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Sufficiency conditions for quantum reflection

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Abstract. – The mathematics of low-energy scattering from asymptotic power law potentials are examined to extract characteristic lengths of the scattering problem in the limit of low velocity. These are then used to characterize the limiting behavior of the scattering wave function, leading immediately to general, explicit, sufficiency conditions for quantum reflection for arbitrary gas and surface species.

A particle striking a surface at sufficiently low incident velocity does not stick. This behavior is a direct consequence of quantum-mechanical limitations on gas-surface energy transfer at low incident velocity, prompting the name "quantum reflection". Although the first experimental evidence of this phenomenon emerged only recently [1], theoretical study of quantum reflection dates back nearly two decades [2]. Given recent advances in ultra-slow atom beams [3], it is of great interest to demarcate, for arbitrary choice of atom and surface, the velocity regime that yields quantum reflection. Relevant to this characterization is the sticking probability $S(k)$ and its dependence on the incident wave vector k. For appropriately short-ranged potentials, a wave vector $k_{\rm QR}$ exists such that $S(k) \sim k$ for all $k \ll k_{\rm QR}$ (see, *e.g.*, [4]). To delineate the quantum reflection regime, it therefore suffices to establish $k_{\rm QR}$.

In his seminal work on quantum reflection, Brenig [2] invoked WKB failure as a possible criterion for $k_{\rm QR}$. A detailed mathematical treatment was supplied by Böheim, Brenig and Stutzki (BBS) [5]. WKB breakdown implies mismatch of the de Broglie wavelength of the particle ($\lambda = 2\pi/k$) *vis à vis* characteristic length scales of the potential. Most recent work invokes either WKB breakdown [5,6] or length scale mismatch [6,7] as a "cause" of quantum reflection. Choosing as a causal criterion the failure of an approximate computational method is worrisome, however, unless such failure can be uniquely linked to a more fundamental behavior. This paper supplies a rigorous criterion for $k_{\rm QR}$ in the case of interaction potentials having a physically correct power law dependence at large separation x [8],

$$V(x) \sim -C_s/x^s \qquad (s > 0 \text{ and } C_s > 0)\,. \tag{1}$$

The fundamental, underlying quantum mechanics is a spatial "scission" of the scattering wave function in the limit $k \to 0$, as discussed by BBS [5] for $s = 3$ and by Chung and George (CG) [9] for general s. We show that WKB failure results from this scission, provided $s > 2$. CG applied their analysis to calculate $k_{\rm QR}$ numerically for several gas-surface systems, but did not develop a general analytical expression. Moreover, the CG criterion fails in the presence of a threshold (zero energy) bound state, as is evident from numerical computations of $S(k)$ as a function of well capacity [2, 10], and this must be included in any general $k_{\rm QR}$ formula. Accordingly, we extend and generalize the CG approach to develop within the Born approximation a fundamental, general, complete definition of $k_{\rm QR}$ [11]. On this basis, it is verified that the H:He(liq) experiments of Yu *et al.* [1] did indeed reach the quantum reflection regime. Possible systems for future quantum reflection measurements are discussed on the basis of our $k_{\rm QR}$.

Gas-surface interaction potentials are strongly repulsive at small gas-surface separation x, weakly attractive at intermediate x, and have the power law form of eq. (1) at large x. The pertinent exponents are $s = 3$ and 4 for unretarded and retarded potentials, respectively. The WKB validity criterion, $|{\rm d}\lambda/{\rm d}x| \ll 2\pi$, delivers a wave vector $k_{\rm WKB}$, below which WKB fails. BBS [5] applied this criterion to a $s = 3$ potential truncated to an infinite hard wall at $x < a$. Normalizing distances with respect to a and energies with respect to $\hbar^2/(2ma^2)$, they obtained a non-dimensional expression for $k_{\rm WKB}$. This formula was later extended to general exponent s by Carraro and Cole (CC) [12]. Denoting the non-dimensional quantities explicitly with carets, the CC formula is

$$\hat{k}_{\rm WKB} = f_{\rm WKB}(s)\hat{C}_s^{\left(\frac{1}{(2-s)}\right)}\,, \quad f_{\rm WKB}(s) = 2^{\left(\frac{1}{s-2}\right)}\sqrt{(s-2)}(s+1)^{\left(\frac{s+1}{s-2}\right)}3^{\left(\frac{-3s}{2(s-2)}\right)}s^{\left(\frac{-s}{2(s-2)}\right)}\,. \quad (2)$$

