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TOPICS IN BOUND-STATE AND DYNAMICAL PROCESSES:
SEMICLASSICAL EIGENVALUES, REACTIVE SCATTERING KERNELS
AND GAS-SURFACE SCATTERING MODELS

by

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To my parents and grandmother

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I. Semiclassical Eigenvalues for Potentials Defined on a Finite Interval.

It has been many years since Langer¹ and others² noted the difficulties which occur when one attempts to apply the ordinary WKB approximation³ to problems involving arbitrary potentials. Specifically, for a general one-dimensional Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) - E\right)\psi(x) = 0 \quad (1.1)$$

one knows that the usual semiclassical expressions for the eigenvalues (if $V(x)$ supports bound states) or for the phase shift (if $V(x)$ is a scattering potential) are not in principle valid if x is confined to only a part of the entire real axis. Such a situation is hardly uncommon, however; for example, the radial Schrödinger equation which involves a spherically symmetric two-body potential falls into this category, since in this case the coordinate (which is customarily denoted by r) is restricted to the semi-infinite domain $(0, \infty)$. It is for this particular problem that Langer derived the correction term¹ $\frac{\hbar^2}{8mr^2}$ which, when added to $V(r)$, yields the correct behavior of the phase shift as $r \rightarrow 0$.

More recently Fröman and Fröman^{2,4} have examined in detail not only the basic problem of the applicability of the conventional WKB formalism but also the even more general question of the validity of various phase integral approximations. Their work has produced a convenient expression for the potential correction term for which Langer's modification represents a special case. As shall be discussed more fully in the following section, however, this particular approach does not yield a unique

correction term and hence cannot alone be used to construct the proper modification.

The present work seeks to overcome the uniqueness difficulties by imposing a criterion which permits identification of the correct modification. In order to demonstrate the utility of the overall method, sample problems are examined which require that the domain of x be limited to the finite interval (a,b) . Specifically, Section C treats first the limiting case in which a particle is confined to a square potential well and second the somewhat more complex problem in which a simple harmonic oscillator is placed in such a well. In either case one finds that by inserting the derived effective potential into the usual Bohr-Sommerfeld quantum condition it is possible to obtain essentially the exact quantum mechanical results. (Although at face value the oscillator-in-a-box problem might seem to be only of pedagogical value, such a model has been proposed for certain nuclear interactions⁵ and for frequency-doubling waveguides.⁶) Furthermore, the obvious inadequacy of the unmodified WKB eigenvalues calculated for these systems points to the importance of using a "corrected" formalism.

A. Mapping Functions

In order to develop a criterion for determining a unique potential modification, it is necessary to explore the more general problem of restricting the coordinate domain to only a portion of the entire real axis. Mathematically this restriction may be handled by mapping the interval of interest (a,b) , over which the WKB approximation is not rigorously valid, onto the line $(-\infty,\infty)$. This is indeed the method adopted by Langer¹ and discussed extensively by Fröman and Fröman.²

Formally, one requires a one-to-one mapping function $z(x)$ which satisfies the following conditions for all $x \in (a,b)$:

$$\begin{aligned} z(a) &= -\infty \\ z(b) &= +\infty \quad , \quad \text{and} \\ z'(x) &> 0 \quad . \end{aligned} \tag{1.2}$$

Having thus defined the mapping function, the Schrödinger equation, Eq. (1.1), may be transformed into an equivalent expression which is a function of z . Following Reference 2, the eigenvalue condition is then given by

$$(n + \frac{1}{2})\pi = \int_{x_<}^{x_>} dx \sqrt{2m[E - V(x) - \Delta V(x)]/\hbar^2} \quad , \tag{1.3}$$

where $\Delta V(x)$ is the potential correction term, constructed via the equation

$$\Delta V(x) = -\frac{\hbar^2}{2m} z'(x)^{1/2} \frac{d^2}{dx^2} z'(x)^{-1/2} \quad . \tag{1.4}$$

[Of course, if $z(x) = x$, i.e., the interval of interest is itself the whole real axis, $\Delta V \equiv 0$ and Eq. (1.3) trivially reduces to the conventional WKB eigenvalue condition,³ as expected.]

One should notice, however, that Eq. (1.4) will yield a non-zero value of $\Delta V(x)$ whenever the quantity $z'(x)^{-1/2}$ is twice differentiable. Certainly there are a great many mapping functions $z(x)$ which can be used to obtain a corresponding number of possibilities for $\Delta V(x)$. Suppose, for example, the particular restriction described by Langer is imposed

such that the coordinate x is confined to a semi-infinite interval, i.e., $(a,b) = (0,\infty)$. A possible choice for the mapping function is then that one which was employed by Langer,

$$z(x) = \ln x \quad . \quad (1.5)$$

It is then a simple matter to substitute this function into the general expression Eq. (1.4) and to find that

$$\Delta V(x) = \frac{\hbar^2}{8mx^2} \quad , \quad (1.6)$$

which is, of course, the usual Langer correction term.¹

As a matter of fact, it is not at all difficult to guess other formulae for $z(x)$. For instance, a set of functions of the form

$$z(x) = x^n - x^{-n} \quad , \quad (1.7)$$

(n being some positive integer) when introduced into Eq. (1.4) leads one to a whole family of correction terms,

$$\Delta V(x) = \frac{\hbar^2}{4m} \left\{ \frac{(n-1)(n-2)x^{n-3} + (n+1)(n+2)x^{-n-3}}{x^{n-1} + x^{-n-1}} - \frac{3}{2} \left[\frac{(n-1)x^{n-2} - (n+1)x^{-n-2}}{x^{n-1} + x^{-n-1}} \right]^2 \right\} .$$

For each value of n , $x \in (0,\infty)$ is mapped onto $z \in (-\infty,\infty)$ with $z'(x) > 0$, but surely not all of these functional forms yield equally good approximations to the quantum mechanical solution. This lack of invariance of $\Delta V(x)$ with

respect to the form taken for the mapping function lends an extremely unsettling aspect to the use of Eq. (1.4) as the sole criterion for determining the modified potential.

In passing it should be also noted that the non-unique character of the interval transformation method described above is by no means peculiar to the particular case in which x is defined over the semi-infinite interval. If x is confined to the finite interval (a,b) , a possible choice for the mapping function is

$$z(x) = \ln \left(\frac{x-a}{b-x} \right) , \quad (1.7)$$

a function which is quite reminiscent of Langer's, Eq. (1.5). Using Eq. (1.7) one finds that

$$\Delta V(x) = \frac{\hbar^2}{8m} \frac{(b-a)^2}{(x-a)^2 (b-x)^2} , \quad (1.8)$$

which is actually very similar to the Langer correction term for values of x near the endpoints.

$$\lim_{x \rightarrow a} \Delta V(x) = \frac{\hbar^2}{8m} \frac{1}{(x-a)^2}$$

$$\lim_{x \rightarrow b} \Delta V(x) = \frac{\hbar^2}{8m} \frac{1}{(b-x)^2} .$$

However, as found previously, there are certainly other mapping functions which may be used to modify the WKB eigenvalue condition. To indicate just one alternative, the function

$$z(x) = \tan \left[\frac{\pi}{2} \left(\frac{2x-a-b}{b-a} \right) \right]$$

certainly satisfies the conditions given by Eqs. (1.2) but unlike Eq. (1.7) yields the correction term

$$\Delta V(x) = \frac{\hbar^2}{2m} \left(\frac{\pi}{b-a} \right)^2 ,$$

which seems to be a clearly unphysical result, inasmuch as the potential correction is independent of x for this mapping.

Hence, to determine a mapping function uniquely, the use of Eqs. (1.2) and (1.4) is, as has been indicated by Fröman and Fröman, quite insufficient--an additional criterion must be found. Fortunately the required criterion may be deduced from a consideration of why Langer's correction term has met with such success in describing scattering processes. Consider for a moment the case $V(x) \equiv 0$ on the restricted interval $x \in (0, \infty)$, for which the phase shift must certainly vanish if the correct physics is to be obeyed. Substituting Langer's correction, Eq. (1.6), into the modified equation for the WKB approximation to the phase shift,

$$\eta = \frac{\pi}{4} + \lim_{k \rightarrow \infty} \left[-kx + \int_{x \ll}^x dx' \sqrt{2m[E - V(x') - \Delta V(x')] / \hbar^2} \right] ,$$

and setting $V(x')$ to zero, one obtains

$$\eta = \frac{\pi}{4} + \lim_{k \rightarrow \infty} \left[-kx + \int_{x \ll}^x dx' \sqrt{2m \left(E - \frac{\hbar^2}{8m x'^2} \right) / \hbar^2} \right] .$$

The above integral is then easily evaluated, yielding

$$\eta = \frac{\pi}{4} + \lim_{k \rightarrow \infty} \left[-kx + \sqrt{k^2 x^2 - \frac{1}{4}} - \frac{1}{2} \sec^{-1} 2kx \right] = 0 ,$$

the expected quantum mechanical result. More important, only Langer's correction term can be shown to reproduce this exact result for the case $V(x) = 0$. Since a nonvanishing phase shift does not represent the known physics, the transformations which lead to such an erroneous prediction may be immediately rejected. Thus, yet another general condition on the correct mapping function $z(x)$ may be imposed in addition to the conditions of Eqs. (1.2), namely the mapping function must lead to a potential correction term ΔV which causes the exact quantum mechanical result to be reproduced in the limit that the potential $V(x)$ is set to zero. The section which follows indicates a way to implement this added requirement for a potential which constrains motion to the finite interval $x \in (a, b)$.

B. Correction Function for Finite Intervals

The application of the ideas of Section A to the case of a potential which is defined over a finite interval requires that the modified Bohr-Sommerfeld quantum condition, Eq. (1.3), give the exact quantum mechanical eigenvalues for zero potential $V(x)$, i.e.,

$$(n + \frac{1}{2})\pi = \int_{x_<}^{x_>} dx \sqrt{2m[E - \Delta V(x)]/\hbar^2} \quad . \quad (1.9)$$

Physically, setting $V(x)$ to zero within the finite interval $x \in (a, b)$ and to infinity outside the interval is equivalent to assuming that the system is described by a particle-in-a-box model. Hence, the eigenvalues obtained via Eq. (1.9) must take on the corresponding well-known values.

$$E_n = \frac{\hbar^2}{2m} \left[\frac{(n+1)\pi}{b-a} \right]^2 \quad , \quad (1.10)$$

where $n = 0, 1, 2, \dots$. Substitution then results in an equation which may be inverted so as to give the correction term $\Delta V(x)$.

