Asymptotics of distorted-wave matrix elements for strongly singular potentials

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A simple and asymptotically exact relation is derived for the ratio of the quantum matrix element $\langle E|W|E'\rangle$ to its classical counterpart in the limit of large energy E'. The method is based on an idea from Landau and works for a large class of potentials including the Lennard-Jones and the exponential potential. The result should be of interest in problems where large energy transfer is involved. Examples are the high-frequency wings of collisionally broadened spectra, or vibrational energy transfer of high-frequency oscillators.

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I. INTRODUCTION

Many problems in perturbation theory reduce to an estimate of the distorted wave matrix element

$$\langle E|W|E'\rangle = \int_0^\infty \psi_E(r)W(r)\psi_{E'}(r)dr. \tag{1}$$

Here $W(r)$ is some interaction potential and the wave functions $\psi_E(r)$ belong to bound or continuum states. Integrals of this kind appear in vibrational energy relaxation [1,2], line broadening [3], and collision-induced absorption [4]. In the simplest cases Fermi's golden rule is invoked, according to which the transition rate $w_{E\to E'}$ of a system weakly perturbed by potential $W(r)$ is proportional to the square of the corresponding matrix element

$$w_{E\to E'} = \frac{2\pi}{\hbar}\rho(E')|\langle E|W|E'\rangle|^2, \tag{2}$$

where $\rho(E')$ is the density of final states.

In some of the problems mentioned above, the final energy E' is very large compared to the initial energy E. This happens, for example, in the high-frequency wings of spectra [5,6]. Another interesting problem where large differences are involved is vibrational energy transfer. In this case the energy of the oscillator, $\hbar\omega$, must be compared with the thermal energy k_BT. For high-frequency oscillators at low temperature the ratio $\hbar\omega/k_BT$ may become very large. In these situations it is important to have some control over the asymptotic behavior of the matrix elements when one (but not both) of the energies becomes very large.

It has been known for a long time that straightforward numerical methods become difficult in the high energy domain. The reason is, that the corresponding wave function oscillates very rapidly and renders the matrix element exponentially small. Particularly severe are the numerical problems for large heavy particles near the classical limit. Various analytical or semianalytical methods have been used to cope with this problem [7]. Most methods rely on an idea due to Landau [8] where the WKB wave functions are continued analytically into the complex plane and the integrals are evaluated by the method of steepest descent [4,9,10]. Because the region near the classical turning point supplies the dominant contribution to the matrix elements, Airy functions and Langer's uniform asymptotic wave functions have also been employed [11].

While the numerical methods have provided useful information on the specific potentials studied, they supply little information on the dependence of the matrix elements on pair potential $V(r)$ or interaction potential $W(r)$. Furthermore, they seem not to have been used to determine the true asymptotic behavior of the matrix elements.

In this paper we study the asymptotics of matrix elements for the simplest two-body problem where the wave functions refer to the Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\psi''_E(r) + V(r)\psi_E(r) = E\psi_E(r). \tag{3}$$

We want to determine the exact asymptotic behavior of the matrix elements for large E without having to determine the exact wave functions and try to answer the following questions.

What is the asymptotic behavior of the matrix element if one of the energies tends to infinity?

How do the asymptotic matrix elements depend on the pair potential $V(r)$ and the interaction potential $W(r)$?

How do the quantum mechanical matrix elements compare to their classical limits?

The analytical methods employ well known techniques. These are the WKB approximation for the "fast" wave function and Landau's analytic continuation into the complex plane. While both methods have been utilized extensively for numerical and analytical purposes, they do not seem to have been applied to determine the exact asymptotic expressions for the matrix elements.

II. NORMALIZATION AND CLASSICAL LIMIT

For large positive r the wave function has the form

$$\psi_E(r) \sim \gamma_E\cos(kr + \varphi_E), \tag{4}$$

where

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$$k^2 = \frac{2\mu E}{\hbar^2} \tag{5}$$

is the wave number and γ_E is a normalization constant. It is advantageous to put

$$\gamma_E = 2\left(\frac{\mu}{2E}\right)^{1/4}. \tag{6}$$

With this normalization $|\psi_E(r)|^2$ tends to the classical probability density

$$|\psi_E(r)|^2 \to \frac{1}{2}\gamma_E^2 = \frac{2}{v_\infty} \tag{7}$$

in the classical limit. Here v_∞ is the (relative) velocity of the classical particles far from the collision center. The factor of 2 is due to the particles approaching and receding.

If there are no bound states the above normalization is equivalent to

$$\int_0^\infty \psi_E^*(r)\psi_E(s)dE = 2\pi\hbar\,\delta(r-s) \tag{8}$$

and

$$\int_0^\infty \psi_E(r)\psi_{E'}^*(r)dr = 2\pi\hbar\,\delta(E-E'). \tag{9}$$

The classical limit of the matrix elements is found from the quasiclassical wave functions

$$2\sqrt{\frac{\mu}{p(r)}}\cos\left(\frac{1}{\hbar}\int_{r_0}^r p(s)ds - \frac{\pi}{4}\right) \tag{10}$$

for $r > r_0$ where r_0 is the classical turning point and $p(r)$ is the classical momentum. This leads in the classical limit to

$$\begin{aligned}\langle\psi_E|W|\psi_{E+\hbar\omega}\rangle &\to 2\int_{r_0}^\infty W(r)\cos\left(\omega\int_{r_0}^r \frac{dy}{v}\right)\frac{dr}{v}\\ &= \int_{-\infty}^\infty W(r(t))\cos(\omega t)dt.\end{aligned} \tag{11}$$

The matrix elements of operator W tend to the Fourier transform of the corresponding classical function $W(r(t))$.

III. MATRIX ELEMENTS AND STRONGLY SINGULAR POTENTIALS

Before we proceed, it is useful to review some qualitative arguments connecting the decay properties of the matrix elements with the properties of the potential.

In the following we consider potentials with a singularity at $r=0$ where V becomes infinite. The asymptotic behavior of the matrix elements then is determined by the nature of the repulsive inner part of the potential. This is true classically as well as quantum mechanically.