However, simple dimensional analysis delivers a fundamental length scale L_s of the power law potential,

$$L_s = \left(\frac{2MC_s}{\hbar^2}\right)^{\left(\frac{1}{(s-2)}\right)} = a\hat{C}^{\left(\frac{1}{(s-2)}\right)} \quad (3)$$

from which it follows that eq. (2) is an unnecessary re-scaling by a of a more fundamental expression,

$$k_{\rm WKB} = f_{\rm WKB}(s)L_s^{-1} \quad (4)$$

or simply that $k_{\rm WKB}$ in units of L_s^{-1} is equal to $f_{\rm WKB}(s)$. BBS's numerical calculations [5] showed the wave function to vanish in the near-surface region for $k < k_{\rm WKB}$, prompting them to adopt $k_{\rm WKB}$ to delineate the quantum reflection regime. A length mismatch is indeed involved, namely $\lambda > \{2\pi/f_{\rm WKB}(s)\}L_s$, but it is not obvious that quantum reflection is a rigorous consequence of this mismatch or even of $k < k_{\rm WKB}$.

To resolve this issue, we consider scattering wave functions in the limit $k \to 0$ and illustrate the discussion with numerical calculations for realistic gas-surface potentials [13]. Typical numerical wave functions are provided in fig. 1(a) for an unretarded He:Cu(111) potential. The governing equation for scattering from an uncorrugated surface is the 1D time-independent Schrödinger equation for an atom of mass M in a potential $V(x) = \hbar^2 U(x)/2M$,

$$\frac{{\rm d}^2\Psi(x;k)}{{\rm d}x^2} + (k^2 - U(x))\Psi(x;k) = 0\,. \quad (5)$$

Restricting consideration to $k^2 \ll |U_{\rm min}|$, eq. (5) clearly displays different $k \to 0$ limiting forms at small and large x [9, 11], as discussed by BBS [5] and CG [9]. A k-independent equation

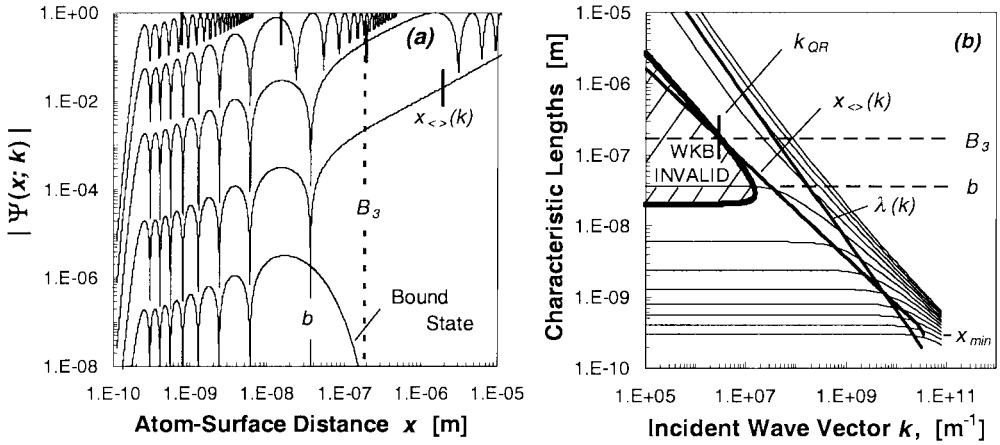

Fig. 1 – (a) Wave function magnitudes for unretarded ($s = 3$) He:Cu(111), plotted as a function of atom-surface separation. The upper four curves are scattering wave functions, scaled to unity at large x. Incident wave vectors are, from top, $k = 10^{10}$, 10^8, 10^6, 10^4 m^{-1}, corresponding to incident energies of 0.52 meV, 52 neV, 5.2 peV and 0.52 feV. The lowest curve is the wave function of the weakest bound state, scaled arbitrarily. Characteristic lengths are marked, specifically the linearity boundary, B_3 (dashed vertical line), the binding length b, and the scission boundary $x_{<>}(k)$ (short vertical bar for each k). (b) Graphical depiction for He:Cu(111) of characteristic lengths as a function of k. Light solid line curves mark the nodal positions of the scattering wave function, the lowest eight corresponding to the eight bound states of He:Cu(111). Boundary at the middle left encloses the region of WKB failure. For He:Cu(111), $B_3 \gg b$ so that the critical binding does not play a role and the quantum reflection regime is entered when $x_{<>}(k)$ exceeds B_3. This $k_{\rm QR}$ is marked (short vertical bar).