Of course, the general prescription for inverting Eq. (1.9) is already known, namely the RKR inversion method.⁷ Briefly, the RKR formalism may be used to construct a potential function which within the WKB approximation has the given set of bound energy levels. For the particular case under consideration here, the appropriate RKR formula is⁷

$$x - \frac{1}{2} (a+b) = \sqrt{\frac{\hbar^2}{2m}} \int_{-\frac{1}{2}}^{n_0} dn [\Delta V - E(n)]^{-1/2} \quad , \quad (1.11)$$

where the correction potential $\Delta V(x)$ is assumed to be symmetric about $x = \frac{1}{2} (a+b)$, the midpoint of the interval, and where n_0 is the zero of the integrand. Inserting the expression for $E(n)$ given by Eq. (1.10) into the above equation, one finds that

$$x - \frac{1}{2} (a+b) = \sqrt{\frac{\hbar^2}{2m}} \int_{-\frac{1}{2}}^{n_0} dn \left[\Delta V - \frac{\hbar^2}{2m} \frac{(n+1)^2 \pi^2}{(b-a)^2} \right]^{-1/2} \quad ,$$

which, when integrated, becomes

$$x - \frac{1}{2} (a+b) = \frac{b-a}{2} \cos^{-1} \left[\frac{\pi}{b-a} \sqrt{\frac{\hbar^2}{8m\Delta V}} \right] \quad .$$

It is then a simple matter to invert $x = x(\Delta V)$ algebraically and to obtain the desired result,

$$\Delta V(x) = \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b-a}\right)^2}{\cos^2 \left[\frac{\pi}{b-a} \left(x - \frac{a+b}{2}\right) \right]} \quad . \quad (1.12)$$

Therefore, for any potential which is defined on the finite interval (a,b), one may generate the modified WKB eigenvalues by substituting into Eq. (1.3), with the potential correction term being given by Eq. (1.12). Since the derivation has explicitly incorporated the correct quantum mechanical behavior in the limit $V(x) = 0$, the ambiguity present when one tries to guess the "best" mapping function has been avoided.

Before proceeding to the consideration of some specific examples, one should note the relationship of the potential modification obtained herein to that derived by Langer, Eq. (1.6). First consider the general form of $\Delta V(x)$ in the particular limit that x is near one of the turning points. If, for example, $x \approx a$, then Eq. (1.12) may be transformed as follows:

$$\begin{aligned} \Delta V &= \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b-a}\right)^2}{\cos^2\left[\frac{\pi}{b-a}\left(x - \frac{b-a}{2} - a\right)\right]} \\ &= \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b-a}\right)^2}{\cos^2\left[\frac{\pi}{b-a}(x-a) - \frac{\pi}{2}\right]} \\ &= \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b-a}\right)^2}{\sin^2\left[\frac{\pi}{b-a}(x-a)\right]} \\ &\xrightarrow{x \approx a} \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b-a}\right)^2}{\left(\frac{\pi}{b-a}\right)^2 (x-a)^2} \\ &= \frac{\hbar^2}{8m(x-a)^2} \end{aligned}$$

which is of the canonical Langer form. If instead $x \approx b$, then similar manipulations yield

$$\Delta V \xrightarrow{x \approx b} \frac{\hbar^2}{8m(b-x)^2} .$$

[In passing, it is interesting to observe that these same limits are obtained from the "guessed" mapping function given in Eq. (1.7); however, the corresponding potential correction, Eq. (1.8), differs substantially from the proper result as constructed above.] Then, by considering the limit $(a,b) \rightarrow (0,\infty)$, i.e., the radial Schrödinger equation case, Eq. (1.12) takes the form

$$\begin{aligned} \Delta V(x) &= \lim_{b \rightarrow \infty} \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b}\right)^2}{\cos^2\left[\frac{\pi}{b}\left(x - \frac{b}{2}\right)\right]} \\ &= \lim_{b \rightarrow \infty} \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b}\right)^2}{\sin^2\left(\frac{\pi}{b}x\right)} \\ &= \frac{\hbar^2}{8m} \frac{\left(\frac{\pi}{b}\right)^2}{\left(\frac{\pi}{b}x\right)^2} \\ &= \frac{\hbar^2}{8mx^2} \end{aligned}$$

which is, of course, the correct Langer correction term. Thus, the results of the Langer formalism may be viewed as just a special case of the more general development proposed in this Section.

C. Specific Examples

1. $V(x) = 0$

In order to get some indication of just how much of a difference exists between the modified and unmodified WKB eigenvalues, first consider the trivial example, $V(x) = 0$, i.e., the case in which the uncorrected potential is set to zero. With the inclusion of the potential correction term, the eigenvalues are, by construction, exactly the particle-in-a-box eigenvalues given by Eq. (1.10). If, however, the correction term is not included, one finds that the energy levels are obtainable via the following manipulations:

$$\begin{aligned} (n + \frac{1}{2})\pi &= \int_a^b dx \sqrt{\frac{2m}{\hbar^2} E_n} \\ &= (b-a) \sqrt{\frac{2m}{\hbar^2} E_n} \end{aligned} ,$$

and so by inverting,

$$E_n = \frac{\hbar^2}{2m} \left[\frac{(n + \frac{1}{2})\pi}{b-a} \right]^2 . \quad (1.13)$$

A few of the eigenvalues calculated using Eqs. (1.13) and (1.10) are listed in Table 1 and also plotted in Figure 1 for the case $m = 1$ and $(a,b) = (-\frac{\pi}{2}, \frac{\pi}{2})$, the units being chosen such that $\hbar = 1$. For example, for $n = 0$ (admittedly the worst case) the unmodified value is too low by a factor of 4; for $n = 1$, although the agreement is improved, the uncorrected eigenvalue is still nearly a factor of 2 too small. Even though the deviation of the results given by the ordinary WKB formulae from those obtained from the modified formalism will not, in general,

be as large as that which is observed for this extreme case, it is clear that the inclusion of the potential correction may in certain instances substantially shift the calculated energy levels.

2. Harmonic Oscillator in a Box

Since the situation described in Case 1 above may by its very simplicity not provide a particularly critical test of the validity of the modified WKB quantum condition, it is useful to examine a slightly more complex example, that of a harmonic oscillator which is confined to a box having infinite-potential walls. Specifically, consider such an oscillator of unit mass which is constrained to the interval $(-\frac{L}{2}, \frac{L}{2})$, i.e.,

$$V(x) = \frac{1}{2} \omega^2 x^2 \quad , \quad |x| < \frac{L}{2}$$

$$= \infty \quad , \quad |x| > \frac{L}{2} \quad .$$

Adopting atomic units ($\hbar=1$), one then writes the effective system potential as

$$V_{\text{eff}} = V(x) + \Delta V(x) = \frac{1}{2} \omega^2 x^2 + \frac{1}{8} \frac{\left(\frac{\pi}{L}\right)^2}{\cos^2\left(\frac{\pi}{L}x\right)} \quad . \quad (1.14)$$

From this form for V_{eff} , it is easy to recognize two familiar limiting cases. If the box is very wide, i.e., $L \rightarrow \infty$, then $\Delta V(x) \rightarrow 0$, and the effective potential is just the unperturbed harmonic oscillator potential. Thus the eigenvalues will be given by the well-known
8
formula

$$E_n = (n + \frac{1}{2})\omega \quad , \quad (1.15)$$

$n = 0, 1, 2, \dots$. Obviously, this limit corresponds to a consideration of the infinite interval $(-\infty, \infty)$, for which Eq. (1.3) necessarily reduces to the customary unmodified WKB quantum condition. The other limit is $L \rightarrow 0$, an infinitely narrow box, in which case $V_{\text{eff}} \approx \Delta V(x)$ ($V(x)$ being negligible compared to $\Delta V(x)$). Now one finds that the situation is for all practical purposes that which was described by Case 1, the correct eigenvalues being those predicted by Eq. (1.10),

$$E_n = \frac{1}{2} \left[\frac{(n+1)\pi}{L} \right]^2 \quad ,$$

$n = 0, 1, 2, \dots$. As has been previously indicated, in this limit the inclusion of a potential correction term is absolutely essential if one is to extract the proper results.

Substitution of Eq. (1.14) into the modified quantum condition, Eq. (1.3), then yields an equation which may be solved iteratively for the eigenvalue E_n ,

$$(n + \frac{1}{2})\pi = \int_{x_<}^{x_>} dx \sqrt{2E_n - \omega^2 x^2 - \frac{\pi^2}{4L^2} \frac{1}{\cos^2(\frac{\pi}{L} x)}} \quad . \quad (1.16)$$

The actual computation procedure is as follows: for given quantum number n , box length L , and oscillator frequency ω , one may write the iteration scheme for E_n as

$$E_n^{(m)} = E_n^{(m-1)} - \frac{I_n(E_n^{(m-1)})}{I_n'(E_n^{(m-1)})} \quad , \quad (1.17a)$$

where

$$I_n(E_n^{(m)}) \equiv \int_{x_<}^{x_>} dx \sqrt{2E_n^{(m)} - \omega^2 x^2 - \frac{\pi^2}{4L^2} \frac{1}{\cos^2(\frac{\pi}{L} x)}} \quad (1.17b)$$

$$- (n + \frac{1}{2})\pi \quad ,$$

$$I_n'(E_n^{(m)}) = \frac{\partial}{\partial E_n^{(m)}} I_n(E_n^{(m)}) \quad , \quad (1.17c)$$

and the integer m counts the iterations. (Eqs. (1.17) will be recognized as being just the well-known Newton root search algorithm.⁹) The iteration is begun by making an initial guess for E_n , conveniently taken to be the oscillator eigenvalue predicted by Eq. (1.15). Once the first approximation, $E_n^{(0)}$, has been obtained, one substitutes this value into Eq. (1.17b), the integral being computed numerically by first determining the zeros of the integrand via a straightforward Newton search and then performing the integration by Gaussian quadrature. Furthermore, the derivative term, Eq. (1.17c), is obtained in a directly analogous manner, with the derivative being approximated by application of the finite-difference formula,

$$I_n'(E_n^{(m)}) \approx \frac{I_n(E_n^{(m)} + \Delta E_n^{(m)}) - I_n(E_n^{(m)})}{\Delta E_n^{(m)}} \quad ,$$

where $\Delta E_n^{(m)} = E_n^{(m)} - E_n^{(m-1)}$. (Note that the use of the above form for I_n' requires that two initial guesses be made, $E_n^{(-1)}$ and $E_n^{(0)}$ -- $E_n^{(-1)}$ is taken to be just $E_n^{(0)}$ plus some small increment.) Once I_n and I_n' are calculated, an "improved" value for E_n may be found by using Eq. (1.17a). The iterative procedure is then repeated until $E_n^{(m)} = E_n^{(m-1)}$ to the accuracy desired.

The computations described herein, coded in Fortran, required less than 10 seconds of minicomputer time for each choice of box length. The only point in the calculation at which special care must be taken is in the determination of the classical turning points which appear in Eq. (1.17b). Since in general the integrand may have more than two real roots, one must be sure that the roots upon which the Newton search ultimately converges are the proper ones, i.e., those roots which lie within the interval $(-\frac{L}{2}, \frac{L}{2})$.