Classically the matrix elements always decay exponentially with frequency [12]. The reason for this is simply that (at fixed energy E) two particles cannot approach arbitrarily closely. The mathematical singularity associated with collision is "shielded" and corresponds to an imaginary time it^* [12]. This leads to exponential decay.

In quantum mechanics two particles in a collision always have a nonzero probability of occupying the same place. The corresponding singularity is no longer shielded. This suggests, that the decay of the matrix elements is always slower than exponentially. It also suggests, that the decay properties are determined by the steepness of the potential near its singularity.

In the following we consider potentials with a singularity at $r=0$ which is stronger than r^{-2}, i.e., we assume that near $r=0$

$$V(r) \sim Ar^{-n}, \quad n > 2. \tag{12}$$

Typical members of this class are the homogeneous potential

$$V_n(r) = Ar^{-n}, \quad n > 2, \tag{13}$$

or the Lennard-Jones potential

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]. \tag{14}$$

We call them "strongly singular potentials."

The exponential potential $\exp(-r/L)$ is analytic on the real axis and has an essential singularity at $r=-\infty$. Therefore it is also a "strongly singular potential" and shares many properties with them. It is discussed in detail in Sec. V B.

The matrix elements of these potentials are qualitatively different from matrix elements of "weakly singular potential" where the singularity is weaker that r^{-2}. In the following we argue that matrix elements of the former decay faster than any power but slower than exponentially (and typically like $\exp\{-\text{const}\ \omega^\nu\}, 0 < \nu \leq 1/2$). One can also show (unpublished) that matrix elements of weakly singular potentials decay algebraically for high frequency. For example, for the Coulomb potential the matrix element with $W=V$ decays like $E'^{-3/4}$ for large E'. The inverse square potential still decays algebraically but with an A-dependent exponent.

Strongly singular potentials have the nice property that the WKB approximation is asymptotically exact. Using Landau's method, this permits an asymptotically exact evaluation of the matrix elements for high frequency.

A. WKB approximation of strongly singular potentials

In most previous approaches the true wave functions are been replaced by their WKB approximations. If this is done, one can proceed using numerical methods or employ Landau's analytical continuation into the complex plane. In these approaches the quality of the WKB approximation is usually not studied and it is simply assumed, that the approximation is sufficiently accurate for the purpose considered.

Despite this neglect, the method seems to work very well in many instances. It does not seem to have been recognized, however, that this approximation is not only surprisingly accurate in most cases, but actually becomes asymptotically exact for high energies for some of the most important potentials.

The simplest way to see this, is to consider the homogeneous potential Eq. (13). The Schrödinger equation reads

$$-\frac{\hbar^2}{2\mu}\psi_E''(r) + Ar^{-n}\psi_E(r) = E\psi_E(r). \tag{15}$$

Putting

$$\psi_E(r) = \gamma_E \phi_{\mathcal{E}}(\lambda r) \tag{16}$$

with the inverse length

$$\lambda = \left(\frac{\hbar^2}{2\mu A}\right)^{1/(n-2)} \tag{17}$$

we obtain

$$-\phi_{\mathcal{E}}''(y) + y^{-n}\phi_{\mathcal{E}}(y) = \mathcal{E}\phi_{\mathcal{E}}(y), \tag{18}$$

where

$$\mathcal{E} = E\left(\frac{\sqrt{2\mu}}{\hbar}A^{1/n}\right)^{2n/(n-2)}. \tag{19}$$

This equation depends on a single parameter, the dimensionless energy $\mathcal{E}$. For $n>2$ the high energy limit is identical to the classical limit $\hbar\to 0$. Since the WKB limit also corresponds to $\hbar\to 0$, this indicates, that the high-energy limit is asymptotically equal to the WKB limit provided $n>2$.

There is another way to draw the same conclusion. The criterion for the applicability of the WKB approximation to the potential $V(r)$ is [8,13]

$$\left|\frac{d}{dx}\frac{\hbar}{\sqrt{2\mu[E-V(r)]}}\right| \ll 1. \tag{20}$$

For high energy this inequality is satisfied away from the classical turning point. However, we need the inequality for all z along the path of integration in Landau's method. Landau studies certain paths in the complex plane which avoid the classical turning point. Putting $r=(A/E)^{1/n}z$, the turning point is at $z=1$ and the inequality becomes

$$\frac{n}{2}\frac{\hbar}{\sqrt{2\mu E}}\left(\frac{E}{A}\right)^{1/n}\frac{|z|^{-n-1}}{|z^{-n}-1|^{3/2}} \ll 1. \tag{21}$$

The last term is bounded on the paths and we find again that WKB is valid for high energy provided $n>2$. In the marginal case $n=2$ the energy cancels, but the inequality is satisfied if A is sufficiently large.

B. Initial amplitude for strongly singular potentials

We expect, that the dominant contribution to the matrix element Eq. (1) for large E' stems from the region near the classical turning point. The larger E', the smaller the turning point, and the smaller the relevant integration range. This indicates that we need the behavior of the "slow" wave function $\psi_E(r)$ for small r.

For $E'\gg E$ and near or below the turning point of the "fast" wave function $\psi_{E'}$ we have $V(r)\gg E$. In this region we may neglect the energy in the "slow" wave function so that ψ_E satisfies

$$-\frac{\hbar^2}{2\mu}\psi_E''(r) + V(r)\psi_E(r) \sim 0. \tag{22}$$

For the homogeneous potential Eq. (13) this equation can be solved exactly. The solution which vanishes at $r=0$ is proportional to

$$\sqrt{r}K_{1/(n-2)}\left(\frac{2}{n-2}\frac{\sqrt{2\mu A}}{\hbar}r^{-(n-2)/2}\right), \tag{23}$$

where $K_\nu(x)$ is the modified Bessel function. For $n>2$ and small r this becomes

$$\psi_E(r) \sim c_E r^{n/4}\exp\left\{-\frac{2}{n-2}\frac{\sqrt{2\mu A}}{\hbar}r^{-(n-2)/2}\right\}, \tag{24}$$

where c_E is a constant. In the general case, were $V(r)\sim Ar^{-n}$, $n>2$ only near the singularity, the small r behavior is the same. Another approach to derive this result is to introduce the ansatz $\psi(r)=e^{P(r)}$ and compare the most divergent terms.

