Low Energy Behavior of Quantum Adsorption

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We present an exact solution of a 1D model: a particle of incident energy $E$ colliding with a target which is a 1D harmonic “solid slab” with $N$ atoms in its ground state; the Hilbert space of the target is restricted to the $(N + 1)$ states with zero or one phonon present. For the case of a short range interaction, $V(z)$, between the particle and the surface atom supporting a bound state, an explicit non-perturbative solution of the collision problem is presented. For finite and large $N$, there is no true sticking but only so-called Feshbach resonances. A finite sticking coefficient $s(E)$ is obtained by introducing a small phonon decay rate $\eta$ and letting $N \to \infty$. Our main interest is in the behavior of $s(E)$ as $E \to 0$. For a short range $V(z)$, we find $s(E) \sim E^{1/2}$, regardless of the strength of the particle-phonon coupling. However, if $V(z)$ has a Coulomb $z^{-1}$ tail, we find $s(E) \to \alpha$, where $0 < \alpha < 1$. [A fully classical calculation gives $s(E) \to 1$ in both cases.]

We conclude that the same threshold laws apply to 3D systems of neutral and charged particles respectively.

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The low energy behavior of the sticking coefficient \( s(E) \) of a particle striking a surface and being trapped in a surface bound state is still a matter of experimental\(^1\)–\(^4\) and theoretical\(^5\)–\(^9\) controversy. We consider here only a zero temperature target. For a particle treated classically which interacts with a classical elastic solid, it is known\(^10\) that the sticking probability, \( s(E) \), tends to 1, as the incident energy of the particle \( E \to 0 \). In contrast, a particle whose motion is treated quantum mechanically can have a dramatically different threshold behavior for sticking; it is known\(^5\)–\(^7\) that for sufficiently weak particle-phonon coupling, if perturbation theory is valid, a quantum particle experiencing a short range interaction will have a sticking probability vanishing as \( s(E) \sim E^{1/2} \) due to “quantum reflection.”

A number of experiments have attempted to explore the low energy region where quantum effects should dictate the form of the threshold behavior of \( s(E) \). Nayak \textit{et al.}\(^1\) found for \(^4\)He atoms striking a liquid-\(^4\)He surface, \( s \to 0 \), in agreement with the quantum prediction. Similarly, results\(^2\) of low energy scattering of Ne from Ru(001) indicate the vanishing of \( s(E) \) as \( E \to 0 \). However, more recently, \( s(E) \) was determined experimentally\(^3\) for ultra-low energy atomic H striking a liquid-\(^4\)He surface, and did not appear to have quantum threshold behavior. Further threshold behavior apparently contrary to quantum predictions was found for positronium (Ps) on Al(111) surfaces.\(^4\) We shall return to these experiments at the end.

Theoretically the threshold behavior of \( s(E) \) for a particle coupled to a solid by a short range interaction was formally studied by Brenig\(^6\) who expressed many-body effects in a non-local, complex, energy dependent potential \( U_{\text{eff}}(r, r'; E) \). Assuming that \( U_{\text{eff}} \) is
also short range in \( r \) and \( r' \) and has a well defined finite limit as \( E \to 0 \), he found \( s(0) = 0 \), in keeping with quantum perturbation theory. The same conclusion\(^{11} \) was reached for the important case of van der Waals interactions \(( \sim z^{-3} \) for large \( z \)).

Polarization effects due to virtual (non-resonant) phonon excitations that are quantitatively important are neglected in Refs. 6 and 11. Knowles and Suhl\(^{12} \) have shown that surface polarization effects increase \( s(E) \) at low energies. As a result of the polarization, the penetration of the particle’s effective wavefunction into the surface region is increased. This effect is known to be in competition with quantum reflection in the determination of \( s(E) \) as \( E \to 0 \).

For the case of a charged particle which experiences a long range image potential, Martin et al.\(^7 \) calculated \( s(E) \) using perturbation theory and concluded (mistakenly) that \( s(E) \propto E^{1/4} \) for small \( E \), so that \( s(0) = 0 \). Their subsequent numerical calculations using the time dependent Hartree approximation indicated to them that \( s(0) \neq 0 \) if the particle-phonon coupling \( \lambda \) exceeded a critical value \( \lambda_c \). They concluded that when \( \lambda > \lambda_c \), polarization effects dominate the quantum reflection.