Fortunately, an exact quantum mechanical analysis of the boxed harmonic oscillator problem has been recently reported.¹⁰ Thus it is a simple matter to compare the results obtained via the modified WKB formalism with the correct quantum eigenvalues. In order to reveal the significance of the addition of the potential correction term to the usual WKB quantum condition, calculations have also been performed with the unmodified formulae, i.e., $\Delta V(x)$ has been set to zero in the iteration scheme described above. These three sets of results are displayed in Table 2 and plotted in Figure 2 for an oscillator frequency $\omega = \frac{1}{2}$. In each case note that the eigenvalues for the ground state ($n=0$) and the first excited state ($n=1$) are given as a function of the box length L , since it has previously been indicated that the physical nature of the system is expected to show a strong L dependence.

Even a cursory examination of Figure 2 reveals that the modified WKB eigenvalues do reproduce the exact quantum mechanical values quite well. In particular note that for small L values (corresponding physically to the case of a very shallow oscillator potential), the modified eigenvalues represent a very substantial improvement over the conventional WKB energies. As mentioned earlier, for large L values the contribution from

the potential correction term becomes negligible, and indeed this behavior may be confirmed by observing that both the modified and the unmodified WKB results converge to the proper quantum mechanical values as $L \rightarrow \infty$. There does, indeed, appear to be an intermediate region in which the finite interval modification tends to "over-correct" somewhat to the point that the ordinary WKB eigenvalues are slightly more accurate than the modified ones, although the actual deviation involved is fairly small. The more important observation to be made is that when the ordinary unmodified formalism does prove to be inadequate, the modifications indicated herein provide a means for restoring the agreement with the quantum mechanical answers.

D. Observations

The present work has shown that for potential functions which are defined over the finite interval (a,b) the ordinary WKB quantum condition does not in general yield an adequate description of the true energy levels. However, by adding a correction term to the actual system potential, one may modify the usual semiclassical formulae and as a result may obtain quite accurate results. A particularly attractive feature of the modification derived in the present work is that the correction term reduces to the well-known Langer form in the limit $(a,b) = (0,\infty)$. The two specific examples treated in Section C then give a demonstration of the significant extent to which these modified formulae improve the agreement with the fully quantum mechanical formalism.

Perhaps the most important lesson to be derived from this study is that the ordinary WKB quantum condition cannot be applied blindly to a system involving an arbitrary potential function. The particular case

considered here points to one of the pitfalls, namely that the WKB wavefunction vanishes only at $\pm \infty$ (disregarding, of course, any isolated nodes). If, therefore, the potential requires that the wavefunction vanish at finite boundaries, the semiclassical method should not be expected to describe adequately the physics. For such a potential one must then introduce an extra potential contribution in order that the correct boundary conditions be satisfied, that extra potential being the correction term which has been derived here.

II. Reactive Scattering Exchange Kernels.

Although in principle a reactive atom-diatom collision is no more difficult to handle than the corresponding nonreactive process, one knows that in practice it is necessary to overcome the additional problem which arises due to the fact that the coordinates appropriate for describing the reactants are quite inappropriate for describing the asymptotic product arrangement. Historically, there have been two methods which have gained popularity as means for surmounting this added difficulty. The first of these methods, one which was suggested by Marcus,¹¹ involves the construction of special coordinates (the so-called "natural collision coordinates") which smoothly follow the progress of the reaction from reactants to products. The second approach¹² to the problem permits one to carry out the integration of the individual channel differential equations in the coordinates appropriate to their respective asymptotic arrangements, however subsequently one must perform a coordinate matching on some hypersurface within the interaction region of the potential surface. Clearly though, regardless of which of these two procedures is adopted for use, one is forced to adapt the formalism explicitly to the particular collision partners being investigated.

Thus, in order to obtain a more general description which avoids the coordinate difficulties altogether, Miller¹³ has chosen to reformulate the reactive scattering problem within a framework which is directly analogous to the conventional Hartree-Fock equations appearing in electronic structure theory. Inherent in this alternate formulation is the appearance of a nonlocal, non-separable exchange kernel, the treatment of which presents the only real obstacle to the application of

the method to a general reactive collision system. The recent application of Miller's work to the $H + H_2$ collinear reaction by Garrett and Miller¹⁴ has shown that while the exchange interaction may be adequately described by an expansion in a suitable basis set, the rather large number of basis functions needed for such an expansion appears to make the extension of the methodology to any larger systems quite cumbersome. If, however, it should prove possible to obtain an improved characterization of the non-separable interaction such that calculations performed on more complex bimolecular collisions become tractable, this particular method is likely to provide an attractive means for studying processes of real chemical interest.

In the present work two different approaches to the improvement of the exchange kernel treatment are examined. The first concerns what might be considered the most straightforward way to construct solutions to the coupled integro-differential equations which arise from the theory, namely an iterative procedure ("a la SCF"). As shall be shown, however, such an iterative scheme does not appear to be convergent in its present form due to the large magnitude of the kernel for those situations which lead to appreciable reaction probabilities. A second approach investigated herein is in the same spirit as that taken by Garrett and Miller,¹⁴ i.e., a separable expansion of the exchange kernel is constructed. The particular expansion chosen here differs from the previous one in that it allows more knowledge of the interaction to be built directly into the description. Calculations using this improved kernel characterization do indeed indicate that the number of expansion functions required can be significantly reduced, thereby enhancing

prospects that Miller's formalism will find general applicability in the study of chemical reaction dynamics.

A. Review of the Theory

Inasmuch as the details of Miller's formulation of the reactive scattering problem are reported elsewhere,^{13,14} only the important features of the formalism will be reproduced here. For a collinear atom-diatom reaction of the general form $A + BC \rightarrow AB + C$ for which the collision energy is such that only the ground vibrational states of reactants and products are open, one writes the wavefunction describing scattering from the initial channel α_0 ($\alpha_0 = a$ or c) as

$$\Psi_{\alpha_0}(r, R) = \phi_a(r_a) f_{a+\alpha_0}(R_a) + \phi_c(r_c) f_{c+\alpha_0}(R_c) + \sum_n C_n \chi_n(r, R)$$

where $a(A+BC)$ and $c(AB+C)$ label the two possible asymptotic arrangements for which (r_a, R_a) and (r_c, R_c) respectively are the appropriate Jacobi coordinates, only two of the four coordinates being independent. Initially one presumes knowledge both of the wavefunctions which characterize the asymptotic diatomic vibrational states, $\phi_a(r_a)$ and $\phi_c(r_c)$, and also of a finite set of square-integrable functions $\{\chi_n\}$ which describe the effect of the energetically closed channels. One needs only, therefore, to determine the expansion coefficients $\{C_n\}$ and the unknown radial functions, $f_{a+\alpha_0}(R_a)$ and $f_{c+\alpha_0}(R_c)$. This determination may be made through the use of a variational principle, specifically by extremizing the functional

$$I\{C_n, f_{a+\alpha_0}, f_{c+\alpha_0}\} = \langle \Psi_{\alpha_0} | H - E | \Psi_{\alpha_0} \rangle$$

(H being the total Hamiltonian) via a variation of first the constants and then the radial functions. As a result of this procedure, a set of coupled equations is obtained which may be solved for the f-functions.

If, however, the discussion is specialized to the H + H₂ exchange reaction, one may take advantage of the symmetry of the resulting equations and construct a set of decoupled equations for the functions f₊(R) and f₋(R) defined by

$$f_{\pm}(R) = f_{a+\alpha_0}(R) \pm f_{c+\alpha_0}(R)$$

Thus, by addition and subtraction of the coupled equations, the following independent integro-differential equations are obtained:

$$\begin{aligned} \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E_0 \right] f_{\pm}(R) \pm \int dR' V_{\text{ex}}(R, R') f_{\pm}(R') \\ + 2 \sum_{n,m}^{\pm} A_n(R) (M_{\approx}^{-1})_{n,m} \langle A_m | f_{\pm} \rangle = 0 \end{aligned} \quad (2.1)$$

where

$$\begin{aligned} V_0(R) &= \int dr \phi_0(r)^* [V - v_0(r)] \phi_0(r) \\ V_{\text{ex}}(R, R') &= \frac{\partial r(R, R')}{\partial R'} \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR'^2} + V - v_0(r') - E_0 \right] \\ &\quad \cdot \phi_0[r(R, R')] \phi_0[r'(R, R')] \end{aligned} \quad (2.2)$$

$$M_{n,m} = \langle \chi_n | E - H | \chi_m \rangle$$

$$A_n(R) = \int dr \phi_0(r)^* (H - E) \chi_n(r, R)$$

$$\phi_0(R) = \phi_a(R) = \phi_c(R)$$

$$E_0 = E - \epsilon_0$$

In the above equations H is the total Hamiltonian, V is the total potential energy, $v_0(r)$ is the asymptotic ground vibrational potential function for H_2 , and ϵ_0 is the vibrational eigenvalue corresponding to $\phi_0(r)$. Since the correlation functions $\{\chi_n\}$ are chosen to have a definite parity upon the exchange $(r_a, R_a) \leftrightarrow (r_c, R_c)$ and furthermore since the matrix M does not contain matrix elements which connect states of differing parity, the summation in Eq. (2.1) retains only the correlation terms of + or - parity.

An examination of Eq. (2.1) reveals that the term which describes the interaction between the open and closed channels is manifestly separable and is therefore inherently easy to handle via a basis set expansion. Calculations performed by Garrett and Miller¹⁴ have indeed verified that such an expansion can provide a quite adequate description of the closed-channel term even when only a few basis functions are employed. Hence in the present work interest will be confined to the nature of the open-channel exchange effect. In order to isolate that effect, the treatment which follows takes as the equation of interest

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E_0\right] f_{\pm}(R) = \int dR' V_{\text{ex}}(R, R') f_{\pm}(R') \quad , \quad (2.3)$$

which includes only the energetically open channels, rather than the complete expression given by Eq. (2.1).

B. Characterization of the Exchange Kernel

Before proceeding to a discussion of the methods which may be used to solve Eq. (2.3), one should obtain some idea of the actual structure of the exchange kernel. It is not difficult to generate numerical values for the kernel via Eq. (2.2) once a choice is made for the H_3 potential.

Throughout this work the popular Porter-Karplus¹⁵ potential surface has been adopted (in its collinear form), making the evaluation of $V_{\text{ex}}(R,R')$ particularly convenient in that the asymptotic reactant and product diatomics are described as simple Morse oscillators.

A calculation of the exchange kernel for an (R,R') coordinate grid was performed at a total energy of 0.4898 eV. The results of this calculation were then plotted as a three-dimensional surface using a Cal-Comp plotter, this surface being shown in Figure 3. One should note first of all that the kernel is quite strongly peaked along the diagonal. Second, it is clear that the effect of the exchange interaction will be limited to a fairly small region of configuration space, the maximum effect occurring at $R = R' \approx 2$ bohr radii (one should recall that for the Porter-Karplus surface, the saddle point is located at $R = R' = 2.55$ bohr radii). The reported need for the inclusion of many basis functions in the separable expansion of this kernel¹⁴ certainly seems, therefore, to be understandable. Hence in the discussion which follows, an investigation is made to determine whether or not the exchange is amenable to the application of a more efficient solution scheme.