Equation (24) is valid for any admissible solution of the Schrödinger equation in the small-r region if the potential is $\sim Ar^{-n}$, $n>2$ near $r=0$. The constant is determined by the condition that $\psi_E(r)$ has the correct asymptotic behavior for large r, Eq. (4). It can in general only be determined by a numerical solution of the Schrödinger equation.

Consider now the WKB approximation for small r. If r_0 is the classical turning point defined by $V(r_0)=E$, the WKB approximation for $r<r_0$ is

$$\psi_E^{\mathrm{WKB}}(r) = \left(\frac{\mu}{2}\right)^{1/4}\frac{1}{(V(r)-E)^{1/4}} \times\exp\left\{-\frac{\sqrt{2\mu}}{\hbar}\int_r^{r_0}\sqrt{V(y)-E}dy\right\}. \tag{25}$$

Comparing with Eq. (24) and we observe, that both wave functions have the same small-r behavior up to a constant factor. We therefore may write in the small-r region

$$\psi_E(r) \sim a_E\psi_E^{\mathrm{WKB}}(r) \tag{26}$$

with a dimensionless factor a_E.

In general the amplitude ratio a_E must be calculated numerically. Figure 2 shows a_E for the homogeneous potential Eq. (13) with $n=12$.

Implications for the matrix elements

We noted above, that the dominant contribution to the matrix element stems from the small-r range. The larger E', the smaller the relevant range. This indicates that we may replace the "slow" wave function by its small-r limit Eq. (24) or Eq. (26). Using the former we find that the matrix elements factorize

$$\langle E|W|E'\rangle \sim c_E d_{E'} \tag{27}$$

in the asymptotic region $E'\gg E$. This factorization will become more explicit below. Using the latter we obtain

$$\langle E|W|E'\rangle \sim a_E \int_0^\infty W(r)\psi_E^{\mathrm{WKB}}(r)\psi_{E'}(r)dr \qquad (28)$$

and we may expect this relation to become asymptotically exact in the limit $E' \gg E$. We noted in Sec. III A that the "fast" wave function can also asymptotically be replaced by its WKB approximation, provided the potential is strongly singular. Therefore both wave functions can effectively be replaced by their WKB approximation up to the factor a_E.

Because the dominant contribution to the matrix element stems from the small-r range, we may replace $W(r)$ by its small-r expansion. In some of the most interesting applications $W=V$ or $W=-V'$. Therefore we suppose

$$W(r) \sim r^{-p} \qquad (29)$$

for small r. If $W=V$ or $W=-V'$ we have $p>2$. However, the results below, Eq. (49) and Eq. (53), are not restricted to positive values of p. In Sec. VIII A we will discuss an exponential $W(r)=e^{-r/L}$ which corresponds to $p=0$.

IV. LANDAU'S METHOD FOR THE EVALUATION OF MATRIX ELEMENTS

In their book [8] Landau and Lifshitz describe a procedure for the asymptotic estimate of the matrix elements. They introduce the wave function $\psi_{E'}^{+}(z)$ which solves the Schrödinger equation in the whole complex plane and satisfies $\mathrm{Re}\{\psi_{E'}^{+}(r)\}=\psi_{E'}(r)$ on the real axis. For large real r, $\psi_{E'}^{+}(r) \sim \gamma_{E'} e^{i(k'r+\varphi_{E'})}$. $\psi_{E'}^{+}(z)$ has the same relation to the real function $\psi_{E'}(r)$ as e^{ikz} has to $\cos kr$. $\psi_{E'}^{+}(z)$ decays like $e^{-k'\,\mathrm{Im}(z)}$ in the upper half plane.

Landau expresses the matrix element Eq. (1) where $E < E'$ as

$$\langle E|W|E'\rangle = \mathrm{Re}\left\{\int_0^\infty W(r)\psi_E(r)\psi_{E'}^{+}(r)dr\right\}. \qquad (30)$$

Since $\psi_E(z)\psi_{E'}^{+}(z)$ decays exponentially in the upper half plane like $e^{-(k'-k)\mathrm{Im}(z)}$, the path of integration can be moved to any path $\mathcal{C}$ which starts at $z=0$ and ends at $i\infty$. Therefore

$$\langle E|W|E'\rangle = \mathrm{Re}\left\{\int_C W(z)\psi_E(z)\psi_{E'}^{+}(z)dz\right\}. \qquad (31)$$

Section III A indicates that $\psi_{E'}^{+}(z)$ asymptotically tends to the WKB approximation on $\mathcal{C}$, provided $\mathcal{C}$ remains within a sector $0<\epsilon<\arg z<(2\pi/n)-\epsilon$ for small z and some $\epsilon>0$. The WKB approximation of $\psi_{E'}^{+}(z)$ has been determined by Landau [8] as

$$-2i\left(\frac{\mu}{2(V(z)-E')}\right)^{1/4} \exp\left\{\frac{\sqrt{2\mu}}{\hbar}\int_z^{r_0'} \sqrt{V(y)-E'}\,dy\right\}. \qquad (32)$$

where r_0' is the turning point satisfying $V(r_0')=E'$. The square root is real and positive for $0<z<r_0'$.

Inserting and using Eq. (28) we obtain

$$\langle E|W|E'\rangle \sim 2a_E\sqrt{\frac{\mu}{2}}\,\mathrm{Im}\left\{\int_C (V(z)-E)^{-1/4} \times (V(z)-E')^{-1/4}W(z)e^{G(z)}dz\right\}, \qquad (33)$$

where

$$G(z) = \frac{\sqrt{2\mu}}{\hbar}\int_z^{r_0''}\sqrt{V(w)-E'}\,dw - \frac{\sqrt{2\mu}}{\hbar}\int_z^{r_0}\sqrt{V(w)-E}\,dw. \qquad (34)$$

For $z\to 0$, $G(z)$ tends to a limit $G(0)$. Writing

$$\langle E|W|E'\rangle \sim 2a_E\sqrt{\frac{\mu}{2}}e^{G(0)}\,\mathrm{Im}\left\{\int_C (V(z)-E)^{-1/4}(V(z) - E')^{-1/4}W(z)e^{G(z)-G(0)}dz\right\}, \qquad (35)$$

we note that $e^{G(0)}$ is the dominant exponential factor in the matrix element found by Landau [8].

