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Trajectory approach to the calculation of sticking probability

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Abstract. Using a path integral approach, we propose a method for the calculation of sticking probability of atoms on solid surfaces. The method makes use of a sticking trajectory for the calculation. The formalism is illustrated by applying it to the collision of an atom with a solid, the solid being modelled as a collection of bosons, the interaction term in the Hamiltonian being linear in the boson coordinates.

Keywords. Sticking probability; trajectory approach; boson coordinates; path integral approach.

1. Introduction

Both in atomic and surface physics, some attention has been paid to methods of finding trajectories, suited for the description of specified processes. Pechukas (1969) and Pechukas and Davis (1972) have considered the problem of finding a trajectory for a particle, interacting with a quantum mechanical system, which as a result of the interaction undergoes a transition from a given initial state to a specified final state. They make use of the "path integral as a functional" approach (Feynman and Hibbs 1965) for this purpose. In surface physics, the question of finding trajectories for particles interacting with surfaces has been studied using the same technique. The infinite degrees of freedom of the solid have prompted search for an average description in which the solid's degrees of freedom have been traced out (Sebastian 1981; Mohring and Smilansky 1980; Nourtier 1985; Newns 1985). Newns (1985) advocates the opposite case of finding trajectories which are suitable for a given loss of energy and momentum. This is in the same spirit as Pechukas (1969) and Metiu and Schön (1984). For interesting related work, see Brenig (1982) and Nourtier (1985).

2. Formalism

In this paper, we consider the problem of sticking of atoms on surfaces. An approach which has been used to calculate the probability of sticking (Brako and Newns 1980; Schönhammer and Gunnarsson 1981) is to assume that the particle follows the elastic trajectory, find the spectrum of excitations produced in the solid, and calculate the sticking probability as the probability that excitations of energy greater than the initial kinetic energy of the atom are produced in the solid. This elastic trajectory approach, while justifiable when applied to inelastic scattering, is not so in the case of sticking. It also has the defect of not conserving the energy,

i.e. the energy gained by the solid is not equal to the energy lost by the atom. One possibility of improving the situation is to modify the classical equations of motion of the projectile by including the effect of energy loss to the solid. This would, however, lead to a trajectory that would either stick or not; a priori there is no way of predicting what would happen. In the following, we propose a method which overcomes these difficulties. It conserves energy and is guaranteed to stick. Our procedure is similar to the one already used by Sebastian (1981) and Mohring and Smilansky (1980, 1981). However, we do not perform a full trace over all the final states of the solid, but only over those final states that have an excitation energy greater than ε, the initial kinetic energy of the incident atom.

To keep the notation simple, we assume a one-dimensional model for both the solid and the incoming atom as done by Newns (1985). We assume the atom to be at the position Q_i at the time t_i, sufficiently far from the solid so that the interaction between the two can be neglected. At this time the solid is assumed to be in the ground state $|0\rangle$. Using quantum mechanical descriptions for both the atom and the solid, we write the probability of finding the atom at Q_f at the time t_f, given that the solid has been excited to states having excitation energy greater than ε, as the double path integral in (1),

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DQ \int D\tilde{Q} \exp\left[\frac{i}{\hbar}\{S_0[Q] - S_0[\tilde{Q}]\}\right] F[Q, \tilde{Q} | \varepsilon]. \tag{1}$$

The path integration is to be carried out over all pairs of paths $Q(t)$ and $\tilde{Q}(t)$ of the atom, obeying

$$\left.\begin{aligned} Q(t_i) = \tilde{Q}(t_i) = Q_i, \quad \text{and} \\ Q(t_f) = \tilde{Q}(t_f) = Q_f. \end{aligned}\right\} \tag{2}$$

$$S_0[Q] = \int_{t_i}^{t_f} dt \left\{\frac{m}{2} Q^2 - V_0(Q)\right\}.$$

$S_0[Q]$ is the action for the atom, m the mass and $V_0(Q)$ the static part of the potential of the interaction between the atom and the solid. All the dynamical interactions are contained in the *modified influence functional*,

$$F[Q, \tilde{Q} | \varepsilon] = \langle 0 | U^+(t_f, t_i; \tilde{Q}) \hat{P}(\varepsilon) U(t_f, t_i; Q) | 0 \rangle. \tag{3}$$