results in the vicinity of the attractive well, where $k^2 \ll |U(x)|$. A k-dependent equation results at large x, where $U(x) \to 0$ and $k^2 \gg |U(x)|$. Thus the scattering wave function $\Psi(x;k)$ "scissions" into functionally different forms $\Psi_<(x)$ and $\Psi_>(x;k)$, respectively. The inner and outer regions are separated by a "scission boundary" $x_{<>}(k)$, defined as the position at which the total energy and potential are equal in magnitude,

$$k^2 = |U(x_{<>}(k))| \,. \tag{6}$$

This $x_{<>}(k)$ moves outward with decreasing k. Since $\Psi(x;k)$ is box-normalized at large x, an asymptotic matching of $\Psi_<(x)$ and $\Psi_>(x;k)$ at $x_{<>}(k)$ in the limit $k \to 0$ imposes an overall linear k-dependence on $\Psi_<(x)$, with the result that the overlap of the scattering state with all bound states vanishes as $k \to 0$. This behavior is clearly seen in fig. 1(a). Consequently, $S(k) \sim k$ and quantum reflection ensues, as discussed by numerous authors [4, 9, 10]. The conditions leading to scission and boundary matching therefore constitute sufficiency conditions for quantum reflection, establishing $k_{\rm QR}$. To extract an analytical expression, consider the scattering wave function $\Psi_<(x;0)$ obtained by setting by $k = 0$ in eq. (5). In accordance with Levinson's Theorem, $\Psi_<(x;0)$ displays one node per bound state, as is easily discerned in the low k wave functions of fig. 1(a). Inserting eq. (1) into eq. (5) yields [14, 15]

$$\Psi_<(x;0) = \sqrt{\frac{x}{B_s}}\mathcal{C}_{\frac{1}{2-s}}\left(-(x/B_s)^{(2-s)/2}\right) . \tag{7}$$

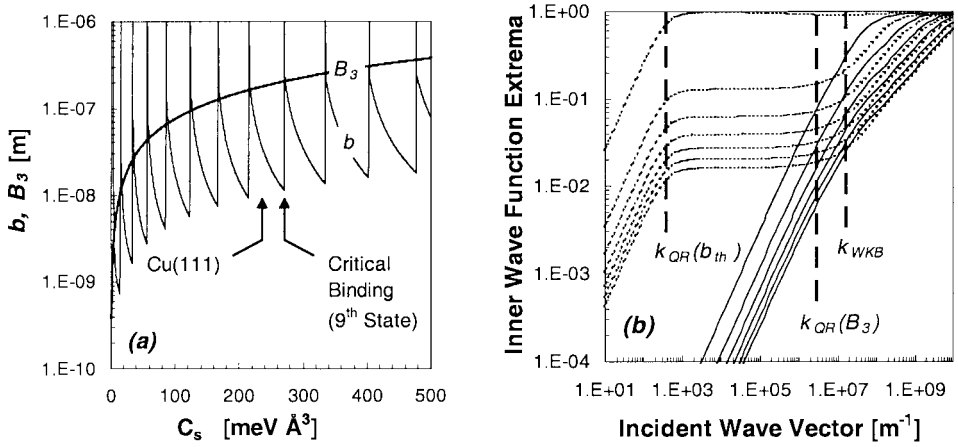

Fig. 2 – (a) Model calculations for a flat-bottomed, hard wall potentials having C_3/x^3 asymptotic power law dependence. The value of C_3 is varied to alter the number of bound states. With the emergence of each new state, the binding length b jumps discontinuously to infinity. For $s \sim 3$ the spikes to $b > B_3$ are narrow, so $B_3 > b$ will be the statistically prevalent case. Arrows mark values of C_3 used in graph (b). (b) Magnitudes of near-surface extrema of the scattering wave function, $\Psi(x;k)$, plotted as a function of k for potentials modeling i) Cu(111) ($C_3 = 235$ meV Å^3 to yield $b = 358$ Å and $B_3 = 1800$ Å, solid line curves) and ii) a near-threshold ninth bound state ($C_3 = 262.15$ meV Å^3 to yield $b = 2.82$ mm and $B_3 = 2010$ Å, dashed line curves). Since $b \ll B_3$ in case i), B_3 determines the onset quantum reflection, labeled $k_{\rm QR}(B_3)$ in the plot. $\Psi(x;k)$ is seen to drop linearly in amplitude with k once $k < k_{\rm QR}(B_3)$. In case ii), $b \gg B_3$ and b determines a much smaller critical wave vector, labeled $k_{\rm QR}(b_{\rm th})$. The region of linear decrease in $\Psi(x;k)$ amplitude is shifted to $k < k_{\rm QR}(b_{\rm th})$. Onset of WKB breakdown, $k_{\rm WKB}$, is indicated (it is essentially the same for both C_3 values).