Asymptotic evaluation of the integral

The integral can be evaluated by steepest descent. The corresponding contour $\mathcal{C}$ starts from $z=0$ and must satisfy the condition

$$\mathrm{Im}\{G(z)-G(0)\}=0. \qquad (36)$$

On this contour

$$G(z)-G(0) = \frac{\sqrt{2\mu}}{\hbar}\int_0^z [\sqrt{V(w)-E}-\sqrt{V(w)-E'}]dw \qquad (37)$$

is real and decays monotonically. For small w the integrand of $G(z)-G(0)$ is

$$\sim \sqrt{V(w)}\left(1-\frac{E}{2V(w)}-1+\frac{E'}{2V(w)}\right) \sim \frac{E'-E}{2\sqrt{A}}w^{n/2} \qquad (38)$$

and therefore for small z

$$G(z)-G(0) \sim \sqrt{\frac{\mu}{2A}}\frac{E'-E}{\hbar}\frac{2}{n+2}z^{(n+2)/2}. \qquad (39)$$

Since $G(z)-G(0)$ should be real and monotonically decreasing on $\mathcal{C}$ for small $|z|$, in this region $\mathcal{C}$ is given by

$$z = te^{2\pi i/(n+2)}. \qquad (40)$$

Then

$$G(z)-G(0) \sim -\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\omega t^{(n+2)/2} \qquad (41)$$

with

$$\omega = \frac{E' - E}{\hbar}. \tag{42}$$

Since $G(z) - G(0)$ appears in the exponent inside the integral, it must effectively be bounded for $\omega \to \infty$ and the relevant z in the integral satisfy

$$\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\omega|z|^{(n+2)/2} = O(1). \tag{43}$$

For these z it is easy to verify that $|V(z)| \gg E'$ (which is equivalent to $\mathcal{E}' \gg 1$). The integral in question then becomes for large ω

$$\frac{1}{\sqrt{A}}\int_{\mathcal{C}} z^{n/2} W(z) \exp\left\{-\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\omega|z|^{(n+2)/2}\right\}dz. \tag{44}$$

Because the relevant z are so small we may replace $\mathcal{C}$ by the initial section Eq. (40). For the same reason only the behavior of $W(z)$ for small z is relevant which we assume to have the form Eq. (29). With $dz = e^{2\pi i/(n+2)}dt$ the integral becomes

$$-\frac{1}{\sqrt{A}}e^{-[2\pi i/(n+2)]p}\int_0^\infty t^{n/2-p}\exp\left\{-\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\omega t^{(n+2)/2}\right\}dt = -\sqrt{\frac{2}{\mu}}e^{-[2\pi i/(n+2)]p}\left(\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\right)^{2p/(n+2)}\Gamma\left(1 - \frac{2p}{n+2}\right)\omega^{-1+[2p/(n+2)]}. \tag{45}$$

V. ASYMPTOTIC MATRIX ELEMENT

Inserting into Eq. (35) we obtain

$$\langle E|W|E'\rangle \sim 2a_E \sin\frac{2\pi p}{n+2}\left(\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\right)^{2p/(n+2)} \times \Gamma\left(1 - \frac{2p}{n+2}\right)\omega^{-1+[2p/(n+2)]}e^{G(0)}. \tag{46}$$

The exponent can be written as

$$G(0) = F(E) - F(E') \tag{47}$$

with

$$F(E) = \frac{\sqrt{2\mu}}{\hbar}\int_0^{r_0}[\sqrt{V(w)} - \sqrt{V(w) - E}] + \frac{\sqrt{2\mu}}{\hbar}\int_{r_0}^\infty \sqrt{V(w)}dw. \tag{48}$$

Thus we obtain finally

$$\langle E|W|E'\rangle \sim a_E\frac{2\pi}{\Gamma\left(\frac{2p}{n+2}\right)}\left(\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\right)^{2p/(n+2)} \times \omega^{-1+[2p/(n+2)]}e^{F(E)-F(E')}. \tag{49}$$

This is the main result of this paper. It is the exact asymptotic expression for the matrix element in the limit $E' \to \infty$. It is valid for potentials with a singularity $\sim Ar^{-n}$, $n > 2$ near $r = 0$. E is fixed, $E' - E = \hbar\omega$, and $W(r) \sim r^{-p}$ near $r = 0$.

In the special case where $V(r) = Ar^{-n}$ for all r we have

$$F(E) = \frac{\sqrt{\pi}}{n-2}\frac{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)}{\Gamma\left(1 + \frac{1}{n}\right)}\mathcal{E}^{(n-2)/2n}. \tag{50}$$

A. Discussion and comparison with classical matrix element

What is the ultimate decay of the matrix element for $\omega \to \infty$? We have

$$\frac{d}{dE}F(E) = \frac{\sqrt{2\mu}}{2\hbar}\int_0^{r_0}\frac{dw}{\sqrt{V(w) - E}}dw \equiv \hbar^{-1}t^*(E). \tag{51}$$

In a previous publication [12] it has been argued, that $t^*(E')$ for large E' decays at least as fast as $E'^{-1/2}$ regardless of the detailed nature of the potential. This indicates, that $F(E')$ for large E' does not increase faster that $\sqrt{E'}$. Therefore the matrix element for large ω decays not faster than $\exp\{-\mathrm{const}\sqrt{\omega}\}$. This is different from the classical matrix elements which all decay exponentially for large frequency [12].