$U(t_f, t_i; Q)$ is the time development operator for the solid which is under the influence of the atom, following the trajectory $Q(t)$. $\hat{P}(\varepsilon)$ is a projection operator which projects out all those states of the solid having an excitation energy greater than ε. It can be written as

$$\hat{P}(\varepsilon) = \Theta(\hat{H}_s - E_0 - \varepsilon), \tag{4}$$

where $\hat{H}_s$ is an appropriately chosen Hamiltonian for the solid (see below). $\Theta(x)$ is the step function, defined by $\Theta(x) = 1$, if $x \geq 0$, and $\Theta(x) = 0$, when $x < 0$. If we put $\varepsilon = -\infty$ then $F[Q, \tilde{Q} | \varepsilon]$ becomes identical with the influence functional used earlier (Sebastian 1981; Mohring and Smilansky 1980). $\hat{P}(\varepsilon)$ can also be written as

$$\hat{P}(\varepsilon) = \sum_{\substack{n \\ E_n - E_0 \geq \varepsilon}} |n\rangle\langle n|, \tag{5}$$

where $|n\rangle$ are eigenstates of $\hat{H}_s$ having energy E_n.

We shall take $\hat{H}_s$ as the Hamiltonian for the solid, interacting with the atom, which is kept fixed at its equilibrium adsorbed position. Defining $\Phi[Q, \tilde{Q}]$ by

$$\exp\{(i/\hbar)\Phi[Q, \tilde{Q}]\} = F[Q, \tilde{Q} \mid \varepsilon], \tag{6}$$

we have

$$P(Q_f, t_f; Q_i, t_i \mid \varepsilon) = \int DQ \int D\tilde{Q} \exp\left[\frac{i}{\hbar}\{S_0[Q] - S_0[\tilde{Q}] + \Phi[Q, \tilde{Q}]\}\right]. \tag{7}$$

We now go over to the centre of mass and relative coordinates (Schmid 1982; Newns 1985). Defining

$$R(t) = \tfrac{1}{2}[Q(t) + \tilde{Q}(t)], \text{ and}$$
$$r(t) = Q(t) - \tilde{Q}(t), \tag{8}$$

we obtain

$$P(Q_f, t_f; Q_i, t_i \mid \varepsilon) = \int DR \int Dr \exp\left[\frac{i}{\hbar}\{S_0[R + \tfrac{r}{2}] - S_0[R - \tfrac{r}{2}] + \Phi[R + \tfrac{r}{2}, R - \tfrac{r}{2}]\}\right]. \tag{9}$$

Clearly

$$R(t_i) = Q_i,\ R(t_f) = Q_f \text{ and } r(t_i) = r(t_f) = 0. \tag{10}$$

From the definition of the functional $\Phi[Q, \tilde{Q}]$ it is easy to see that $\Phi[Q, \tilde{Q}] = -\Phi[\tilde{Q}, Q]^*$. Denoting the real and imaginary parts of $\Phi[Q, \tilde{Q}]$ by $\Pi[R, r]$ and $\Sigma[R, r]$, we see that

$$\Pi[R, r] = -\Pi[R, -r],$$

and

$$\Sigma[R, r] = \Sigma[R, -r]. \tag{11}$$

Now expanding the functionals S_0, $\Pi[R, r]$ and $\Sigma[R, r]$ as functional Taylor series in $r(t)$, we get

$$P(Q_f, t_f; Q_i, t_i \mid \varepsilon) = \int DR \int Dr \exp\left[\frac{i}{\hbar}\int_{t_i}^{t_f} dt\{m\dot{R}(t)\dot{r}(t) - V_0'(R(t))r(t)\} + \left(\frac{\delta\Pi[R, r]}{\delta r(t)}\right)_{r(t)=0} r(t) + i\,\Sigma[R, 0] + \frac{i}{2}\int_{t_i}^{t_f} dt_1\, r(t_1)\left(\frac{\delta^2\Sigma[R, r]}{\delta r(t)\,\delta r(t_1)}\right)_{r(t)=0} r(t) + \ldots\right]. \tag{12}$$

V_0' denotes the first derivative of V_0. Note that some of the terms in the Taylor expansion vanish, due to the properties of $\Pi[R, r]$ and $\Sigma[R, r]$, given in (11). As done by earlier workers (Newns 1985; Schmid 1983), we shall neglect terms of cubical and higher order in $r(t)$ (see these papers for a discussion of the validity of this approximation). Introducing a Gaussian random function $\xi(t)$ obeying

$$\langle \xi(t) \rangle = 0 \text{ and } \langle \xi(t)\xi(s) \rangle = \frac{1}{\hbar} \left(\frac{\delta^2 \Sigma[R, r]}{\delta r(t)\, \delta r(s)} \right)_{r(t_i)=0}, \tag{13}$$

where $\langle \ldots . \rangle$ denotes averaging over the random function, we can write (12) as