1. Iterative Solution

As has been previously indicated,¹⁴ there is an obvious analogy between these scattering equations and the conventional Hartree-Fock expansions of electronic structure theory. One is tempted, therefore, to try to solve the equations via an iteration scheme analogous to an SCF calculation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E_0\right] f_{\pm}^{(n)}(R) = \int dR' V_{\text{ex}}(R,R') f_{\pm}^{(n-1)}(R') \quad (2.4)$$

where n counts the iterations.

If $f_0(R)$ is the regular solution of the homogeneous differential equation, i.e.,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E_0\right] f_0(R) = 0 \quad , \quad (2.5)$$

then the iterative process is begun by taking $f_{\pm}^{(0)}(R) \equiv f_0(R)$, substituting the zeroth order solution into the right hand side of Eq. (3.1), integrating this inhomogeneous equation to determine $f_{\pm}^{(1)}(R)$, then repeating the cycle until $f_{\pm}^{(n)}(R) = f_{\pm}^{(n-1)}(R)$ to the accuracy desired. Note also that such an operation is equivalent to summing a Born series;¹⁶ for example, a single iteration yields the solution obtained via the usual distorted-wave Born approximation.

The difficulty with such an approach lies, of course, in the convergence properties of Eq. (2.4). To get an idea of the conditions under which a solution may be obtained by iteration, consider a simple separable approximation to the exchange kernel,

$$V_{ex}(R, R') = A g(R) g(R') \quad , \quad (2.6)$$

where $g(R)$ might, for example, be a gaussian centered about the maximum of V_{ex} . For this case, Eq. (2.3) then reduces to

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E_0\right] f_{\pm}(R) = \mp A g(R) \langle g | f_{\pm} \rangle \quad (2.7)$$

which is known to be solvable in a closed form,

$$f_{\pm}(R) = f_0(R) \pm G_0 g \cdot A \langle g | f_0 \rangle (1 \mp A \langle g | G_0 | g \rangle)^{-1} \quad ,$$

where G_0 is the Green's function corresponding to Eq. (2.5). Once the solution is in this form, one can identify the convergence criterion by noting that the second term on the right has the form of the sum of a geometric series, for which the convergence properties are well known.¹⁷ Thus one sees that an iterative solution will be obtainable if and only if

$$|A\langle g|G_0|g\rangle| < 1 \quad . \quad (2.8)$$

Model calculations were therefore performed for the $H + H_2$ collinear system using a simplified form for the exchange kernel, namely a separable product of gaussians (as was suggested above), the parameters for which were determined by roughly fitting the actual calculated values for $V_{ex}(R, R')$ to the assumed functional form. Although admittedly the parameter fit is rather crude due to the fact that Eq. (2.6) yields a poor approximation to the true kernel, it appears that in general Eq. (2.8) will not be satisfied for such a model potential at those collision energies for which the reaction probabilities are non-negligible. [By no means does this particular model calculation indicate that there is no function $g(R)$ such that Eq. (2.8) will be satisfied for a particular choice of potential parameters, but rather it does suggest that poor convergence can make the iterative solution method unreliable for a general collision process.] Physically the lack of convergence merely points to the fact that the inclusion of the rearrangement effects produces a significant additional phase shift, making $f_0(R)$ a poor approximation to $f_{\pm}(R)$. Consequently, the higher terms in the Born series will make a non-negligible contribution to the scattering, and hence the distorted-wave Born approximation may be expected to be inadequate.

One also notices that the analogy between this development and Hartree-Fock theory is not as close as might be hoped. In practice the exchange kernel, although manifestly nonlocal, is confined to a relatively small region of space ($R, R' = [1., 5.]$ bohr) and as such does not produce the average potential field which is characteristic of electron exchange. Therefore one should not be too surprised that an SCF-like approach to equations describing molecular rearrangement is not particularly successful.

2. Separable Expansion of V_{ex}

Garrett and Miller,¹⁴ in the initial complete application of the exchange kernel formalism, make a separable approximation to V_{ex} , namely

$$V_{ex}(R, R') = \sum_{i,j} u_i(R) \langle u_i | V_{ex} | u_j \rangle u_j(R') \quad , \quad (2.9)$$

where $\{u_i\}$ is a convenient basis set. Since their calculations were converged with respect to an increase in the number of basis functions, Eq. (2.9) represents an essentially exact treatment of the direct exchange contribution. In addition, the use of a separable expansion greatly facilitates computation in that all of the inhomogeneous terms in Eq. (2.1) are then separable. Consequently one can obtain a solution for $f_{\pm}(R)$ in a closed form. However, as mentioned previously, this "outer" expansion of the kernel requires that a large number of functions be included if convergence is to be achieved, and hence this particular approach would likely prove to be unwieldy for systems larger than $H + H_2$.

One is lead, therefore, to explore the possibility that some other separable expansion might provide a superior description of the exchange

kernel. Specifically, the present work examines an "inner" expansion defined by

$$\begin{aligned} V_{\text{ex}}(R, R') &= \langle R | V_{\text{ex}} V_{\text{ex}}^{-1} V_{\text{ex}} | R' \rangle \\ &= \sum_{i,j} \langle R | V_{\text{ex}} | u_i \rangle \langle u_i | V_{\text{ex}} | u_j \rangle^{-1} \langle u_j | V_{\text{ex}} | R' \rangle \end{aligned} \quad (2.10)$$

where $\langle u_i | V_{\text{ex}} | u_j \rangle^{-1}$ denotes the (i,j) matrix element of the matrix inverse of the matrix $\langle u_i | V_{\text{ex}} | u_j \rangle$. Note that now the expansion vectors are $\{V_{\text{ex}} u_i\}$ rather than $\{u_i\}$, and accordingly more knowledge of the exchange is built directly into the development.

To see the consequences of improving the approximation for V_{ex} , consider another very simple model for the exchange,

$$V_{\text{ex}}(R, R') = A \delta(R - R_0) \delta(R' - R_0) \quad ,$$

a model which is localized (in the extreme) at $R = R' = R_0$; note that the actual kernel for $H + H_2$ in reference 14 is qualitatively of this form. Applying Eq. (2.9) one obtains the outer expansion,

$$V_{\text{ex}}(R, R') = A \sum_{i,j} u_i(R) u_i(R_0) u_j(R') u_j(R_0) \quad .$$

On the other hand, using the inner expansion, Eq. (2.10),

$$\begin{aligned} V_{\text{ex}}(R, R') &= \sum_{i,j} \frac{A^2 \delta(R - R_0) \delta(R' - R_0) u_i(R_0) u_j(R_0)}{A u_i(R_0) u_j(R_0)} \\ &= A \delta(R - R_0) \delta(R' - R_0) \end{aligned}$$

identically, regardless of the form taken for $\{u_i\}$ or of the number of functions used. Clearly, unless a rather large number of expansion functions are retained, these two expressions will differ significantly. One is therefore encouraged that this inner expansion may substantially improve the characterization of the kernel and in doing so decrease the size of the basis set required for an accurate solution.

C. Results and Observations

Utilizing the improved separable expansion of the exchange kernel described in Section B(2), calculations were performed in order to determine the $H + H_2$ collinear reaction probability at a collision energy of 0.4898 eV. (As was previously indicated, the Porter-Karplus¹⁵ H_3 potential surface has been used in all calculations appearing herein.) There was, in fact, little difference between these computations and those which have been heretofore reported¹⁴ except for the way in which V_{ex} has been treated, although in the present work the emphasis has been placed on a characterization of the direct exchange contribution since the effects arising from the indirect exchange via the closed channels already seem to be adequately incorporated. [Details of the calculation are presented in the Appendix to this chapter.]

In order to generate a "best" separable expansion of V_{ex} (i.e., one which yields the most accurate description for a minimal number of basis functions), a search was made for the optimal choice of parameters for the $\{u_i\}$ appearing in Eq. (2.10). These functions, conveniently taken to be harmonic oscillator wavefunctions,¹⁸ contain two free parameters--the point about which the functions are centered, R_0 , and a quantity related inversely to the "width" of the functions, β . The results of this search

are displayed in Table 3, where the open-channel reaction probability is given for various values of β^2 (R_0 being chosen in all cases as the point at which the exchange kernel is a maximum). It is quite evident that the number of functions required in order that a converged expansion may be obtained is strongly dependent upon the choice for β . In contrast, calculations summarized in Table 4 which were performed using the outer expansion (Eq. (2.9)) show convergence which is virtually independent of the function width. [Of course, one should also observe from a comparison of the two sets of results that the inner expansion yields converged results with a substantially smaller basis set.] This difference in the behavior of the two descriptions suggests that whereas the outer expansion is sufficiently poor that many basis functions must be included regardless of the details of the functional forms, the inner expansion, by providing more flexibility in fitting a specific form of the exchange kernel, requires that the basis functions be "tuned" in order that the fit be optimized. Thus, for large values of β , one is obliged to use many functions just to span the coordinate space over which the rearrangement is most likely to occur simply because the spanning functions are themselves too localized. On the other hand, for very small β , the functions become so spread out that they have a substantial amplitude in the region of the repulsive wall of the potential, a region which is poorly described in general. Therefore one expects the optimum choice for β to appear in an intermediate region, this expectation being borne out by the tabulated results.

The principal conclusion to be drawn from Tables 3 and 4 is then that there exists a much more efficient representation of the exchange kernel than that which was previously reported. For the optimum choice of β , for example, a reaction probability converged to three significant

figures may be obtained by including only 8 basis functions in an inner expansion of the kernel, while on the other hand roughly 25 functions must be retained in order to generate results of comparable accuracy via an outer expansion. Of course if one desires to characterize more complex reactive processes, in particular those reactions which involve reactants and products that are not the same chemical species and thus which lead to unsymmetrical exchange kernels, then one should expect that a somewhat larger set of expansion functions might be required. However, inasmuch as the inner expansion automatically incorporates more knowledge of V_{ex} than does the outer expansion, it is not unreasonable to anticipate that for such cases the computational advantages of adopting the description proposed here will actually be enhanced.

Overall this improved expansion of the exchange kernel provides a significant reduction in the magnitude of the computational problem which is associated with Miller's reactive scattering formalism. Such a reduction, hopefully, has made the extension of this method to higher dimensions or to more chemically interesting collision partners much more feasible.

Appendix: Collinear H + H₂ Open-Channel Reaction Probability Calculation

In this section the details of the method used to calculate the reactive scattering phase shifts (and hence the reaction probability) are presented for the particular case in which the exchange kernel is handled via an inner expansion (Eq. (2.10)). Since for this case both the open-channel and closed-channel exchange terms are manifestly separable, it is a fairly simple matter to incorporate both of these contributions into the calculation; however, for the sake of illustration, the solution described herein will be only that for the situation of specific interest in the present study, namely the open-channel exchange.