Let us formally take the classical limit of the right-hand side in Eq. (49). In this limit $a_E \to 1$ and the right-hand side becomes

$$\langle E|W|E'\rangle \sim \frac{2\pi}{\Gamma\left(\frac{2p}{n+2}\right)}\left(\frac{2}{n+2}\sqrt{\frac{\mu}{2A}}\right)^{2p/(n+2)}\omega^{-1+[2p/(n+2)]}e^{-\omega t^*}. \tag{52}$$

This is precisely the asymptotic matrix element of the corresponding classical problem derived previously by a purely classical method [see Eq. (87) in Ref. [12]]. It is satisfying that these two very different methods lead to the same result.

Denoting the quantum or classical meaning of the matrix element by an index, we can write the main result in the form

$$\frac{\langle E|W|E+\hbar\omega\rangle_{quant}}{\langle E|W|E+\hbar\omega\rangle_{class}} \sim a_E e^{-F(E+\hbar\omega)+F(E)+\hbar\omega F'(E)}. \tag{53}$$

In particular, in the asymptotic region of large ω the ratio of the matrix elements is independent of the operator W.

B. Exponential potential

Let us compare with the exactly solvable exponential potential. It has an essential singularity at infinity and the results of the previous section are applicable after some trivial modifications.

The Schrödinger equation for the potential

$$V(r) = Ae^{-r/L} \tag{54}$$

was solved exactly by Jackson and Mott [14]. Putting

$$\psi_E(r) = \gamma_E \varphi_\kappa\left(\frac{r}{L} + \rho\right) \tag{55}$$

with

$$\frac{2\mu A L^2}{\hbar^2} e^{\rho} = 1 \tag{56}$$

the Schrödinger equation becomes

$$-\varphi_\kappa''(y) + e^{-y}\varphi_\kappa(y) = \kappa^2 \varphi_\kappa(y), \tag{57}$$

where κ is the dimensionless wave number

$$\kappa^2 = \frac{2\mu L^2}{\hbar^2} E. \tag{58}$$

The normalized solution is

$$\varphi_\kappa(y) = \sqrt{\frac{2\kappa \sinh(2\pi\kappa)}{\pi}} K_{2i\kappa}(2e^{-y/2}), \tag{59}$$

where K_ν is the modified Bessel function. The matrix element of the potential has also been calculated exactly by Jackson and Mott [14]. It is given by

$$\langle E|V|E'\rangle = 4\pi\mu L^2 \omega \frac{\sqrt{\sinh(2\pi\kappa)\sinh(2\pi\kappa')}}{\cosh 2\pi\kappa' - \cosh 2\pi\kappa}, \tag{60}$$

where $E - E' = \hbar\omega$. The classical matrix element is

$$\int_{-\infty}^{\infty} e^{i\omega t} V(r(t)) dt = \frac{2\pi\mu L^2 \omega}{\sinh\left(\pi L \sqrt{\frac{\mu}{2E}}\omega\right)}. \tag{61}$$

Let us compare with our asymptotic results in the previous section. One finds after some algebra

$$a_E = e^{-\pi\kappa}\sqrt{2 \sinh 2\pi\kappa}. \tag{62}$$

and

$$G(0) = \lim_{z->-\infty} \frac{\sqrt{2\mu}}{\hbar}\left\{\int_z^{r_0'} \sqrt{Ae^{-w/L} - E'}\,dw - \int_z^{r_0} \sqrt{Ae^{-w/L} - E}\,dw\right\} = \pi(\kappa - \kappa'). \tag{63}$$

To calculate the asymptotic matrix element we cannot use Eq. (49) directly since this assumes a singularity of the form r^{-n}. However we can use Eq. (53). From Eq. (61) we observe that the factor multiplying the exponent in the classical matrix element is $4\pi\mu L^2\omega$. Equation (53) then predicts for the asymptotic quantum matrix element

$$4\pi\mu L^2 \omega e^{-\pi\kappa}\sqrt{2 \sinh 2\pi\kappa} e^{\pi(\kappa-\kappa')} = 4\pi\mu L^2 \omega \sqrt{2 \sinh 2\pi\kappa} e^{-\pi\kappa'} \tag{64}$$

and this is indeed the correct asymptotic form of Jackson-Mott's result.

At zero frequency classical and quantum matrix elements coincide. The reason is that for the exponential potential the force is proportional to the potential. In general quantum and classical matrix elements coincide [15] at $\omega = 0$ if $W = V'$.

VI. NUMERICAL METHODS

In this section some methods for the numerical calculations of the matrix elements are discussed. The numerical calculations were done using Mathematica, usually with a precision of 16 or 24 digits. In a few cases up to 44 digits were needed in the high energy region.

The matrix elements pose numerical problems only for very large energy where the wave function oscillates very rapidly. In such a case the path of integration must be deformed into some curve in the complex plane which dampens the amplitude of the oscillations. However it turns out, that this is not necessary for our purposes. The frequencies accessible by integration on the real axis alone are amply sufficient to verify the analytic predictions.

A. Potential $V = Ar^{-12}$

As mentioned previously, the Schrödinger equation for the homogeneous potential can be reduced by rescaling to Eq. (18). We must calculate the amplitude ratio a_E and the matrix elements proper.

To obtain accurate values of the wave function, we split the integration region into two parts. From the classical turning point at $\mathcal{E}^{-1/n}$ to infinity the original Eq. (18) is solved. From 0 to the classical turning point we extract the asymptotic factor Eq. (24) and write

$$\varphi(z) = u(z) z^{n/4} \exp\left\{-\frac{2}{n-2} z^{-(n-2)/2}\right\}. \tag{65}$$

The resulting differential equation for $u(z)$

$$u'' + \left(\frac{n}{2z} + 2z^{-n/2}\right)u' + \left(\mathcal{E} + \frac{n^2 - 4n}{16z^2}\right)u = 0 \tag{66}$$

is less singular at $z = 0$. It can numerically be solved for $z \gtrsim 0.01$. For small z the relevant solution satisfies

$$u(z) = 1 - \frac{n(n-4)}{16(n-2)} z^{(n-2)/2} + \dots, \tag{67}$$

which furnishes the boundary condition. Pasting the two solutions together yields the wave function.

Although we do not need it for the matrix elements, it is interesting to determine the contour $\mathcal{C}$ of steepest descent discussed in Sec. IV.