We shall present results of an exactly solvable one dimensional (1D) model for quantum sticking. The model is sketched in Fig. 1a. It has an external particle interacting with a 1D “solid slab.” All motions are constrained to 1D. The surface atom and the particle interact by a short range potential whose generic form is sketched in Fig. 1b. We take for the Hamiltonian of the system\(^{13} \)

\[
\mathcal{H} = \mathcal{H}_{ph} + \mathcal{H}_p + \mathcal{H}_I, \tag{1}
\]
where
\[
\mathcal{H}_{ph} = \sum_q \hbar \Omega_q a^\dagger_q a_q,
\]
\[
\mathcal{H}_p = \frac{P^2}{2m} + V(z),
\]
\[
\mathcal{H}_I = \frac{1}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{M \Omega_q}} \cos \left( \frac{q a}{2} \right) (a^\dagger_q + a_q) V'(z);
\]
\[
(2)
\]
\(\mathcal{H}_p\) is the Hamiltonian for the particle moving in the static potential, \(V(z)\). \(\mathcal{H}_{ph}\) is the Hamiltonian for the phonons in the solid; \(\mathcal{H}_I\) contains the particle–phonon coupling; \(m\) is the particle mass; \(\Omega_q\) is the frequency of the phonon with wavenumber \(q\); and \(a^\dagger_q\) and \(a_q\) are phonon creation and annihilation operators respectively. \(N\) is the number of atoms in the solid, \(M\) is the mass of a lattice atom, and \(a\) is the equilibrium lattice spacing.

The phonon Hamiltonian describes a chain of \(N\) atoms coupled harmonically to their nearest neighbors and to fixed sites as illustrated in Fig. 1. (The coupling to fixed sites, which introduces a lower cut-off frequency \(\Omega_c\), is needed in this 1D model to prevent a well-known infrared divergence which does not exist in higher dimensions.) The interaction potential, \(V\), is sufficiently deep so as to support a bound state with energy \(-E_b\).

We next restrict the Hilbert space to states with 0 or 1 phonon present\(^{14}\). However we allow a particle-lattice interaction of arbitrary strength.

We expand the wavefunction using 0– and 1–phonon eigenstates, \(\psi_0\) and \(\{\psi_i\}\):
\[
\Psi(z_1, z_2, \ldots, z_N, z) = \phi_0(z) \psi_0(z_1, z_2, \ldots, z_N) + \sum_{i=1}^N \phi_i(z) \psi_i(z_1, z_2, \ldots, z_N),
\]
\[
(3)
\]
where \((z_1, z_2, \ldots, z_N)\) are the positions of the chain atoms, \(i\) labels its modes, and \(z\) is the position of the particle. The following coupled system of equations results:
\[
(\mathcal{H}_p - E)\phi_0(z) + \sum_{i=1}^N V_{0i}(z) \phi_i(z) = 0,
\]
\[
(4a)
\]
\[(\mathcal{H}_p + h\Omega_i - E) \phi_i(z) + V_{i0}(z) \phi_0(z) = 0, \quad i = 1, \ldots, N\]  \hspace{1cm} (4b)

where

\[V_{i0}(z) = V_{0i}(z) = \frac{1}{\sqrt{N}} \sqrt{\frac{\hbar}{M\Omega_i}} V'(z) \cos\left(\frac{q_i a}{2}\right),\]  \hspace{1cm} (5)

\(\phi_i\) is the wavefunction for the particle in the \(i^{th}\) channel. \(h\Omega_i\) is the excitation energy, \(q_i\) is the wavenumber of the \(i^{th}\) mode, and \(E\) is the total energy of the system.

The coupled system of Eq. (4) may be reduced to an effective one-particle equation by first solving Eqs. (4 b) for the \(\phi_i\) in terms of \(\phi_0\). Substitution into Eq. (4 a) gives a single equation for the particle wavefunction in the elastic channel, \(\phi_0\).

\[\left(\frac{d^2}{dz^2} + k^2 - U(z)\right) \phi_0(z) - \int dz' U_{\text{eff}}(z, z'; k) \phi_0(z') = 0,\]  \hspace{1cm} (6)

where

\[U_{\text{eff}}(z, z'; k) \equiv \sum_{i=1}^{N} U_{0i}(z) U_{0i}(z') G_i(z, z')\]  \hspace{1cm} (7)

and

\[G_i(z, z') = \frac{\Phi_b(z)}{\omega_i - k^2 - \epsilon_b} + \int_0^{\infty} dk' \frac{\Phi(z, k')\Phi(z', k')}{\omega_i - k^2 + k'^2 - i\eta},\]  \hspace{1cm} (8)

\(k \equiv \sqrt{2mE/\hbar}, \quad \omega_i \equiv \frac{2m}{\hbar^2} h\Omega_i, \quad \text{and} \quad \epsilon_b \equiv \frac{2mE_b}{\hbar^2}.\) \(\Phi(z, k)\) and \(\Phi_b(z)\) are normalized continuum and bound state eigenfunctions respectively for the static potential \(U(z)\). \(\eta \rightarrow 0^+\), so as to satisfy the outgoing boundary conditions for the scattered particle.