Substituting Eq. (2.10) into (2.3), one obtains the equation to be solved:

$$(H_0 - E_0) f_{\pm}(R) = \mp \sum_{ij} \langle R | v_{\text{ex}} | u_i \rangle (\langle u_i | v_{\text{ex}} | u_j \rangle)^{-1} \langle u_j | v_{\text{ex}} | f_{\pm} \rangle \quad , \quad (\text{A.1})$$

where H_0 is the Hamiltonian for the nonreactive single-channel scattering. Then, by defining a new set of expansion vectors by the expression

$$|v_i\rangle = v_{\text{ex}} |u_i\rangle$$

and furthermore by defining a matrix \tilde{v}_{ex} , the elements of which are given by

$$(\tilde{v}_{\text{ex}})_{ij} = \langle u_i | v_{\text{ex}} | u_j \rangle \quad ,$$

one may rewrite Eq. (A.1) as

$$(H_0 - E_0) f_{\pm}(R) = \mp \sum_{ij} v_i(R) (\tilde{v}_{\text{ex}}^{-1})_{ij} \langle v_j | f_{\pm} \rangle \quad . \quad (\text{A.2})$$

Notice that this equation is then of the same form as Eq. (2.7), the solution of which has been previously given. Similarly, one may easily construct the solution to the scattering problem described by Eq. (A.2) in a closed form, the result being that the phase shifts may be obtained via the expression

$$\tan \eta_{\pm} = \tan \eta_0 \mp \frac{2\mu}{\hbar^2 k} f_0 \cdot (1 \underset{\approx}{V}^{-1} \underset{\approx}{G_0})^{-1} \cdot \underset{\approx}{V}^{-1} \cdot f_0 \quad (\text{A.3})$$

where

$$(f_0)_i = \langle v_i | f_0 \rangle$$

and

$$(G_0)_{ij} = \langle v_i | G_0 | v_j \rangle = \int dR \int dR' v_i^*(R) G_0(R, R') v_j(R')$$

(G_0 is just the Green's operator described in Section 2a, the coordinate matrix elements of which are products of the homogeneous solutions,¹⁹ namely

$$G_0(R, R') = -\frac{2\mu}{\hbar^2 k} f_0(R_{<}) f_1(R_{>})$$

where $f_0(R)$ and $f_1(R)$ are respectively the regular and irregular solutions.)

The actual computation proceeds as follows: first, the linearly independent solutions to the homogenous equation are obtained via direct numerical integration of Eq. (2.5) using the well-known Numerov method.²⁰ Having thus found the radial functions at an evenly spaced coordinate grid, the matrix elements may be calculated by a straightforward application of

Simpson's rule²¹ once one has constructed the set of expansion vectors $\{v_i\}$ (since the vectors $\{u_i\}$ are chosen to be just harmonic oscillator wavefunctions, it is a simple matter to compute these new vectors using the form for $V_{ex}(R,R')$ given by Eq. (2.2)). Only standard matrix manipulations are then required in order to determine the phase shifts from Eq. (A.3).

III. A Unified Model for Elastic and Inelastic Scattering from a Solid Surface.

Ever since the early days of quantum mechanics, there has been an abiding interest in trying to understand and describe the microscopic nature of the scattering of gaseous atoms and molecules from various types of solid surfaces. The first real progress followed the discovery of discrete diffraction peaks in the observed intensity of a helium beam scattered from a lithium fluoride crystal plane, a revelation which prompted theorists to propose the first crude models for the gas-surface interaction giving rise to such diffractive phenomena.²² Not until more recently, however, have there been many real advances which significantly relate to the development of a truly global theory, i.e., a theory which would allow one actually to identify essentially all of the structure yielded by experiments. Notably, Goodman²³ and subsequently Goodman and Tan,²⁴ using a continuum model of the solid and obtaining transition probabilities via the method of Cabrera, Celli, Goodman, and Manson²⁵ (CCGM), were able to calculate a scattering distribution for the He-LiF(001) system which at least qualitatively reproduces the experimental inelastic results. Other work by Lin and Wolken²⁶ (who performed a close-coupling calculation) and by Metiu²⁷ has also helped to clarify the physics of the gas-surface collision, although both of the approaches taken by these investigators require extensive numerical computation before the scattering structure can be revealed. On the other hand, the state of the theory has also benefited substantially from the consideration of simplified scattering models which permit one to identify unambiguously the particular constituent effects that generate the composite intensity

pattern. A good example of just such an approach is to be found in the work of Weare,²⁸ who has examined the specific case in which the surface and gas temperatures are sufficiently low that a first-order perturbative treatment of the inelasticity adequately describes the scattering from a smooth potential contour.

It should not be inferred from the above comments that the sole contributions to the understanding of the surface scattering processes have been made within a quantum mechanical framework. In particular, a paper by Garrison and Adelman²⁹ has considered the collisional energy transfer from a classical many-body standpoint by taking advantage of the computational tractability afforded by the generalized Langevin equation formalism.³⁰ In addition, these workers have investigated the conditions under which various simplified solid models might be expected to mimic accurately the actual surface behavior.

The present work provides a simple, alternative one-dimensional surface model which manifestly displays the principal features of both the elastic and the inelastic processes. Although the basic formalism employed has been previously described elsewhere,³¹ the model adopted herein does in fact permit an analytic determination of the scattering intensities, thereby making immediately evident the consequences of such a formulation.

There appear to be two major stumbling blocks in evidence in the bulk of the previous inelastic studies. The first is the assumption that in the absence of phonon excitations the crystal surface is perfectly flat.^{23,28,32} Such an assumption is clearly inadequate if a unified model is to be constructed due to the fact that for a flat surface

specular scattering is the only elastic process allowed. Consequently, one should select a form for the gas-surface interaction potential (the surface contour being classically just the turning-point surface for this potential at the specified collision energy) which yields a version of the corrugated hardwall potential in the limit of zero phonon displacement inasmuch as such a corrugated contour is known to produce the desired gross diffraction peak structure.³³

Secondly, there is always a problem involved in treating the phonon mode enumeration and averaging. Elaborate treatments, such as that by Beeby,³² have all of the proper phonon dynamics incorporated in them; however, the difficulty of that inclusion makes such formalisms somewhat cumbersome to use while apparently adding little to the construction of a straightforward physical picture of the scattering. Furthermore it is desirable to avoid ad hoc averaging procedures³⁴ whose accuracy is hard to evaluate. In the model described below, these modes have been handled in a very intuitive way which does indeed seem to generate the aggregate phonon structure but at the same time does not obscure the fundamental physics.

This work takes advantage of the widely used assumption that the fundamental scattering pattern arises as a result of a more or less purely repulsive two-body short-range component of the gas-surface interaction. Such an assumption logically prompts the use of an impulsive collision model, which itself has a firm basis in experimental findings,³⁵ so that the motion of the surface may be effectively decoupled from the actual collision dynamics within the interaction time interval. Equivalently, this particular model has been obtained by Weare²⁸ in the

limit that for a given initial energy state of the solid the translational energy of the incident gas atom is allowed to become large. By making this sudden approximation, one does, however, necessarily restrict the application of the formalism to the collision of light atoms such as helium with the surface, although in practice these are the very systems which are amenable to experimental study and which might be expected to exhibit the most detailed scattering intensity patterns. A more thorough discussion of the impulsive collision assumption is given in Section A.

A. Impulsive Collision Approximation

The fundamental problem of interest is the calculation of a transition probability (i.e., a scattering intensity) from some initial wavevector \vec{k}_i , which describes the unperturbed motion of the incident gas atom, to a final wavevector for the scattered atom \vec{k}_f with a concurrent translational energy gain (or loss) due to inelasticity, ΔE . Practically, since at present one cannot experimentally characterize precisely the quantum states of the solid before or after the collision, it is necessary to average appropriately over the phonon modes if one is to obtain a quantity which can actually be observed. Thus, the scattering intensity may be written in terms of an S-matrix element as

$$I_{\Delta E, \vec{k}_f \leftrightarrow \vec{k}_i} = \sum_{\vec{n}_2} \sum_{\vec{n}_1} \frac{e^{-\beta \epsilon_{\vec{n}_1}}}{Q} \delta[\Delta E + (\epsilon_{\vec{n}_2} - \epsilon_{\vec{n}_1})] |S_{\vec{k}_f, \vec{n}_2 \leftrightarrow \vec{k}_i, \vec{n}_1}^+|^2 \quad (3.1)$$

where \vec{n}_1 and \vec{n}_2 label respectively the initial and final phonon states having energies $\epsilon_{\vec{n}_1}$ and $\epsilon_{\vec{n}_2}$. [In addition, Q is the phonon partition function, and $\beta = (k_B T_S)^{-1}$ (with k_B being Boltzmann's constant and T_S the characteristic surface temperature).]

As indicated in the introductory discussion, one then commonly proceeds by taking the short-range gas-surface interaction to be repulsive, the limit of which being a simple hard wall. Certainly if diffractive elastic scattering dominates the intensity pattern, then it is reasonable to assume that the collision may be modeled in zeroth order by a hard sphere rebounding elastically from an infinitely hard surface. More realistically, the surface is described as being a corrugated wall which undergoes distortions due to the excitation of phonon modes in the solid, these distortions presumed to be a small percentage of a lattice dimension, and that this motion is slow compared to the collision time (which, of course, in the case of interaction with a perfectly hard wall is infinitesimal).

The above impulsive collision assumption may be introduced into Eq. (3.1) by writing the S-matrix element in the sudden approximation form,³⁶

$$S_{\vec{k}_{f2}, \vec{k}_{i1}}^{\vec{k}_{f2}, \vec{k}_{i1}} = \langle \vec{k}_{f2} | e^{2i\eta(x; \vec{q})} | \vec{k}_{i1} \rangle, \quad (3.2)$$

where in this particular case the phase shift η depends not only upon the coordinate parallel to the surface plane, x , but also parametrically upon the vector of phonon normal mode displacement coordinates, $\vec{q} = \{q_j\}$. Since the repulsive gas-surface interaction is assumed to be well modeled by a hardwall potential, it then follows that the phase shift is given by the hard sphere scattering result,³⁷ i.e.,

$$\eta(x; \vec{q}) = -kZ(x; \vec{q}),$$

where $Z(x; \underline{q})$ is the equation of the surface contour.

But now how does one actually determine a form for this surface contour? Presumably, if the distortions which arise as a result of the excitation of the phonon modes are, as was previously suggested, sufficiently small in amplitude, then the contour should be adequately described by a truncated Taylor series, the expansion being made about the equilibrium surface position,

$$Z(x; \underline{q}) = Z(x; 0) + \left. \frac{\partial Z(x; \underline{q})}{\partial \underline{q}} \right|_{\underline{q}=0} \cdot \underline{q} \quad (3.3)$$

($\underline{q} = 0$ corresponding to the undistorted surface). In order that the notation might be simplified somewhat, Eq. (3.3) is at this point rewritten in the following form:

$$Z(x; \underline{q}) = Z(x) + \underline{\zeta}(x) \cdot \underline{q} \quad , \quad (3.4)$$

with the vector $\underline{\zeta}(x)$ having components given by

$$\zeta_j(x) = \left. \frac{\partial Z(x; \underline{q})}{\partial q_j} \right|_{\underline{q}=0} \quad .$$

Within this expansion the product $\zeta_j(x)q_j$ may be interpreted then as being the displacement of the surface contour at some position x as a result of the excitation of the j^{th} normal mode, the total displacement at x being obtained by summing over all of the N modes of the surface atoms. It should be clear, though, that in general one will not be able to determine $\underline{\zeta}(x)$ analytically; however, for the particular case examined in Section C, these vectors may indeed be constructed, and hence the phase shift (and thus the S-matrix elements) may be obtained.