Figure 1 shows the contours $\mathcal{C}$ of steepest descent for the homogeneous potential with $n = 12$ and $\mathcal{E} = 0$. The contours are linear near the origin with slope $\tan \pi/7$ and bend upwards near the classical turning point $\mathcal{E}'^{-1/12}$. Far from the origin they become vertical since $\mathrm{Im}\{\xi(z)\} \sim \mathrm{const} - \sqrt{\mathcal{E}'}x$ for large $|z|$. $\xi(z)$ is real and decays monotonically on $\mathcal{C}$.

B. Lennard-Jones potential

To rescale the Schrödinger equation for the LJ potential

$$-\frac{\hbar^2}{2\mu}\psi''(r) + 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]\psi(r) = E\psi(r), \tag{68}$$

we put

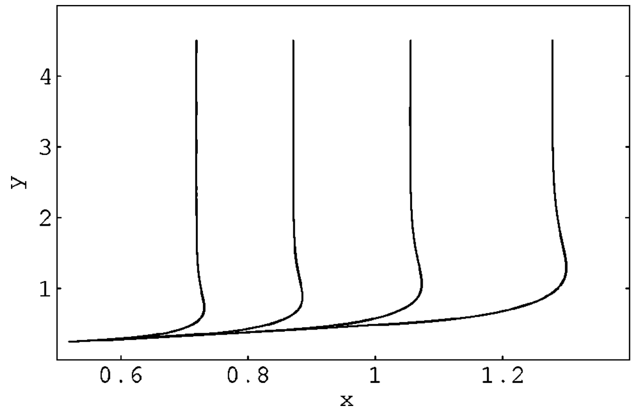

FIG. 1. Contours $\mathcal{C}$ of steepest descent in the complex plane. From left to right $\mathcal{E}'=100$, 10, 1, and 0.1.

$$\psi(r) = \varphi(r/\sigma) \tag{69}$$

and obtain

$$-\varphi''(x) + \eta(x^{-12} - x^{-6})\varphi(x) = \kappa^2\varphi(x), \tag{70}$$

where

$$\kappa^2 = E\frac{2\mu}{\hbar^2}\sigma^2 \tag{71}$$

is a dimensionless wave number and

$$\eta = 4\epsilon\frac{2\mu}{\hbar^2}\sigma^2 \tag{72}$$

is a dimensionless parameter.

The numerical procedure for the LJ potential is very similar to the homogeneous potential.

VII. INITIAL AMPLITUDES

As mentioned previously, the factor a_E is needed to correct for the fact that the WKB approximation is not exact for the "slow" wave function ψ_E near $r=0$. $1-a_E$ is a measure for the corresponding error.

In general, the amplitude ratio a_E must be calculated numerically. For very small and large energies, however, additional information is available.

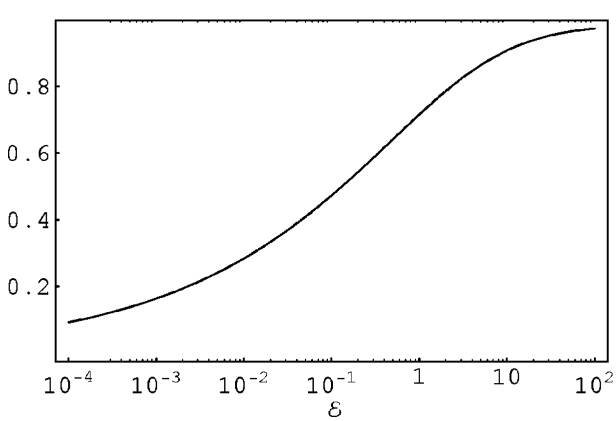

FIG. 2. Amplitude ratio a_E for V_{12} potential.

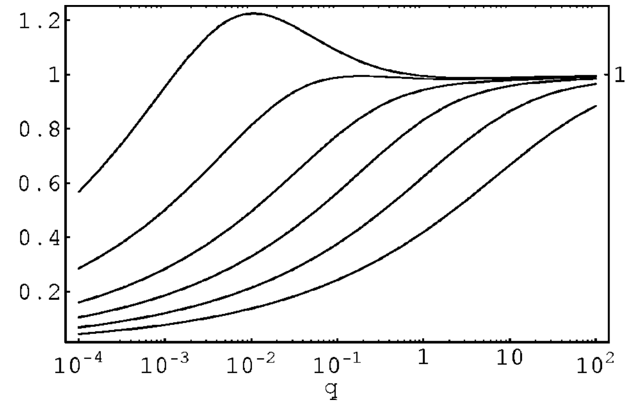

FIG. 3. Amplitude ratio a_E for for the Lennard-Jones potential versus q. From top to bottom: $\eta=15$, 10, 5, 2, 0.5, and 0.1.

We noted in Sec. III A that the large-E limit is identical to the classical limit. In particular, the initial WKB amplitude is asymptotically exact for large E. Therefore a_E tends to 1 for $E\to\infty$. For small E one can show that a_E is proportional to $E^{1/4}$.

Figure 2 shows the amplitude ratio versus the scaled energy $\mathcal{E}$ for the homogeneous potential V_{12}.

For the Lennard-Jones potential the amplitude ratio a_E depends on the dimensionless parameters η and on the energy via $q=E/4\epsilon$.

Figure 3 shows the dependence on q for various η. For large energy the WKB approximation becomes exact and a_E tends to 1 for all η. For small energy it is again proportional to $E^{1/4}$. For fixed q and $\eta\to\infty$ the system becomes classical and $a_E\to 1$ again. For very small energies, however, a_E oscillates as a function of η.

Figure 4 displays the amplitude versus η for $q=10^{-1}$, 10^{-2}, and 10^{-3}. For $q\to 0$ the amplitude diverges for certain values of η. This is due to the appearance of zero eigenvalues at $\eta=22.36, 148, 385, \ldots$. For large η the oscillations decrease rapidly.

VIII. ASYMPTOTIC MATRIX ELEMENTS: COMPARING ANALYTICAL AND NUMERICAL RESULTS

We are finally in a position to compare the analytical prediction for the matrix elements with numerical results.

