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# A quantum–semiclassical comparison of the scattering of H<sub>2</sub>–Cu

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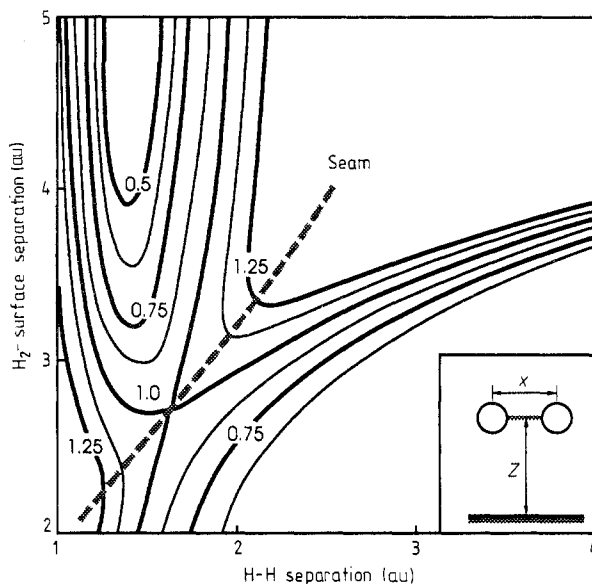
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**Abstract.** The dissociative adsorption of H<sub>2</sub>–Cu is studied as representing that class of adsorption systems displaying an activation barrier. In this work we use an established potential energy surface and compare results obtained from ‘exact’ quantum wave-packet calculations with a previously discussed semiclassical model. Results show that for qualitative purposes, the semiclassical method captures the essential physics. Tunnelling through the activation barrier is an important feature and dissociation probabilities show clear evidence of this effect.

## 1. Introduction

In the general areas of reaction kinetics and dynamics, quantum mechanics is frequently treated in an inconsistent manner [1]. Clearly in order to obtain a potential energy surface (PES) for the reaction, the electronic problem has to be solved and it would be a *cause célèbre* if classical mechanics were employed for this purpose! Now assuming that a PES has been obtained (either calculated or inverted from experimental data), then to investigate the dynamics of a particular process, it remains to solve for the evolution of the nuclear motion. Classical or quantum?

When faced with this question it is normal to examine the de Broglie criterion for wavelength  $\lambda \lesssim a$ , where  $a$  is some length scale which serves to define the problem [2]. Intuition tells us that for the case of a surface reaction, the breaking of molecular bonds and the making of adsorption bonds, both involve length scales  $\sim 3$  a.u. [3]. Specifically, consider the scattering of a beam of molecules from a surface. Current technology is capable of producing beams with translational energies in the range  $10 \text{ meV} < E_{\text{trans}} < 2 \text{ eV}$ , with both limits being dependent upon the particular molecule in question [4]. Associated de Broglie wavelengths for some light gases are:  $0.3 \text{ a.u.} \leq \lambda_{\text{trans}}(\text{H}_2) \leq 3.9 \text{ a.u.}$ ;  $0.2 \text{ a.u.} \leq \lambda_{\text{trans}}(\text{D}_2) \leq 2.7 \text{ a.u.}$ ;  $0.07 \text{ a.u.} \leq \lambda_{\text{trans}}(\text{N}_2) \leq 1.0 \text{ a.u.}$  and  $0.05 \text{ a.u.} \leq \lambda_{\text{trans}}(\text{Cl}_2) \leq 0.64 \text{ a.u.}$ , which demonstrates that at all but the lowest energies  $a \gg \lambda_{\text{trans}}$ . It would be, however, premature to conclude that quantum motion for the reactants is unimportant since we have only considered the propensity of molecular *translations*. Do things change when length scales are measured in the direction of the vibrational coordinate of the molecule? By associating the vibrational wavelength with the classical extent of the  $v = 1$  vibrational state  $\lambda_{\text{vib}} = (12/\mu\omega)^{1/2}$ , where  $\mu$  is the reduced mass of the molecule ( $M_{\text{mol}}/4$ ) and  $\omega$  is the molecular frequency. For the same



**Figure 1.** The potential energy surface for  $\text{H}_2$  interacting with a Cu surface. The inset defines the  $x$  and  $Z$  coordinates and contour energies are measured in eV, the zero of energy corresponding to a stationary molecule infinitely far from the surface.