B. Formal Theory

Using the results of the previous section (Eqs. (3.1), (3.2), and (3.4)), the scattering intensity is given in the impulsive approximation by

$$I_{\Delta E, \vec{k}_f \leftarrow \vec{k}_i} = \sum_{\tilde{n}_2} \sum_{\tilde{n}_1} \frac{e^{-\beta \epsilon_{\tilde{n}_1}}}{Q} \delta[\Delta E + (\epsilon_{\tilde{n}_2} - \epsilon_{\tilde{n}_1})] \left| \int dx \int d\tilde{q} e^{-i\Delta k_x x} \cdot \phi_{\tilde{n}_2}(\tilde{q})^* \phi_{\tilde{n}_1}(\tilde{q}) e^{-i\Delta k_z Z(x)} e^{-i\Delta k_z \zeta(x) \cdot \tilde{q}} \right|^2, \quad (3.5)$$

where $\phi_{\tilde{n}_1}$ and $\phi_{\tilde{n}_2}$ are, respectively, the initial and final quantum states of the solid, and Δk_x and Δk_z are the projections of $\Delta k = |\vec{k}_f - \vec{k}_i|$ parallel and perpendicular to the plane of the surface. One then notes that since the coordinate representation of the transition operator is given here by

$$T(\tilde{q}) = \int dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} e^{-i\Delta k_z \zeta(x) \cdot \tilde{q}}, \quad (3.6)$$

Eq. (3.5) may be rewritten as

$$I_{\Delta E, \vec{k}_f \leftarrow \vec{k}_i} = \sum_{\tilde{n}_2} \sum_{\tilde{n}_1} \frac{e^{-\beta \epsilon_{\tilde{n}_1}}}{Q} \delta[\Delta E + (\epsilon_{\tilde{n}_2} - \epsilon_{\tilde{n}_1})] \langle \tilde{n}_1 | T^\dagger | \tilde{n}_2 \rangle \cdot \langle \tilde{n}_2 | T | \tilde{n}_1 \rangle.$$

Furthermore, by employing the Fourier transform identity for the delta function, this last equation may be cast into a particularly convenient form, namely the well-known correlation function expression,³¹ via the

following transformations:

$$\begin{aligned}
 I_{\Delta E, \vec{k}_f \leftrightarrow \vec{k}_i} &= (2\pi\hbar)^{-1} \int dt e^{-i\Delta E t/\hbar} \sum_{\vec{n}_2} \sum_{\vec{n}_1} \frac{e^{-\beta \epsilon_{\vec{n}_1}}}{Q} \langle \vec{n}_1 | T^\dagger(0) | \vec{n}_2 \rangle \\
 &\qquad \qquad \qquad \cdot \langle \vec{n}_2 | T(t) | \vec{n}_1 \rangle \\
 &= (2\pi\hbar)^{-1} \int dt \frac{e^{-i\Delta E t/\hbar}}{Q} \text{Tr} [e^{-\beta H_0} T^\dagger(0) T(t)] \\
 &\equiv (2\pi\hbar)^{-1} \int dt e^{-i\Delta E t/\hbar} \langle T^\dagger(0) T(t) \rangle \quad ,
 \end{aligned}$$

where $T(t)$ is the time-evolved transition operator T in the Heisenberg representation,

$$T(t) = e^{-iH_0 t/\hbar} T e^{iH_0 t/\hbar} \quad ,$$

and H_0 is the phonon Hamiltonian.

The time correlation function thus defined may be evaluated by re-expanding in terms of the T-matrix elements,

$$\begin{aligned}
 \langle T^\dagger(0) T(t) \rangle &= \sum_{\vec{n}_2} \sum_{\vec{n}_1} \frac{e^{-\beta \epsilon_{\vec{n}_1}}}{Q} e^{-i(\epsilon_{\vec{n}_2} - \epsilon_{\vec{n}_1}) t/\hbar} \langle \vec{n}_1 | T^\dagger | \vec{n}_2 \rangle \\
 &\qquad \qquad \qquad \cdot \langle \vec{n}_2 | T | \vec{n}_1 \rangle \\
 &= Q^{-1} \int dx \int dx' \int d\vec{q} \int d\vec{q}' e^{-i\Delta k_x (x-x')} e^{-i\Delta k_z (Z(x)-Z(x'))} \\
 &\quad \cdot e^{-i\Delta k_z \zeta(x) \cdot \vec{q}} e^{i\Delta k_z \zeta(x') \cdot \vec{q}'} \left[\sum_{\vec{n}_2} \langle \vec{q}' | \vec{n}_2 \rangle e^{-i\epsilon_{\vec{n}_2} t/\hbar} \langle \vec{n}_2 | \vec{q} \rangle \right] \\
 &\quad \cdot \left[\sum_{\vec{n}_1} \langle \vec{q} | \vec{n}_1 \rangle e^{-\beta \epsilon_{\vec{n}_1}} e^{i\epsilon_{\vec{n}_1} t/\hbar} \langle \vec{n}_1 | \vec{q}' \rangle \right] \quad . \quad (3.7)
 \end{aligned}$$

Assuming that the phonon modes are harmonic, the terms in square brackets in Eq. (3.7) are just harmonic oscillator propagators in the coordinate representation.³⁸ Thus the above equation may be written

$$\langle T^\dagger(0) T(t) \rangle = \int dx \int dx' e^{-i\Delta k_x(x-x')} e^{-i\Delta k_z(Z(x)-Z(x'))} C(x, x'; t), \quad (3.8)$$

the new instantaneous position correlation function $C(x, x'; t)$ being given by

$$C(x, x'; t) = Q^{-1} \prod_j \int dq_j \int dq'_j e^{-i\Delta k_z(\zeta_j(x)q_j - \zeta_j(x')q'_j)} \\ \cdot \left[\frac{4\pi^2 \hbar^2}{m^2 \omega_j^2} \sin \omega_j t \sin \omega_j(t + i\hbar\beta) \right]^{-1/2} \exp\left\{ \frac{i m \omega_j}{2 \hbar \sin \omega_j t} [(q_j^2 + q'_j{}^2) \cos \omega_j t \right. \\ \left. - 2 q_j q'_j] - \frac{i m \omega_j}{2 \hbar \sin \omega_j(t + i\hbar\beta)} [(q_j^2 + q'_j{}^2) \cos \omega_j(t + i\hbar\beta) - 2 q_j q'_j] \right\},$$

(here m and ω_j are the mass and frequency of the j^{th} mode). The integrals over phonon mode displacement coordinates are of the general gaussian form and therefore may be done analytically, the details of that evaluation not being given here. Suffice to say, after a substantial amount of algebra one obtains

$$C(x, x'; t) = \exp\left\{ - \sum_j \frac{\hbar \Delta k_z^2}{4 m \omega_j} [(\zeta_j(x))^2 + \zeta_j(x')^2 - 2 \zeta_j(x) \zeta_j(x') \cos \omega_j t] \coth \frac{\hbar \omega_j \beta}{2} \right. \\ \left. + 2 i \zeta_j(x) \zeta_j(x') \sin \omega_j t \right\}.$$

Then, by recognizing that the mean square displacement of a harmonic oscillator³⁹ is just

$$\langle q_j^2 \rangle = \left(\frac{2m\omega_j}{\hbar} \tanh \frac{\hbar\omega_j\beta}{2} \right)^{-1},$$

the correlation function may be rewritten as

$$\begin{aligned} C(x, x'; t) &= \exp\left[-\frac{1}{2} \sum_j \Delta k_z^2 \langle q_j^2 \rangle (\zeta_j(x)^2 + \zeta_j(x')^2)\right] \\ &\cdot \exp\left\{\sum_j \Delta k_z^2 \langle q_j^2 \rangle \zeta_j(x)\zeta_j(x') \left[\cos\omega_j t - i \sin\omega_j t \tanh \frac{\hbar\omega_j\beta}{2}\right]\right\}. \end{aligned} \quad (3.9)$$

At this point one may identify the Debye-Waller factor, defined by

$$W(x) = \frac{1}{2} \Delta k_z^2 \sum_j \langle q_j^2 \rangle \zeta_j(x)^2.$$

Furthermore, in passing to the classical limit $\tanh \frac{\hbar\omega_j\beta}{2} \rightarrow \frac{\hbar\omega_j\beta}{2}$, with the result being that Eq. (3.9) takes on the form

$$\begin{aligned} C^{CL}(x, x'; t) &= e^{-W(x)} e^{-W(x')} \left\{ \exp \sum_j \Delta k_z^2 \langle q_j^2 \rangle \zeta_j(x) \zeta_j(x') \right. \\ &\quad \left. \cdot \left[\cos\omega_j t - i \frac{\hbar\omega_j\beta}{2} \sin\omega_j t \right] \right\} \\ &= e^{-W(x)} e^{-W(x')} \exp\left\{ \left(1 + i \frac{\hbar\beta}{2} \frac{d}{dt}\right) \sum_j \Delta k_z^2 \langle q_j^2 \rangle \right. \\ &\quad \left. \cdot \zeta_j(x) \zeta_j(x') \cos\omega_j t \right\} \\ &= e^{-W(x)} e^{-W(x')} \exp\left\{ \left(1 + i \frac{\hbar\beta}{2} \frac{d}{dt}\right) \Delta W(x, x'; t) \right\}. \end{aligned} \quad (3.10)$$

(Note that the completely classical result ($\hbar = 0$) is obtained by totally neglecting the imaginary part of ΔW .)