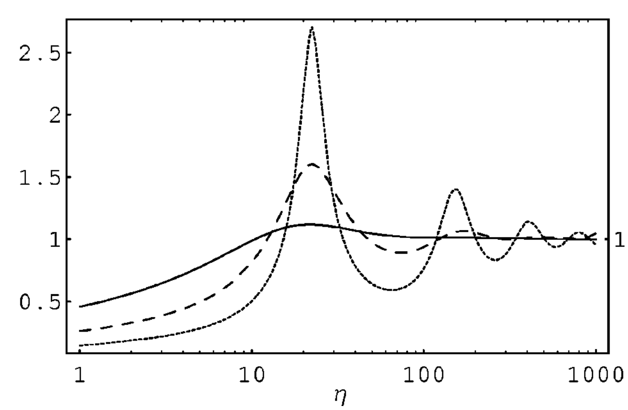

FIG. 4. Amplitude ratio a_E for for the Lennard-Jones potential versus η. Dotted curve: $q=10^{-3}$; dashed curve: $q=10^{-2}$; full curve: $q=10^{-1}$.

In order to test approximation Eq. (53), we consider the ratio of the two sides, i.e., we numerically calculate the quality factor

$$Q = \frac{\langle E|W|E+\hbar\omega\rangle_{quant}}{\langle E|W|E+\hbar\omega\rangle_{class}} a_E^{-1} e^{F(E+\hbar\omega)-F(E)-\hbar\omega F'(E)}. \tag{73}$$

Any deviation of Q from 1 directly measures the error in approximation Eq. (53).

A. Potential $V=Ar^{-12}$

From Eq. (18) we obtain for the matrix element

$$\langle E|r^{-p}|E'\rangle = \gamma_E\gamma_{E'}\lambda^{p-1}\int_0^\infty x^{-p}\phi_{\mathcal{E}}(x)\phi_{\mathcal{E}'}(x)dx. \tag{74}$$

The corresponding classical matrix element is

$$\int_{-\infty}^{\infty} r^{-p}(t)\cos(\omega t)dt, \tag{75}$$

where $r(t)$ satisfies the equation of motion

$$\frac{\mu}{2}\dot{r}^2 + Ar^{-n} = E. \tag{76}$$

We get rid of the constants by rescaling

$$r(t) = \left(\frac{A}{E}\right)^{1/n} y(\omega_0 t), \tag{77}$$

where

$$\omega_0 = \sqrt{\frac{E}{2\mu}}\left(\frac{E}{A}\right)^{1/n} \tag{78}$$

is the natural frequency scale of the classical system [12]. $y(x)$ satisfies

$$\frac{1}{4}y'^2 + y^{-n} = 1 \tag{79}$$

and the classical matrix element becomes

$$\sqrt{\frac{2\mu}{E}}\left(\frac{E}{A}\right)^{(p-1)/n}\int_{-\infty}^{\infty} y^{-p}(z)\cos\left(\frac{\omega}{\omega_0}z\right)dz. \tag{80}$$

The ratio of the matrix elements then is

$$\frac{\langle E|r^{-p}|E'\rangle_{quant}}{\langle E|r^{-p}|E'\rangle_{class}} = 2\left(\frac{\mathcal{E}}{\mathcal{E}'}\right)^{1/4}\mathcal{E}^{-(p-1)/n}\frac{\int_0^\infty x^{-p}\phi_{\mathcal{E}}(x)\phi_{\mathcal{E}'}(x)dx}{\int_{-\infty}^{\infty} y^{-p}(z)\cos\left(\frac{\omega}{\omega_0}z\right)dz}, \tag{81}$$

with $E'=E+\hbar\omega$ as usual. $\mathcal{E}'$ is related to ω by

$$\mathcal{E}' = \mathcal{E} + \frac{\omega}{\omega_0}\mathcal{E}^{(n+2)/2n}. \tag{82}$$

The exponent in Eq. (73) is

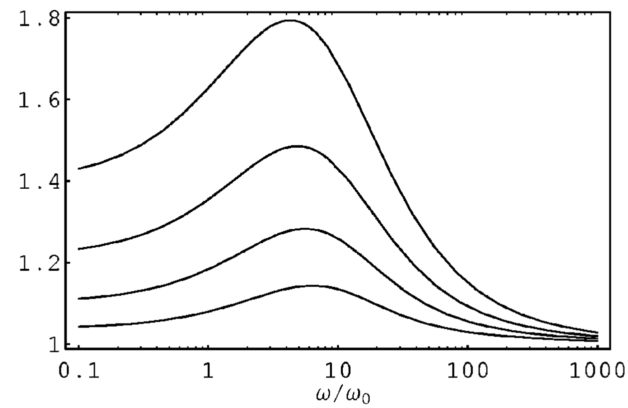

FIG. 5. Quality factor Q for V_{12} potential and $p=13$. From top to bottom: $\mathcal{E}=1$, 3, 10, and 50.

$$\sqrt{\pi}\frac{\Gamma\left(\frac{1}{2}+\frac{1}{n}\right)}{\Gamma\left(\frac{1}{n}\right)}\left[\frac{n}{n-2}(\mathcal{E}'^{(n-2)/2n} - \mathcal{E}^{(n-2)/2n}) - \frac{\omega}{2\omega_0}\right], \tag{83}$$

where Eq. (50) has been used.

Figure 5 shows the quality factor for $p=13$, i.e., $W=V'$. As expected $Q\to 1$ for $\omega \gg \omega_0$ or $\mathcal{E}\gg 1$. In this case quantum and classical matrix element coincide for $\omega=0$. For $\omega\to 0$, Q tends to a_E^{-1} (compare Fig. 2).