gases as before:  $\lambda_{\text{vib}}(\text{H}_2) = 0.81$  a.u.;  $\lambda_{\text{vib}}(\text{D}_2) = 0.57$  a.u.;  $\lambda_{\text{vib}}(\text{N}_2) = 0.31$  a.u. and  $\lambda_{\text{vib}}(\text{Cl}_2) = 0.19$  a.u. Now the situation is rather different and, whereas on the basis of  $\lambda_{\text{trans}}\text{N}_2$  would be deemed a classical particle, unless the PES softens  $\omega$  by order of magnitude, a quantum treatment of  $\text{N}_2$  dissociation dynamics should not be discounted.

On the basis of a semiclassical model, it has been suggested that  $\text{N}_2$  dissociation does in fact show behaviour characteristic of a quantum system [5, 6]. The aim of this present work is to examine the basis for this claim by performing ‘exact’ calculations against which to test the model. In order to remove the arbitrariness of the potential, we present calculations for the dissociative adsorption of  $\text{H}_2$  molecules on a Cu surface where a PES exists. A discussion of the dynamical simulations, PES and results are presented in § 2 and a summary with conclusions follows in § 3.

## 2. Results

In a series of previous works [5, 7–12] we have considered the dynamics of dissociative adsorption based upon a simple model where molecular motion is constrained (i) to be normally incident and (ii) to have its molecular axis parallel to the surface (see inset of figure 1). For a 0 K surface, two coordinates serve to define the problem;  $Z$ , the centre of mass location with respect to the surface; and  $x$ , the relative bond length. Figure 1 shows the PES for the interaction of an  $\text{H}_2$  molecule with a Cu surface which, based upon an *ab initio* calculation [13], has formed the basis for several recent dynamical studies [11–14]. While space does not permit a detailed exposition of this PES, its salient topological features for present purposes are as follows.

(i) An *entrance channel* along which the incident molecule moves towards the surface. This has the form of a bound potential in  $x$  (which asymptotically becomes the gas-phase potential) and an exponential repulsion in  $Z$ . This arises as a consequence of the interaction between a closed-shell molecule and the s-p band in the noble metal [13].

(ii) An *exit channel* along which two adsorbed H atoms may diffuse across the surface.

(iii) A crossing seam [10] which marks that region of space where a switch of electronic configuration may occur between states (i) and (ii). This region is critically important when studying dynamical processes and its topology can determine the resulting energetic distributions for reacting species [11, 14]. An activation barrier is located along the seam at the saddle point (or col). For the PES in figure 1, this is located at  $x = 1.79$  a.u. and  $Z = 2.68$  a.u. and has a value of  $E_{\text{act}} = 1.0$  eV.

In a previous work [5] it was suggested that for systems having a PES of this generic form (entrance channel, activation barrier, exit channel), the dynamics could be described by a hybrid model employing a classical description of translations and a quantum analysis of vibrations. The basis for this model was the factor of 4 difference between the masses in the  $x$  and  $Z$  directions. Using a perturbation theory, the dissociation probability for an incident molecule in vibrational state  $v$  was shown to be given by the following analytic form [5]:

$$S_0^v(E_{\text{trans}}) \sim [\omega/E_{\text{trans}}(v + \frac{1}{2})] |\varphi_v(x_s)|^2. \quad (1)$$

The initial vibrational state wavefunction of the diatomic  $\varphi_v$  is evaluated at  $x_s$ , the location of the crossing seam corresponding to the value of  $Z (= Z_{\text{ctp}})$  where the classical kinetic energy has fallen to zero. Results using equation (1) for the PES in figure 1 are presented in figure 2(a). The drawback with this method is that because of its perturbative approach it is strictly valid only in that region where  $E_{\text{trans}} < E_{\text{act}}$ .