While Eq. (3.10) is the exact result for the correlation function within the impulsive collision assumption, in its present form one is not able to identify easily the elementary physical processes which give rise to the observed effect. In order to reveal these processes, the last exponential is expanded in a power series, which when substituted with Eq. (3.8) into (3.5) leads to the following equation for the scattered intensity:

$$\begin{aligned}
 I_{\Delta E, \vec{k}_f \leftarrow \vec{k}_i} &= (2\pi\hbar)^{-1} \int dt e^{-i\Delta E t/\hbar} \int dx \int dx' e^{-i\Delta k_x(x-x')} e^{-i\Delta k_z(Z(x)-Z(x'))} \\
 &\cdot e^{-W(x)} e^{-W(x')} \left\{ 1 + (1 + i \frac{\hbar\beta}{2} \frac{d}{dt}) \Delta W \right. \\
 &\left. + \frac{1}{2} [(1 + i \frac{\hbar\beta}{2} \frac{d}{dt}) \Delta W]^2 + \dots \right\}
 \end{aligned}$$

Since the time enters into ΔW through a cosine term only, the time integral simply yields energy delta functions,

$$\begin{aligned}
 I_{\Delta E, \vec{k}_f \leftarrow \vec{k}_i} &= \delta(\Delta E) \left| \int dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} e^{-W(x)} \right|^2 \\
 &+ \frac{1}{2} \sum_j \left\{ [\delta(\Delta E - \hbar\omega_j) + \delta(\Delta E + \hbar\omega_j)] - \frac{\hbar\omega_j\beta}{4} [\delta(\Delta E - \hbar\omega_j) \right. \\
 &\left. - \delta(\Delta E + \hbar\omega_j)] \right\} \Delta k_z^2 \langle q_j^2 \rangle \left| \int dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} \right. \\
 &\cdot e^{-W(x)} \zeta_j(x) \left|^2 + \dots \right. \\
 &= I_0 + I_1 + \dots
 \end{aligned}$$

(terms through first order in ΔW being shown explicitly). In this form the component elementary scattering process may be easily recognized: the first term produces just the purely elastic spectrum with peak intensities attenuated by Debye-Waller factors, the second term represents the one-phonon inelastic event, and the remaining terms account for higher order phonon processes. Note that in the one-phonon term the phonon annihilation ($\Delta E = +\hbar\omega_j$) and creation ($\Delta E = -\hbar\omega_j$) contributions are symmetric in the completely classical result, and that even when quantum effects begin to become significant and the intensity symmetry is broken, the positions of the inelastic peaks are unaltered.

Due to the periodicity of the surface, it is advantageous to transform the x -integrals into sums of integrals over a unit cell. Since the details of this transformation are set down in Appendix A, only the final results will be indicated here. For the component intensities one finds that

$$\begin{aligned}
 I_0 &= Na^2 \delta(\Delta E) \sum_{\mathbf{k}} \left| \delta\left(\mathbf{k} - \frac{\Delta\mathbf{k}}{2\pi}\right) \right| \frac{1}{a} \int_0^a dx e^{-i\Delta\mathbf{k}_x x} e^{-i\Delta\mathbf{k}_z Z(x)} e^{-W(x)} \Big|^2 \\
 &= Na^2 \delta(\Delta E) \sum_{\mathbf{k}} \left| \delta\left(\mathbf{k} - \frac{\Delta\mathbf{k}}{2\pi}\right) \right| |S_{\mathbf{k}}^0|^2 \quad , \quad (3.11a)
 \end{aligned}$$

and

$$\begin{aligned}
 I_1 &= \frac{1}{2} \sum_j \left\{ [\delta(\Delta E - \hbar\omega_j) + \delta(\Delta E + \hbar\omega_j)] - \frac{\hbar\omega_j \beta}{4} [\delta(\Delta E - \hbar\omega_j) \right. \\
 &\quad \left. - \delta(\Delta E + \hbar\omega_j)] \Delta k_z^2 \langle q_j^2 \rangle \right\} \int_0^a dx e^{-i\Delta\mathbf{k}_x x} e^{-i\Delta\mathbf{k}_z Z(x)} \\
 &\quad \cdot e^{-W(x)} \sum_n e^{-i\Delta\mathbf{k}_x n a} \zeta_j(x+na) \Big|^2 \quad , \quad (3.11b)
 \end{aligned}$$

where N is the number of unit cells within the experimental interaction zone.

Eqs. (3.11) represent the general result for the scattering intensity due to elastic and one-phonon inelastic processes. (For the time being any higher-order processes which give rise to effective elastic or single-phonon transitions, e.g., a two-phonon event in which the same phonon is first annihilated and then created or vice versa, shall be ignored.) Although the multiphonon terms may be similarly constructed, it shall be convenient to restrict the present development to the consideration of only these two contributions; however, one should recognize that there seems to be no general consensus as to the appropriateness of this one-phonon approximation to the total inelastic scattering.^{28,32}

C. Interaction Potential

The formal solution given in the previous section, while perhaps somewhat illustrative, does not really provide a physical picture of the collision due to the presence of the as yet unknown ζ -vectors. In order to obtain analytical formulae which clearly reveal the scattering structure, it is necessary to adopt a model potential which at least qualitatively represents the true gas-surface interaction while at the same time permits a tractable solution to the problem. Inasmuch as the impulse approximation supposes that the interatomic forces are fundamentally repulsive, the present study shall adopt as a model potential the simple two-body form

$$V = V_0 \sum_j e^{-\alpha(x-x_j)^2} e^{-\gamma(z-z_j)} \quad , \quad (3.12)$$

where V_0 is some scaling parameter which also sets the units properly, the adjustable parameters α and γ are measures of the range of the potential, and (x_j, z_j) is the instantaneous position of the j^{th} surface atom.

A further simplification is introduced by assuming that the solid atoms have only two unique vibrational frequencies, ω_x and ω_z , respectively corresponding to oscillation parallel or perpendicular to the surface plane. Such an assumption implies the consideration of some sort of modified Einstein solid [an evaluation of the consequences of using this particular model for the distribution of phonon modes shall be deferred to Section D]. The phonon mode displacement coordinates, q_j^x and q_j^z , are therefore just the displacements of the j^{th} atom from its equilibrium position. Thus, if the coordinate system is fixed with the origin at the equilibrium position of one of the surface atoms,

$$\begin{aligned}x_j &= ja + q_j^x \\z_j &= q_j^z\end{aligned}\quad (3.13)$$

Substituting Eq. (3.13) into (3.12) and defining the surface contour to be the classical turning-point surface for the interatomic potential, i.e., $V(Z(x;q)) = E$, one may solve for the equation of the contour analytically,

$$Z(x;q) = \gamma^{-1} \ln \frac{V_0}{E} + \gamma^{-1} \ln \sum_j e^{-\alpha(x-ja-q_j^x)^2} e^{\gamma q_j^z}.$$

As mentioned in the introductory comments, in the static surface limit ($q = 0$) this contour should resemble a corrugated hard wall. Thus,

$$Z(x;0) \equiv Z(x) = \gamma^{-1} \ln \frac{V_0}{E} + \gamma^{-1} \ln \sum_j e^{-\alpha(x-ja)^2} \quad (3.14)$$

Using the Poisson sum rule,⁴⁰ the summation may be written

$$\begin{aligned} \sum_{\ell} \int_{\ell} e^{2\pi i \ell j} e^{-\alpha(x-ja)^2} &= \frac{\sqrt{\pi}}{a\sqrt{\alpha}} \sum_{\ell} e^{-\pi^2 \ell^2 / \alpha a^2} e^{\frac{2\pi i \ell}{a} x} \\ &\cong \frac{\sqrt{\pi}}{a\sqrt{\alpha}} (1 + 2e^{-\pi^2 / \alpha a^2} \cos \frac{2\pi x}{a}) \end{aligned}$$

(Since the sum is presumed to be rapidly convergent, only the $\ell = 0, \pm 1$ terms are retained.) Consequently, Eq. (3.14) becomes

$$\begin{aligned} Z(x) &\cong \gamma^{-1} \ln \left(\frac{V_0}{E} \frac{\sqrt{\pi}}{a\sqrt{\alpha}} \right) + \gamma^{-1} \ln (1 + 2e^{-\pi^2 / \alpha a^2} \cos \frac{2\pi x}{a}) \\ &\cong Z_0 + \frac{2}{\gamma} e^{-\pi^2 / \alpha a^2} \cos \frac{2\pi x}{a} \quad (\text{assuming } e^{-\pi^2 / \alpha a^2} \ll \frac{1}{2}) \\ &\cong Z_0 + ha \cos \frac{2\pi x}{a} \end{aligned} \quad (3.15)$$

where Z_0 is just a constant (and which therefore only scales $Z(x)$) and ha is the surface amplitude. One may easily see now that $Z(x)$ does indeed have the canonical form of a corrugated surface and is, as required, periodic in x .

Having made the assumption that the surface atoms oscillate with the normal mode frequencies, one may easily generate the required ζ -vectors:

$$\zeta_{z_j}(x) = \frac{\partial Z(x; q)}{\partial q_j} \Big|_{q=0} = \frac{e^{-\alpha(x-ja)^2}}{\sum_{j'} e^{-\alpha(x-j'a)^2}}$$

and

$$\zeta_{x_j}(x) = \frac{\partial Z(x; q)}{\partial q_j} \Big|_{q=0} = \frac{2\alpha}{\gamma} \frac{(x-ja) e^{-\alpha(x-ja)^2}}{\sum_{j'} e^{-\alpha(x-j'a)^2}} \quad (3.16)$$

Before proceeding further, notice that the vector involving displacement of the surface atoms parallel to the surface, $\zeta_{x_j}(x)$, is inversely proportional to the potential parameter γ . Just by looking at the form of Eq. (3.12), it is clear that if the potential function is to mimic a strongly repulsive interaction, then γ must be large, otherwise the impulsive collision approximation is invalid. But for large γ , $\zeta_{x_j}(x) \ll \zeta_{z_j}(x)$, and thus the x-motion of the surface atoms may essentially be neglected with respect to motion perpendicular to the surface. This neglect of in-plane motion is used almost universally in the work of others, and therefore it is particularly encouraging that the model proposed herein exhibits this feature explicitly.

The same methods which lead to the simplification of the summation in Eq. (3.14), namely the use of the Poisson sum rule and retention of only the first harmonic terms, when applied to Eq. (3.16) yield

$$\zeta_{z_j}(x) = \frac{a\sqrt{\alpha}}{\sqrt{\pi}} \frac{e^{-\alpha(x-ja)^2}}{1 + 2e^{-\pi^2/\alpha a^2} \cos \frac{2\pi x}{a}}$$

Introduction of this form into the expression for $W(x)$ followed by application of the above summation convention then permits one to write, after some algebra,

$$W(x) = \frac{a\sqrt{\alpha}}{2\sqrt{2\pi}} \Delta k_z^2 \langle q_z^2 \rangle \frac{1 + 2e^{-\pi^2/2\alpha a^2} \cos \frac{2\pi x}{a}}{(1 + 2e^{-\pi^2/\alpha a^2} \cos \frac{2\pi x}{a})^2} \quad (3.17)$$

Once these last two equations have been obtained, one may construct the one-phonon scattering intensity, I_1 , within the context of the preceding approximations, remembering that for this model the sums over phonon modes have been reduced to sums over individual surface atoms. Inasmuch as that calculation is not particularly instructive, the details are omitted here and only the result is indicated:

$$I_1 = \frac{N}{2} a^2 \Delta k_z^2 \langle q_z^2 \rangle \{ [\delta(\Delta E - \hbar\omega_z) + \delta(\Delta E + \hbar\omega_z)] - \frac{\hbar\omega_z \beta}{4} [\delta(\Delta E - \hbar\omega_z) - \delta(\Delta E + \hbar\omega_z)] \} \sum_{\ell} e^{-\frac{2\pi^2}{\alpha a^2} (\ell - \frac{\Delta k_x a}{2\pi})^2} (|K_{\ell}^{(1)}|^2 + |K_{\ell}^{(2)}|^2 + |K_{\ell}^{(3)}|^2)$$

$$K_{\ell}^{(1)} = \frac{1}{a} \int_0^a dx F(x)$$

$$K_{\ell}^{(2)} = \frac{2}{a} \int_0^a dx F(x) e^{-\pi^2/2\alpha a^2} \cos \frac{\pi x}{a}$$

$$K_{\ell}^{(3)} = \frac{2}{a} \int_0^a dx F(x) e^{-\pi^2/2\alpha a^2} \sin \frac{\pi x}{a}$$

$$F(x) = e^{-\frac{2\pi i \ell}{a} x} e^{-i\Delta k_z Z(x)} e^{-W(x)} [1 + 2e^{-\pi^2/\alpha a^2} \cos \frac{2\pi x}{a}]^{-1} \quad (3.18)$$