$\mathcal{C}_\nu(z)$ denotes any cylinder function, *e.g.*, the Bessel functions $Y_\nu(z)$ and $J_\nu(z)$. Note that the exponent of the argument z is negative for $s > 2$, in which case $x \to \infty$ leads to $z \to 0$. A characteristic length B_s has emerged, dependent solely upon M, s, C_s, and constants,

$$B_s = \left(\frac{8MC_s}{(2-s)^2\hbar^2}\right)^{\frac{1}{s-2}} = \left(\frac{4}{(2-s)^2}\right)^{\frac{1}{s-2}} L_s\,. \tag{8}$$

Expanding the physically appropriate $\mathcal{C}_\nu(z)$ for small z (large x) [14] reveals $\Psi_<(x;0)$ to be linear in x for $x > B_s$ and likewise $\Psi_<(x;k)$ as $k \to 0$. Thus B_s defines a "linearity boundary" for the $k \to 0$ inner wave function. A strictly linear portion of the wave function yields an infinite $\lambda(x)$, whereupon WKB must fail. WKB breakdown is therefore unambiguously associated with the linear portion of the wave function beyond $x > B_s$ and is a consequence of the wave function scission and the asymptotic form of $\Psi_<(x;0)$.

As k is reduced, the scission boundary $x_{<>}(k)$ eventually moves beyond B_s. The k-independent inner portion of the wave function $\Psi_<(x)$ is then linear in x approaching $x_{<>}(k)$ from below. In the absence of any threshold bound states and provided the de Broglie wavelength $\lambda(k)$ appreciably exceeds $x_{<>}(k)$, the outer portion $\Psi_>(x;k)$ is also linear in x, with slope proportional to k, upon approaching $x_{<>}(k)$ from above. Asymptotic boundary matching of $\Psi_<(x)$ and $\Psi_>(x;k)$ at $x_{<>}(k)$ then yields quantum reflection [4, 9, 10]. Consequently, the conditions $x_{<>}(k) > B_s$ and $\lambda > x_{<>}(k)$ suffice to establish $k_{\rm QR}$. For $s > 2$, the wave-

length $\lambda(k)$ increases more rapidly with decreasing k than does $x_{<>}(k)$ and the B_s constraint dominates. Accordingly, via eqs. (1), (6), and (9),

$$k_{\mathrm{QR}} = \left(\frac{(2-s)^2}{4}\right)^{\frac{s}{2(s-2)}} \left(\frac{\hbar^2}{2MC_s}\right)^{\frac{1}{s-2}}, \tag{9}$$

which can be written in the same functional form as eq. (4),

$$k_{\mathrm{QR}} = f_{\mathrm{QR}}(s) L_s^{-1}, \quad f_{\mathrm{QR}}(s) = \left(\frac{|2-s|}{2}\right)^{\frac{s}{s-2}}. \tag{10}$$

A comparison of $f_{\mathrm{QR}}(s)$ and $f_{\mathrm{WKB}}(s)$ shows that the WKB criterion k_{WKB} is coincidentally almost identical to the more rigorous k_{QR} for retarded potentials ($s = 4$) but smaller by a factor of nearly 6 for unretarded potentials ($s = 3$). More importantly, the relevance of the WKB criterion has emerged. WKB failure is linked to the appearance of a linear portion of the wave function in the region of asymptotic boundary matching. In a sense, this region can be viewed as an analog at positive kinetic energy to a classical turning point, whereby quantum reflection is interpreted as scattering of the particle from the attractive outer wall of the potential well rather than from the repulsive inner wall. Identical behavior is found at larger values of s, *e.g.*, $s = 6$ and 7 of unretarded and retarded gas-gas scattering, respectively.