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR \int Dr \left\langle \exp \left\{ \frac{i}{\hbar} \int_{t_i}^{t_f} dt \left(m\dot{R}(t)\dot{r}(t) - V_0'(R(t))r(t) \right.\right.\right.$$
$$\left.\left.\left. + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0} r(t) + r(t)\xi(t) \right) \right\} \right\rangle \exp\left(-\frac{\Sigma[R, 0]}{\hbar} \right). \tag{14}$$

Now performing the path integration over $r(t)$, we obtain

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR \left\langle \delta \left[-m\ddot{R} - \frac{\partial V_0}{\partial R} + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0} \right.\right.$$
$$\left.\left. + \xi(t) \right] \right\rangle \exp\left(-\frac{\Sigma[R, 0]}{\hbar} \right). \tag{15}$$

$\delta[\ldots..]$ stands for the delta functional. From (14), it is clear that only paths $R(t)$, obeying

$$m\ddot{R} + V_0'(R(t)) = \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0} + \xi(t), \tag{16}$$

contribute to the probability. In order to calculate $P(Q_f, t_f; Q_i, t_i | \varepsilon)$, we have to solve (16) for each realization of the random function $\xi(t)$, use the result in (15), perform the path integral and average over $\xi(t)$. This is very tedious. So we replace $\xi(t)$ in (15) by its average value, viz zero. This means that instead of (16), we now have the equation

$$m\ddot{R} + V_0'(R) = \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0}. \tag{17}$$

Let us denote the trajectory which obeys this equation and the boundary conditions $R(t_i) = Q_i$ and $R(t_f) = Q_f$ by $\bar{R}(t)$. In principle, there may be many trajectories obeying these conditions. In the following, we consider the case where there is only one such trajectory. Equation (15) now becomes

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \int DR\ \delta \left[-m\ddot{R} - \frac{\partial V_0}{\partial R} \right.$$
$$\left. + \left(\frac{\delta \Pi[R, r]}{\delta r(t)} \right)_{r(t)=0} \right] \exp\left(-\frac{\Sigma[R, 0]}{\hbar} \right). \tag{18}$$

The path integral in (18) can be evaluated exactly. As the evaluation is long and tedious, we just give the final result here (see Sebastian 1987, for details). It is

$$P(Q_f, t_f; Q_i, t_i | \varepsilon) = \frac{1}{2\pi\hbar} \left| \frac{\partial Q_f}{\partial P_i} \right|^{-1} \exp\left[-\int_{t_i}^{t_f} db\ \ddot{\bar{U}}(b, b) \right] \exp\left(-\frac{\Sigma[\bar{R}, 0]}{\hbar} \right) \tag{19}$$

$\ddot{\tilde{U}}(b, b) = [(\partial^2 \tilde{U}(b, t))/\partial t^2]_{t=b}$ and $\tilde{U}(b, t)$ is the solution of

$$m \frac{\partial^2}{\partial t^2} \tilde{U}(b, t) + \left(\frac{\partial^2 V_0}{\partial R^2}\right)_{\bar{R}(t)} \tilde{U}(b, t) = \int_0^b \mathrm{d}s\, \tilde{U}(b, s) \left(\frac{\delta^2 \Pi[R, r]}{\delta R(s)\, \delta r(t)}\right)_{\substack{r(t)=0, \\ R(s)=\bar{R}(s)}} \tag{20}$$

obeying the conditions $\tilde{U}(b, b) = 0$ and $[(\partial \tilde{U}(b, t))/\partial t]_{t=0} = 0$. P_i is the initial momentum with which the trajectory starts. If $[(\delta^2 \Pi[R, r])/\delta R(s)\, \delta r(t)]_{r(t)=0}$ were local or is causal (i.e. it contains either $\delta(t-s)$ or $\Theta(t-s)$) then (19) simplifies, as $\ddot{\tilde{U}}(b, b) = 0$.

As we had started with a state located at the point Q_i at the time t_i, the number of particles having initial momentum between P_i and $P_i + \mathrm{d}P_i$ is $[(\mathrm{d}P_i)/(2\pi\hbar)]$. If all these particles followed (17), then they would all be found between Q_f and $Q_f + \mathrm{d}Q_f$ and hence $(1/2\pi\hbar)\ (\mathrm{d}P_i/\mathrm{d}Q_f)$ would be the "classical distribution". Equation (19) has a multiplicative correction factor to this as only the sticking particles would obey this equation. Hence the sticking probability is given by

$$s = \exp\left[-\int_{t_i}^{t_f} \mathrm{d}b\, \ddot{\tilde{U}}(b, b)\right] \exp\left[-\frac{\Sigma[\bar{R}, 0]}{\hbar}\right],$$

which can also be written as

$$s = \exp\left[-\int_{t_i}^{t_f} \mathrm{d}b\, \ddot{\tilde{U}}(b, b)\right] \langle 0 | U^+(t_f, t_i, \bar{R})\, \hat{P}(\varepsilon)\, U(t_f, t_i, \bar{R}) | 0 \rangle. \tag{21}$$