To improve upon this calculation we have performed quantum wavepacket calculations in *both* the  $x$  and  $Z$  coordinates for the PES in figure 1 [12]. The initial state is taken to be the product wavefunction

$$\psi_v(x, Z; t = 0) = \varphi_v(x)g(Z - Z_i, p_Z) \quad (2)$$

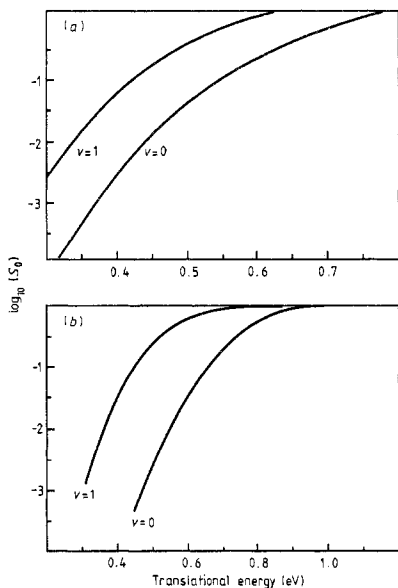
where  $g(Z - Z_i, p_Z)$  is a Gaussian wavepacket centred at  $Z_i$  with momentum  $p_Z$ . This is numerically propagated in time according to the full Hamiltonian until such a time that asymptotic states obtain, which in the most general case will consist of a scattered fragment

$$\psi_{\text{scatt}}(x, Z \rightarrow \infty) = \sum_v g_v(Z)\varphi_v(x) \quad (3)$$

and an adsorbed fraction

$$\psi_{\text{ads}}(x, Z) = \sum_j C_j \chi_j(x, Z) \quad (4)$$

where the states  $\chi_j(x, Z)$  are the eigenstates of the chemisorption potential [15]. The propagation method is based upon the split operator scheme of Feit *et al* which has been discussed in detail elsewhere [16]. The dissociation probability is given by  $|\psi_{\text{ads}}(x, Z)|^2$  and results for molecules in their  $v = 0$  and 1 initial states are presented in figure 2(b). While the results in figure 2(a) appear similar, they are quantitatively correct only in the low  $E_{\text{trans}}$  region. This does not, however, invalidate the general conclusions presented in [5] which have been ratified by the present work:



**Figure 2.** (a) Results for the dissociation probability for  $v = 0$  and  $1$   $\text{H}_2$  molecules as a function of initial translational energy. These results are obtained using the semiclassical model of [10] as described in the text. (b) As (a), but results obtained using a full quantum treatment of nuclear motion in all dimensions. It is seen that while the semiclassical model accounts qualitatively for these results, it fails at high values of the translational energy.

(i) Higher lying vibrational states experience lower *effective* barriers and therefore tunnel more readily;

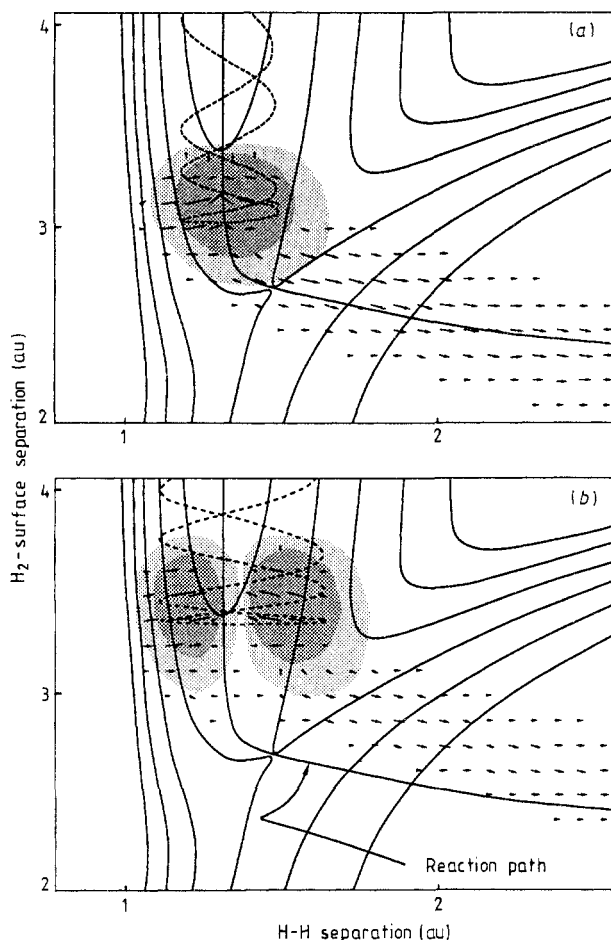
(ii) an increase in  $E_{\text{trans}}$  allows the molecule to penetrate further into the surface and thus sample a lower barrier.

