The results for the transition probabilities when the molecule is initially in excited state $n = 1$ and $n = 2$ are given in Table 2 and Table 3, respectively. The averaged probability distributions for two collision energies when molecule is initially in $n = 2$ state are shown in Fig. 2. The agreement between our results and

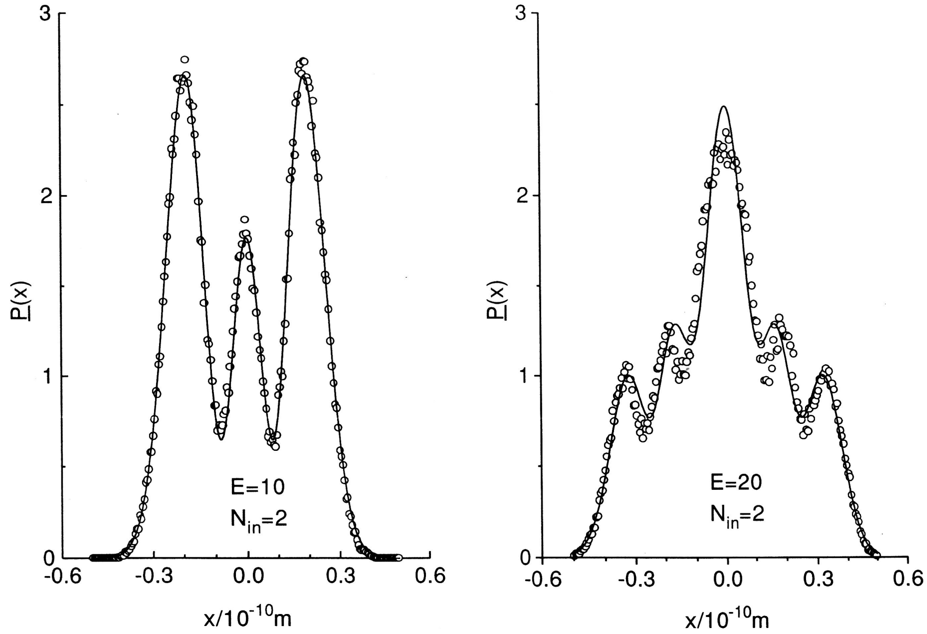

Fig. 2. Quantum time-averaged probability distribution (solid line) and classical time-averaged probability distribution (circles) when the molecule is initially in $n = 2$ state.

Table 2. Transition probabilities for transitions from the first excited state of H_2 molecule for various collision energies. Comparison is made with the quantum results of Secrest and Johnson. Energy is measured in the units of $\hbar\omega/2$.

	$E = 6$		$E = 10$		$E = 16$		$E = 20$	
N_f	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}
0	0.012	0.022	0.260	0.408	0.408	0.394	0.206	0.218
1	0.999	0.977	0.546	0.563	0.184	0.224	0.287	0.286
2	−0.010	0.001	0.204	0.182	0.392	0.345	0.047	0.009
3			−0.010	0.003	0.016	0.037	0.092	0.170
4							0.262	0.240
5							0.112	0.077

Table 3. Transition probabilities for transitions from the second excited state of H_2 molecule for various collision energies. Comparison is made with the quantum results of Secrest and Johnson. Energy is measured in the units of $\hbar\omega/2$.

	$E = 6$		$E = 10$		$E = 16$		$E = 20$	
N_f	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}	P_{class}	P_{quant}
0	0.000	0.001	0.017	0.015	0.065	0.068	0.366	0.366
1	0.031	0.042	0.182	0.182	0.378	0.345	0.027	0.009
2	0.980	0.956	0.751	0.744	0.289	0.348	0.153	0.207
3	−0.010	0.001	0.055	0.059	0.286	0.233	0.105	0.018
4					−0.018	0.006	0.058	0.169
5							0.239	0.194
6							0.060	0.037

quantum results for transition probabilities when molecule is initially in an excited state is good, getting worse at higher energy.

Based on the previous results one concludes that classical theory gives virtually the same results as quantum theory, the deviations being relatively large for higher collision energies. The question which is obvious to ask is whether this is the deficiency of the theory or of the numerical procedure. That the numerical problems are significant can be noted from the tables. Some of the transition probabilities (classical) are negative, and therefore can be regarded as the sign of inaccuracy of our procedure. At the hart of the problem are the fluctuations of random numbers which makes least square fit, of the sort (19), relatively inaccurate. The inaccuracies become significant for higher collision energies, when the pattern $\underline{P(x)}$ becomes more difficult to fit to a series of positive definite functions.

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PRINCIP NEODREĐENOSTI U KLASIČNOJ MEHANICI: PRIMJENA NA KOLINEARNE SUDARE

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Klasična teorija sudara formulirana je uz uvažavanje principa neodređenosti. Izračunali smo prijelazne vjerojatnosti za kolinearni sudar He-H_2 i usporedili rezultate s kvantnim proračunima. Pronašli smo vrlo dobro slaganje.