Notice that $\langle 0 | U^+(t_f, t_i, \bar{R})\, \hat{P}(\varepsilon)\, U(t_f, t_i, \bar{R}) | 0 \rangle$ is exactly the probability of creating excitations of energy greater than or equal to ε, and one would expect this to be the sticking probability from simple considerations.

Solving (17) is not as difficult as it may appear. Using (3) and (6), one can write

$$m\ddot{\bar{R}} + V_0'(\bar{R}) = -\,\mathrm{Re}\left\{\frac{\delta}{\delta r(t)} \ln \left\langle 0 | U^+\left(t_f, t_i; R - \frac{r}{2}\right) \hat{P}(\varepsilon)\right.\right.$$
$$\left.\left. U\left(t_f, t_i; R + \frac{r}{2}\right) | 0 \right\rangle\right\}, \tag{22}$$

$$m\ddot{\bar{R}} + V_0'(\dot{\bar{R}}) = -\,\mathrm{Re}\left\{\frac{\langle 0 | U^+(t_f, t_i; \bar{R})\, \hat{P}(\varepsilon)\, U(t_f, t; \bar{R})\, H_i'[\bar{R}(t)]\, U(t, t_i; \bar{R}) | 0 \rangle}{\langle 0 | U^+(t_f, t_i; \bar{R})\, \hat{P}(\varepsilon)\, U(t_f, t_i; \bar{R}) | 0 \rangle}\right\} \tag{23}$$

Re' stands for the real part. $H_i[\bar{R}(t)]$ is the Hamiltonian for the time development of the solid, when the atom follows a trajectory $\bar{R}(t)$. A nice property of $\bar{R}(t)$, viz energy conservation, is easily illustrated using the above equation. For this we multiply (23) by $\dot{\bar{R}}(t) = [\partial \bar{R}(t)/\partial t]$ and integrate from t_i to t_f. This leads to

$$[\tfrac{1}{2} m \dot{\bar{R}}^2 + V_0(\bar{R})]_{t=t_i} = [\tfrac{1}{2} m \dot{\bar{R}}^2 + V_0(\bar{R})]_{t=t_f}$$
$$+ \mathrm{Re}\left\{\frac{\langle 0 | U^+(t_f, t_i; \bar{R})\, \hat{P}(\varepsilon)\, H_i(Q_f)\, U(t_f, t_i; \bar{R}) | 0 \rangle}{\langle 0 | U^+(t_f, t_i; \bar{R})\, \hat{P}(\varepsilon)\, U(t_f, t_i; \bar{R}) | 0 \rangle}\right\} \tag{24}$$

which shows that the particle loses exactly the same energy as the energy gained by the solid due to all excitations having energy greater than ε.

To solve (23), one can start with the particle at Q_i at the time t_i and take the initial momentum to be P_i. Using these two inputs and neglecting the term on the left hand side, one can calculate the elastic trajectory $\bar{R}_{el}(t)$. This may be used on the left hand side of (23), as an approximation to $\bar{R}(t)$ and the equation solved again, to find a better approximation for $\bar{R}_{el}(t)$. This procedure may be continued until convergence is attained. However, choosing values for t_f and Q_f can be a problem. It appears to be reasonable to take Q_f to be the equilibrium position of the atom and t_f to be the time when the particle has hit the solid and has executed a few oscillations near it. One also expects the sticking probability to be independent of the values of Q_f and t_f so chosen. Numerical calculations are being planned and will be reported later.