To pursue the investigation of the semiclassical model, in figure 3(a) we show the comparison of a quantum and a classical  $v = 0$  ‘molecule’ with  $E_{\text{trans}} = 0.68$  eV. The classical trajectory clearly shows that for a total energy of 0.95 eV there is insufficient energy to surmount the activation barrier and the molecule is scattered back into the gas phase essentially with unchanged vibrational energy. The classical turning point is located at  $Z_{\text{ctp}} = 3.0$  a.u. For the wavepacket,  $|\psi(x, Z)|^2$  is plotted as a shaded region for a time corresponding to  $\langle p_z \rangle = 0$  which defines an approximate quantum turning point. In addition to the probability density, the quantum current density is also shown. This vector field is defined in the usual way [2]:

$$S(x, Z; t) = \text{Re} \left( \psi^*(x, Z; t) \left[ \frac{\hbar}{i\mathbf{M}} \right] \nabla \psi(x, Z; t) \right) \quad (5)$$

where  $\mathbf{M}$  is the mass tensor. In figure 3,  $S(x, Z)$  is denoted by an array of arrows. In this calculation the initial state Gaussian wavepacket is chosen to have a deliberately narrow  $p_z$  spread ( $\sim 7\%$ ), which ensures that all of the observed dissociation flux arises from tunnelling. A similar ‘snapshot’ taken  $\Delta t$  before the quantum turning point shows considerably less tunnelling, while one  $\Delta t$  after shows the formation of a node along the seam separating  $\psi_{\text{scatt}}$  from  $\psi_{\text{ads}}$  [17]. Although these results confirm part of the semiclassical hypothesis, an over-simplification was to assume that the tunnelling occurred primarily in the  $x$  direction. Figure 3(a) shows that the transmitted flux appears to follow the line of the (classical) reaction path [11].

Figure 3(b) shows a similar plot of figure 3(a) but for the case when the initial vibrational state is  $v = 1$  with  $E_{\text{trans}} = 0.47$  eV. This particular choice was selected since both examples have a dissociation probability of  $S_0 = 0.2$ . In the second example,  $Z_{\text{ctp}} =$



**Figure 3.** (a) Classical and quantum scattering of a  $v = 0$   $H_2$  molecule with translational energy 0.68 eV. The broken curve shows a classical trajectory which because of insufficient energy fails to reach the activation barrier and scatters vibrationally adiabatically. The shaded region corresponds to  $|\psi(x, Z)|^2$  evaluated at a time corresponding to  $\langle p_z \rangle = 0$  which defines an approximate quantum turning point. The arrows are a representation of the current density which portrays the tunnelling of flux through the activation barrier into the dissociated state. (b) As (a), but for a  $v = 1$  molecule with translational energy 0.47 eV. Although now the turning point is considerably further from the surface, because of the increased energy in the vibrational coordinate, an equal amount of dissociation occurs as in (a): 20%.

3.3 a.u. and again the classical trajectory is scattered vibrationally adiabatically. The tunnelling is now far from being constrained to the vibrational coordinate and does not even track the reaction path. As previously, however, the majority of the dissociation occurs very close to  $Z_{\text{ctp}}$  and so again the qualitative features of the semiclassical model appear to be valid.

### 3. Summary and conclusions

In this present work we have performed detailed quantum wavepacket scattering calculations to simulate  $H_2$  interacting with a Cu surface. The PES employed was taken from

a previous dynamical simulation of associative desorption where the results agreed well with experimental observations [9]. Dissociation probabilities have been calculated as a function of  $E_{\text{trans}}$  and vibrational state and the exact calculations compared with those obtained using a semiclassical approximation [5]. This scheme gives a good overall understanding of the basic phenomena but fails qualitatively at high  $E_{\text{trans}}$  where the perturbation approach breaks down. Plots of the wavepacket current densities give a detailed insight into the microscopic dynamics in the reaction zone and further work exploiting this method is currently in progress [17].

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