For functions of the type $W(r)=r^{-p}$ the matrix elements depend only on $\mathcal{E}$ and $\mathcal{E}'$. If W is not of this form, new dimensionless parameters are generated which make an overview of the quality of approximation Eq. (53) more time consuming. As a single example let us consider the exponential

$$W(r) = Ae^{-r/L}, \tag{84}$$

again for the homogeneous potential Eq. (13) with $n=12$. Operators W of this kind are of interest in collision-induced absorption [4]. Here the new dimensionless parameter

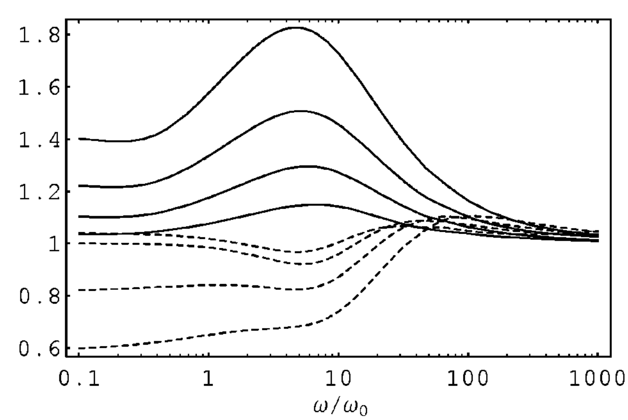

FIG. 6. Quality factor for V_{12} potential and exponential $W=e^{-z/\zeta}$ for $\zeta=0.2$ (broken lines) and $\zeta=5$ (full lines). Values of $\mathcal{E}$ are 1, 3, 10, and 50. $\mathcal{E}$ increases for broken (full) lines from bottom to top (top to bottom).

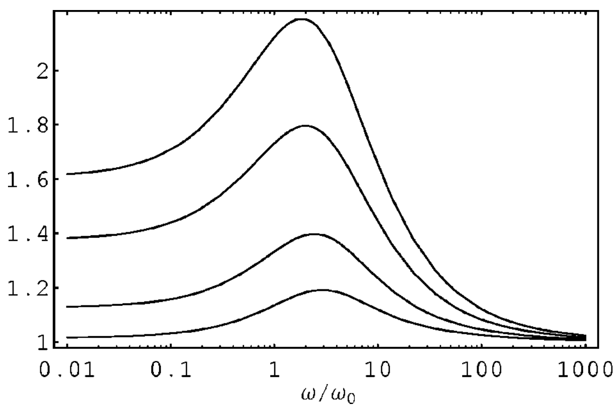

FIG. 7. Quality factor Q for the LJ potential. From top to bottom: η=0.5, 1, 3, and 10.

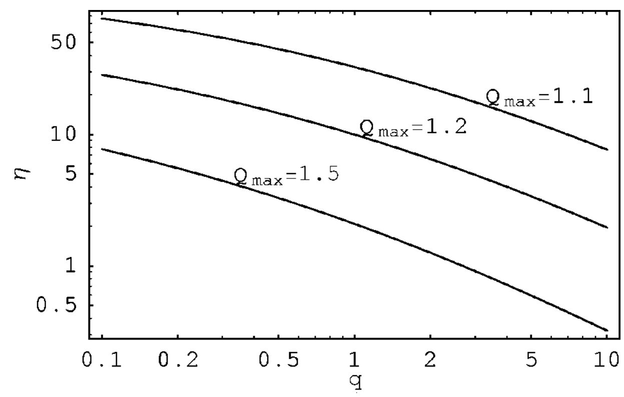

FIG. 8. Contour plot of maximal quality factor Q_{max} for the LJ potential as a function of q and η.

$$\zeta = L\lambda \tag{85}$$

appears where λ is defined in Eq. (17).

Figure 6 displays the quality factor of exponential W for various values of $\mathcal{E}$ and ζ. As expected, approximation (53) becomes exact in the limit $\omega \to \infty$ or $\mathcal{E} \to \infty$.

B. Lennard-Jones potential

For the LJ potential the most interesting operator W is the force. A natural frequency scale is

$$\omega_0 = \sqrt{\frac{8\epsilon}{\mu}}\sigma^{-1}. \tag{86}$$

Figure 7 displays the quality factor for $W=V'$. Different curves refer to different values of η [see Eq. (72)]. As expected, $Q \to 1$ and the approximation (53) becomes exact if ω or η tend to infinity. The energy E of the "slow" component is fixed at $q=1$ in Fig. 7.

The error is maximal for frequencies $1 \lesssim \omega/\omega_0 \lesssim 10$. In order to obtain an overview over the maximal error, Fig. 8 shows a contour plot of the maximal value of Q, Q_{max}, as a function of η and q.

In Fig. 8 the corresponding value of ω varies from $\omega/\omega_0=0.4$ for the smallest q and η to $\omega/\omega_0=8$ for the largest values of q and η. As expected, Q_{max} tends to 1 if q or η tends to infinity.

IX. SUMMARY

A simple and asymptotically exact relation [Eq. (49) or (53)] is derived for the quantum matrix element $\langle E|W|E'\rangle$ if one (but not both) of the energies becomes very large. The matrix elements refer to two-body collisions and it is assumed that the interaction potential is strongly singular. The method is an elaboration of an idea of Landau discussed in Landau-Lifshitz [8].

For potentials with a singularity at $r=0$ the condition of strong singularity is $V(r) \sim r^{-n}$, $n>2$ for small r. An example is the Lennard-Jones potential.

The theory applies to a few other potentials like the exponential potential. The Coulomb potential, however, is not strongly singular and shows qualitatively different decay properties.

In the form Eq. (53) the main approximation shows small to moderate errors over the whole frequency range when compared to numerical calculations. For example, Fig. 7 displays the relative error Q_{max} versus frequency for the Lennard-Jones potential.

For large E the matrix elements of such potentials decay faster than any power but slower than exponentially. For potentials $V(r) \sim r^{-n}$, $n>2$ the ultimate decay is $\sim \exp\{-E^{\sigma}\}$ with $\sigma=(n-2)/2n$. The exponential potential corresponds to $\sigma=1/2$. There are indications that $\sigma \leqslant 1/2$ for all strongly singular potentials.

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[15] At zero frequency the matrix element of the force is given by $-\langle E|V'|E\rangle = 2\sqrt{2\mu E} = 2p$. This "sum rule" is valid quite generally. Classically it simply means $\int_{-\infty}^{\infty} F\, dt = \Delta p = 2p$. In particular, classical and quantum matrix elements are identical if $W = V'$.