The boundary/asymptotic conditions on \(\phi_0\) are

\[\phi_0(-\infty) = 0\]  \hspace{1cm} (9a)

\[\phi_0(z) = e^{-ikz} - R(k)e^{ikz}, \quad z \rightarrow \infty\]  \hspace{1cm} (9b)
where $R(k)$ is the elastic reflection coefficient. Eqs. (5) and (8) can be analytically solved for $s(E)$. Complete details are given elsewhere.\textsuperscript{15} We find that for finite $N$, $s(E) \equiv 0$ for all $E$. Only in the limit of $N \rightarrow \infty$ does sticking occur, and $s(E)$ is given as

$$s(E) = \frac{1}{k} \frac{|P(k)|^2 |\text{Im} \mathcal{I}(k)|}{|1 - W(k)\mathcal{I}(k)|^2}$$

(10)

where

$$W(k) = 2 \left( \frac{m}{M} \right) \int dz' dz'' \Phi_b(z') U'(z') \mathcal{G}(z', z''; k) U'(z'') \Phi_b(z''),$$

(11)

$$\mathcal{I}(k) = \int_{\omega_c}^{\omega_m} d\omega \frac{\rho(\omega) \cos^2 \left( \frac{q(\omega)a}{2} \right)}{(k^2 + \epsilon_b - \omega + i\eta) \omega}$$

(12)

and

$$P(k) = -2ie^{i\delta(k)} \sqrt{\frac{2m}{M}} \int dz' \Phi_b(z') U'(z') \chi_0(z'; k);$$

(13)

$\rho(\omega)$ is the density of vibrational states per atom and $\mathcal{G}$ is a Green’s function for the particle in the potential, $U + U_{\text{pol}}$, consisting of the static part and the part due to virtual excitations of the particle-phonon system, exclusive of virtual particle sticking; $\chi_0$ is a solution in $U + U_{\text{pol}}$, subject to the boundary condition that it vanish as $z \rightarrow -\infty$ and the asymptotic condition that it approach $\sin(kz + \delta)$ as $z \rightarrow \infty$; $\delta$ is the phase shift resulting from $U + U_{\text{pol}}$.

In the low energy regime, for a finite range $U$, $\chi_0(z, k) \xrightarrow{k\rightarrow0} kf(z)$. The factor $k$ is the manifestation of quantum reflection. The result is that regardless of the coupling strength,

$$s(E) \xrightarrow{E \rightarrow 0} E^{1/2}$$

(14)

For a neutral particle which asymptotically experiences a $z^{-3}$ potential, the above result is still valid\textsuperscript{11}. 
A charged particle asymptotically experiences a $z^{-1}$ potential. Here (unlike for $z^{-3}$) the WKB approximation for $\chi_0$ is valid for all $k$ beyond a fixed $z$, and the particle experiences no quantum reflection. In the low energy regime, $\chi_0(z,k) \rightarrow \sqrt{k} g(z)$. We define as $s_n(E)$ the sticking probability for the bound state $n$. In lowest order perturbation theory in the particle-phonon coupling, we find

$$s_n(E) \underset{E \rightarrow 0}{\rightarrow} \alpha_n$$  \hspace{1cm} (15)

where $0 < \alpha_n < 1$.

We must concern ourselves with the convergence of the infinite summation resulting from sticking contributions from the infinite number of Coulomb bound states. The amplitude of high lying bound states near the surface behaves as $n^{-3/2}$ as for pure Coulomb wave functions. Thus the square of the matrix elements decrease as $n^{-3}$, insuring convergence of the summation. In fact, most sticking occurs in the lowest bound state.

In relating quantum sticking to classical sticking we want to point out two quite distinct quantum effects.

1. A Debye-Waller like effect: In quantum mechanics there is a finite probability (even as $N \rightarrow \infty$) that no lattice vibrations are excited and hence the particle is reflected. Thus under all circumstances $s(E) < 1$. By contrast, classically, in the case of an attractive particle-target interaction, a finite amount of impact energy is delivered to the target, even when $E \rightarrow 0$, because of the particle’s acceleration by the interaction potential. When $N \rightarrow \infty$, some of this energy disappears to $z = -\infty$. Thus for $E$ sufficiently small, $E < E_{\text{min}}$, the particle cannot escape and $s(E) = 1$. 