3. Application to a simple Hamiltonian

As an illustration, we derive the equation for the sticking trajectory for the case of an atom interacting with the phonons of the solid, with the total Hamiltonian given by

$$\hat{H}_s = \sum_k \hbar\omega_k b_k^+ b_k + \sum_k F(k, Q)(b_k^+ + b_k) + \frac{p^2}{2m} + V_0(Q). \tag{25}$$

$p^2/2m$ is the kinetic energy of the atom and $V_0(Q)$ is the static part of the interaction between the atom and the solid. That is, it represents the interaction between the atom and the solid, when all the solid atoms occupy their equilibrium positions. $\Sigma_k \hbar\omega_k b_k^+ b_k$ is the phonon Hamiltonian, and the last term in the Hamiltonian represents the interaction between the phonons and the atom. This Hamiltonian has been considered by many authors (Kaplan and Dragulis 1967; Brako and Newns 1982; Newns 1985). One can take Q_f to be Q_e, where Q_e is the minimum of the potential $V_0(Q)$. Let us take $\hat{H}_s$ to be the Hamiltonian for the solid with the atom kept fixed at Q_e, i.e.

$$\hat{H}_s = \sum_k \hbar\omega_k b_k^+ b_k + \sum_k F(k, Q_e)(b_k^+ + b_k). \tag{26}$$

We take $|n\rangle s$ in (5) to be eigenfunctions of this Hamiltonian.

Equation (22) now becomes

$$m\ddot{\bar{R}} + V_0'(\bar{R}) = -\mathrm{Re}\sum_k \frac{\langle 0|U^+(t_f, t_i; \bar{R})\hat{P}(\varepsilon)U(t_f, t; R)(b_k^+ + b_k)U(t, t_i; \bar{R})|0\rangle F'(k, \bar{R})}{\langle 0|U^+(t_f, t_i; \bar{R})\hat{P}(\varepsilon)U(t_f, t_i; \bar{R})|0\rangle}, \tag{27}$$

$F'(k, \bar{R}) = [\partial F(k, R)/\partial R]_{R=\bar{R}(t)}$. In the last term of (27), using the commutation relations of b_k and b_k^+, one can move b_k to the right hand extreme so that it annihilates $|0\rangle$, and similarly, b_k^+ to the left hand extreme. b_k^+, however, has to be moved across $\hat{P}(\varepsilon)$ for which one can make use of the following identity:

$$\hat{P}(\varepsilon)b_k^+ = b_k^+ \hat{P}(\varepsilon - \omega_k) + \frac{F(k, Q_e)}{\hbar\omega_k}\{\hat{P}(\varepsilon - \hbar\omega_k) - \hat{P}(\varepsilon)\}. \tag{28}$$

This can be easily obtained from the definition of $\hat{P}(\varepsilon)$. Equation (27) can now be written as

$$m\ddot{\bar{R}} + V_0'(\bar{R}) = \frac{1}{\hbar}\sum_k F'(k, \bar{R}) \int_{t_i}^{t_f} dt_1 F(k, \bar{R}) \sin \omega_k |t - t_1|$$

$$-\sum_k \frac{F'(k, \bar{R})F(k, \bar{R})}{\hbar\omega_k} \cos w_k(t_f - t) \left\{\frac{\langle\langle \hat{P}(\varepsilon - \omega_k)\rangle\rangle}{\langle\langle \hat{P}(\varepsilon)\rangle\rangle} - 1\right\}$$

$$-\frac{1}{\hbar}\sum \frac{F'(k, \bar{R})}{\langle\langle \hat{P}(\varepsilon)\rangle\rangle} \langle\langle \hat{P}(\varepsilon - \omega_k)\rangle\rangle \int_{t_i}^{t_f} dt_1 F(k, \bar{R}) \sin \omega_k(t - t_1), \tag{29}$$

$$= \frac{1}{\hbar}\sum_k F'(k, \bar{R}) \int_{t_i}^{t_f} dt_1 F(k, \bar{R}(t_1)) \sin \omega_k(t - t_1)$$

$$\left\{\text{sgn } (t - t_1) - \frac{\langle\langle \hat{P}(\varepsilon - \omega_k)\rangle\rangle}{\langle\langle \hat{P}(\varepsilon)\rangle\rangle}\right\}$$

$$-\sum_k \frac{F'(k, \bar{R})F(k, \bar{R}_e)}{\hbar\omega_k} \cos \omega_k(t_f - t) \left\{\frac{\langle\langle \hat{P}(\varepsilon - \omega_k)\rangle\rangle}{\langle\langle \hat{P}(\varepsilon)\rangle\rangle} - 1\right\}. \tag{30}$$

This equation, though it looks complicated, can be applied to the problem of sticking as outlined here: (i) start with the elastic trajectory $\bar{R}_{el}(t)$ as an approximation, (ii) evaluate $\langle\langle \hat{P}(t)\rangle\rangle$ with this, use them to calculate the right hand side of (30), solve this equation to get a better approximation to $\bar{R}(t)$ and continue this until self-consistency is achieved. Calculating $\langle\langle \hat{P}(\varepsilon)\rangle\rangle$ can be done easily as we now have a system of forced harmonic oscillators, for which the explicit formula is given by Muller-Hartman *et al* (1970).

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