Tacit within the above derivation is the assumption that B_s lies beyond all stationary nodes of $\Psi_<(x;0)$. This precludes threshold (zero energy) bound states. Returning to the $k \to 0$ stationary nodes of the scattering wave function, it is obvious that these nodes constitute a family of characteristic lengths representative of the bound state spectrum. Of primary interest is the largest, namely the node associated with the weakest bound state. This we denote the "binding length", in analogy with the scattering length a of effective range theory, and label it b [16]. The binding length depends critically on the potential well capacity. If the well is adjusted to move the weakest state to zero energy binding, the value of b increases to infinity. Once $b > B_s$, the outer portion of the wave function $\Psi_>(x;k)$ need not be linear in

Table I – *van der Waals dispersion coefficient C_3, binding length b, linearity boundary B_3, and the critical wave vector for quantum reflection k_{QR}, for various unretared ($s = 3$) gas-surface systems of interest. Table is arranged in order of decreasing k_{QR}. Polycrystalline faces and liquid surfaces are labeled "poly" and "liq", respectively.*

Gas	Surface	C_3(meVÅ^3)	b(Å)	B_3(Å)	k_{QR}(Å^{-1})
H	^{4}He(liq)	31	*	60	8.4×10^{-3}
^{4}He	Cs(poly)	86	430	660	7.6×10^{-4}
^{4}He	Li(poly)	123	250	940	5.3×10^{-4}
^{4}He	Cu(111)	227	360	1740	2.9×10^{-4}
^{4}He	Ag(111)	250	1240	1910	2.6×10^{-4}
^{4}He	Au(111)	275	150	2110	2.4×10^{-4}
H_2	Cs(poly)	286	1370	4300	2.3×10^{-4}
Ne	Mg(poly)	301	980	11600	4.3×10^{-5}
Ne	Cu(111)	453	2460	17500	2.9×10^{-5}
Ne	Al(111)	401	2560	15500	2.6×10^{-5}
Ar	Cu(111)	1540	19800	118000	4.3×10^{-6}

x at $x_{<>}(k) = B_s$ unless $\lambda(k) > b$. This requirement yields

$$k_{\mathrm{QR}} = \frac{2\pi}{b} \tag{11}$$

For any s, the smaller k_{QR} of eqs. (9) and (11) delineates the quantum reflection regime. Together, these two equations constitute general, fully sufficient conditions for quantum reflection.

Insofar as questions of length mismatch are concerned, the pertinent characteristic lengths are seen to be $x_{<>}(k)$, $\lambda(k)$, b, and B_s. These are plotted in fig. 1(b) as a function of k for He:Cu(111). The eight lowest nodes of this system clearly "lock in" at low k to their stationary x-values in the $\Psi_<(x)$ region of $x < x_{<>}(k)$. Since $b \ll B_s$ for He:Cu(111), critical binding plays no role and quantum reflection then ensues once $x_{<>}(k)$ exceeds B_s, as marked. The region of WKB breakdown is indicated.

Detailed discussions of threshold bound states has been presented [5, 10]. To illustrate their effects on k_{QR}, simple model calculations of b and B_3 suffice, as plotted in fig. 2(a). At $C_3 = 235$ meV Å^3, this model potential approximates the dispersion and bound state spectrum of He:Cu(111). If C_3 is varied to alter the well capacity, the value of b jumps discontinuously to infinity with the emergence of each bound state. Near each singularity, $b \gg B_3$ and eq. (11) determines the onset of quantum reflection. Elsewhere, $B_3 \gg b$ and eq. (9) is the relevant relation. A gas-surface well capacity can be tuned experimentally in this fashion by means of overlayer growth, ion implantation, or even thermal expansion and contraction of quantum solids such as LiH. It is thus possible that threshold bound state behavior can be explored experimentally [17]. Picking cases of non-critical and critical binding, the corresponding extrema of the scattering wave function near the surface are plotted in fig. 2(b). The k_{WKB} criterion of BBS and CC is clearly insufficient in the presence of a threshold bound state.

Using theoretical values of C_3 [13], eqs. (9) and (11) were applied to compute k_{QR} for various gas-surface systems of current interest, as listed in Table I. Note from eq. (9) that k_{QR} varies inversely with MC_s for all short-ranged ($s > 2$) potentials. Large values of k_{QR} therefore require small M and C_s. Of the systems investigated, the largest k_{QR} is that of H:^{4}He(liq). This is the only system for which experimental quantum reflection has been reported [1] and our k_{QR} verifies that those experiments did indeed reach the $S(k) \sim k$ quantum reflection regime. For helium scattering, alkali metals offer the best prospects of observing quantum reflection. Inclusion of retardation improves prospects, due to the increase in $f_{\mathrm{QR}}(s)$ with s. Observation of quantum reflection with heavy inert gases seems unlikely, due to the large M and C_s , yielding correspondingly large L_s and B_s.

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