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2. Quantum reflection: We consider first the particle striking a rigid target in the classical regime. The particle coming in with a low velocity, \(-v_\infty\), spends a time of the order 
\[ t_{\text{res}} \sim \frac{2z_0}{\bar{v}} \]
in the interaction region, where \(z_0\) is the range of interaction and \(\bar{v}\) is a mean speed in the interaction region. As \(v_\infty \to 0\), \(\bar{v}\) approaches a finite limit and the ratio of the time spent by the particle in the interaction region to the time spent in a spatial interval \(z_0\) in the asymptotic region is

\[ \frac{P_i}{P_\infty} \equiv \frac{t_{\text{res}}}{(\frac{z_0}{v_\infty})} \sim \left( \frac{E}{\bar{E}} \right)^{1/2}, \quad (16) \]

where \(\bar{E} \sim \frac{1}{2} m \bar{v}^2\) is a typical kinetic energy in the interaction region, when \(v_\infty \to 0\).

Now consider the problem quantum mechanically for small incident energy. In the rigid target potential, assumed sufficiently short range, the particle is described by a standing wave, \(\chi_0(z, k)\), with the properties

\[ \chi_0(z, k) \bigg|_{z \to \infty} = \mathcal{N} \sqrt{\frac{2}{\pi}} \sin(kz + \delta') \quad (17a) \]

\[ \chi_0(z, k) \bigg|_{z \to 0} \sim \mathcal{N}(kz_0) f(z) \quad (17b) \]

where \(\mathcal{N}\) is an (irrelevant) normalization factor, \(\delta'\) is a phase shift, and \(f(z)\) becomes independent of \(k\) for small \(k\) and is of order 1. (This is well-known from so-called effective range theory\(^{16}\) and can easily be checked for a square well interaction potential backed by an infinite wall.) Thus the ratio of the probability of finding the particle in the interaction region to the probability of finding it in an asymptotic interval of length \(z_0\) is

\[ \frac{P_i}{P_\infty} \approx \int_{0}^{z_0} \frac{[(kz_0)f(z)]^2}{z_0} dz \approx k^2 z_0^2 \approx \frac{2mz_0^2}{k^2} E \quad (18) \]

Note the power of \(E^1\) compared to the classical result, \(E^{1/2}\): as \(E \to 0\) the quantum particle spends less time in the interaction region than the classical particle, by a power \(E^{1/2}\). This
is the so-called quantum reflection. We can also note that for unit incident current, the probability of a quantum particle being in the interaction region is \( \sim E^{1/2} \). This is the physical origin of the sticking threshold behavior of Eq. (14). For a charged particle, on the other hand, one finds \( P_i/P_\infty \) has the form of Eq. (16), as in the classical case; \( i.e., \) there is no quantum reflection.

Very recent experiments with low energy neutral particles striking low temperature targets have failed to find the threshold behavior of Eq. (14) which we expect because of quantum reflection. The sticking of neutral H on liquid \(^4\)He film\(^3\) was analyzed by Carraro and Cole\(^9\) using Ref. 11. They conclude that the energy (\( \sim 10^{-8} \) eV) was still too high to observe quantum reflection in this system.

An ingenious experiment by Mills et al.\(^4\) of desorption of low energy Ps from Al, led to the estimate \( s(0) \approx 1 \) by means of a detailed balance argument. Because of the low mass of Ps, quantum reflection effects are expected to be much more pronounced than for incident atoms and molecules. According to Ref. 8, they would normally be expected at incident energies below 2 eV. The experiments explore energies down to \( 5 \times 10^{-3} \) eV without signs of quantum reflection.

Martin et al.\(^8\) offer as explanation their previous conclusion from numerical work that sufficiently strong inelastic coupling eliminates quantum reflection. Our model shows quantum reflection for neutral particles regardless of the strength of the coupling. We also want to point out that the numerical results of Ref. 8 (Fig. 2) for a charged particle show that \( s(0) \propto \lambda^2 \) for small coupling constant \( \lambda \), in line with our own results, and that, when plotted against \( \lambda \) rather than \( \log \lambda \), there is in our opinion no sign of an abrupt transition.
We therefore consider the apparent absence of quantum reflection observed by Mills et al. as still unexplained.

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Figure 1. (a) Schematic view of a particle with mass $m$ impinging upon a 1D solid consisting of atoms with mass $M$. Lattice atoms are coupled to nearest neighbors and to fixed lattice sites. (b) Particle interacts with the end atom via a finite-range surface potential.