The integrals appearing above as well as the one which appears in the expression for I_0 may all be evaluated as indicated in Appendix B after inserting the forms for $Z(x)$ and $W(x)$ given by Eqs. (3.15) and (3.17). Doing so, the final result for the elastic and one-phonon intensity

contributions through order μ^2 is

$$\begin{aligned}
 I_{\Delta E, \vec{k}_f \leftarrow \vec{k}_i} &= N \delta(\Delta E) a^2 e^{-2\bar{W}} \sum_{\ell} \delta\left(\ell - \frac{\Delta k_x a}{2\pi}\right) J_{\ell}(\lambda)^2 \\
 &+ N \left\{ \frac{1}{2} [\delta(\Delta E - \hbar\omega_z) + \delta(\Delta E + \hbar\omega_z)] - \frac{\hbar\omega_z \beta}{8} [\delta(\Delta E - \hbar\omega_z) \right. \\
 &- \delta(\Delta E + \hbar\omega_z)] \left. \right\} a^2 \Delta k_z^2 \langle q_z^2 \rangle e^{-2\bar{W}} \sum_{\ell} e^{-\frac{2\pi^2}{\alpha a^2} \left(\ell - \frac{\Delta k_x a}{2\pi}\right)^2} \\
 &\cdot [J_{\ell}(\lambda)^2 + 4\mu^2 (J'_{\ell}(\lambda))^2 + |S_{\ell}|^2 + |C_{\ell}|^2] \quad , \quad (3.19)
 \end{aligned}$$

where $\mu = e^{-\pi^2/2\alpha a^2}$ (assumed to be small),

$$\lambda = \Delta k_z h a \quad ,$$

$$\bar{W} = \frac{a\sqrt{\alpha}}{4\pi} \Delta k_z^2 \langle q_z^2 \rangle \quad , \quad (3.20)$$

$J_{\ell}(\lambda)$ = Bessel function of order ℓ ,

$$J'_{\ell}(\lambda) = \frac{d}{d\lambda} J_{\ell}(\lambda) \quad ,$$

and the integrals S_{ℓ} and C_{ℓ} are given by the following series:

$$S_{\ell} = \sum_{n=0}^{\infty} \frac{(i\lambda)^n}{2^n n! \pi} \sum_{m=0}^n \binom{n}{m} \left[-\frac{(-1)^{\ell-n+2m}}{2} \right] \left[\frac{1}{\ell-n+2m+\frac{1}{2}} + \frac{1}{\ell-n+2m-\frac{1}{2}} \right]$$

$$C_{\ell} = \sum_{n=0}^{\infty} \frac{(i\lambda)^n}{2^n n! \pi} \sum_{m=0}^n \binom{n}{m} \frac{(-1)^{\ell-n+2m}}{2} \left[\frac{1}{\ell-n+2m+\frac{1}{2}} - \frac{1}{\ell-n+2m-\frac{1}{2}} \right] \quad ,$$

$\binom{n}{m}$ being the conventional binomial coefficient.

D. Discussion

The final equations of Section C provide an analytic form for the scattering intensity pattern which is produced by the assumed pairwise repulsive potential, Eq. (3.12), through first order in the inelastic phonon effects. Clearly, the basic structure is dominated by the elastic diffraction term, producing delta-function peaks whenever Δk_x is equal to a reciprocal lattice vector, although the intensities of these peaks are attenuated by a Debye-Waller factor. This primary structure is then augmented by the presence of inelastic lobes on either side of each diffraction peak. (Of course, the actual peak profile may be greatly complicated by the overlap of inelastic lobes with nearby elastic structure.) Any direct broadening of the elastic peaks may only occur within the present model as a result of the influence of "experimental" effects such as a finite distribution of incident particle velocities; broadened inelastic peaks, on the other hand, must always be anticipated due to the fact that for a one-phonon energy transfer process the allowed values of Δk_x are determined via a gaussian distribution centered about the diffraction condition rather than by a delta function criterion. One should recognize, however, that if the phonon frequencies are sufficiently low, the predicted peak shape would more closely resemble a sharp spike with broad inelastic "wings" near the base. But even in this limiting case the observed width of any diffraction peak should be expected to correspond roughly to the width of the incident beam velocity distribution.

An additional feature of the inelastic peak structure indicated by Eqs. (3.18) is that there exists in general an intensity asymmetry between

the phonon annihilation lobe, i.e., the peak shifted toward the surface normal, and the corresponding phonon creation lobe. The asymmetry of course vanishes if $\beta \rightarrow 0$, namely for the completely classical case, but should be observable if quantum effects are important. Note that for large β it is the phonon creation peak ($\Delta E = -\hbar\omega_z$) which becomes the dominant contribution. Such a result is to be expected on physical grounds; if the surface is very cold then energy transfer from the gas to the surface should logically be more likely than the reverse process in which the surface gives up energy to the impinging atom simply because there are relatively few excited phonon modes available from which energy can be released. At higher surface temperatures, however, one would expect that phonon annihilation and creation will contribute more or less equally. Thus, the results obtained herein do conform with intuition about the relative importance of the two inelastic components.

A comparison with experimental results by Williams⁴¹ reveals that the present model does indeed qualitatively describe the observed intensity pattern. As previously suggested it would be necessary to "correct" the theoretical model by the introduction of an initial beam velocity distribution and by the appropriate averaging consistent with a finite detector width in order to be able to make a quantitative comparison. (However, since these averaging techniques will reveal no new structure but rather will tend to wash out existing effects, such procedures shall not be applied in this investigation.) But just on the basis of an overall evaluation, it seems likely that the agreement with experiment is sufficiently good so as to lead one to conclude that the proposed formalism is successful in incorporating the fundamental phenomenology into the analysis of the problem.

Inasmuch as there does seem to be fairly good general agreement between the model and experiment, one is obliged to ask why the modified Einstein description of the solid, a description which is usually viewed as being only a crude approximation,⁴² appears to be quite adequate. An obvious conclusion to be drawn is that actually only a narrow range of phonon mode frequencies contributes significantly to the scattering, and thus the Einstein model would be expected to yield essentially the same result as could be obtained with the inclusion of a more accurate phonon distribution. More important, however, is the observation that the present two-frequency phonon model of a solid having a periodic surface structure appears to compare very favorably with the more customarily postulated solid picture, i.e., a Debye solid, the surface of which is taken to be flat. Certainly in the limit in which both of these models do yield effectively identical phonon structures, the ability to describe both diffraction and inelastic transitions within a single unified formalism is indeed a definite advantage.

Perhaps, however, there may be a more fundamental reason that the Einstein model seems to be adequate here. A recent paper by Garrison and Adelman²⁹ describes a classical treatment of inelastic energy transfer during a gas-surface collision via the generalized Langevin theory.³⁰ In connection with that study, a comparison was made of the results obtained by using the full Langevin dynamics with those derived from certain simple solid models, one of which being an Einstein model. Consideration of that model has lead Garrison and Adelman to conclude that the nature of the solid is such that if the gas collision time is less than some characteristic response time, then the simplified picture of the phonon mode distribution can mimic

the actual physical situation. Of course, for the impulsive collision model hypothesized in this work, the collision time is assumed to be infinitesimal. Hence one is prompted to believe that an Einstein description may constitute a much more reasonable depiction of the surface dynamics than might be initially supposed.

Aside from the consideration of any experimental averaging as mentioned above, there is one more general feature of the gas-surface scattering problem which has been ignored. That feature involves the presence of a long-range attractive part in the actual two-body potential. As suggested by others, since the detailed structure of an appropriate attractive potential apparently has little or no bearing on the scattering pattern in the absence of surface trapping, a simple square-well form for the attraction seems adequate. It is reasonable, however, to ignore the well altogether within the present model by making the assumption that the only consequence of considering such a well is the addition of a momentum increment perpendicular to the surface to an approaching gas atom and the subtraction of the corresponding increment from the scattered atom. Naturally, this quasiclassical assumption leads to a change in the actual incident and scattered angles, but these modified angles may, of course, be simply related to the experimentally observed angles by a geometrical argument.⁴³ Still, inasmuch as the scattering pattern has the same qualitative features with or without a well, the presence of any attractive interaction has been neglected completely.

It is important that a final point concerning the results obtained herein be stressed, namely that the width of the inelastic scattering lobes is, as expected, related to the degree of inelasticity present. This

width, arising as a result of the gaussian distribution of Δk_x values in the I_1 term, may be correlated with the effective Debye-Waller factor, Eq. (3.20), which to order μ^2 is just a multiplicative constant. Specifically, for this particular gaussian distribution the standard deviation may be written as

$$\sigma = \frac{a\sqrt{\alpha}}{2\pi} .$$

Notice then that with this definition one may write the effective Debye-Waller exponent as

$$\bar{W} = \frac{\sigma}{2} \Delta k_z^2 \langle q_z^2 \rangle .$$

Hence for smaller σ , i.e., for a narrower distribution in Δk_x , \bar{W} is also smaller, which implies that $e^{-2\bar{W}}$ is closer to unity--this is indeed the expected concerted behavior for a system which is becoming less inelastic. Furthermore, since σ depends on the potential parameter α , one may conclude that a decrease in α , corresponding to a "loosening" of the potential in the x-direction, would simultaneously cause a reduction in the observed inelastic intensity.

Finally, in conclusion, the qualitative features of the results obtained from the scattering model proposed here are briefly summarized:

(1) the elastic scattering peaks are infinitely sharp if the incident atomic beam is monoenergetic;

(2) the inelastic scattering peaks are broadened even for a monoenergetic beam, with the peak widths being dependent upon the interaction potential parameters and not upon either the surface temperature or the collision energy;

(3) the effective Debye-Waller factor, Eq. (3.20), shows the expected temperature dependence (inasmuch as it is a function of $\langle q_z^2 \rangle$), and appears to first order as just a multiplicative term;

(4) the surface amplitude, h_a , is independent of the collision energy in the static surface limit, although the actual position of the potential turning-point contour is a function of E ;

(5) the effect of the in-plane motion of the surface atom is negligible as compared with the effect due to motion perpendicular to the surface plane;

(6) the symmetry of the one-phonon annihilation and creation lobes does exhibit a temperature dependence, with the two being totally symmetric only in the high temperature limit (the positions of the lobes do not, however, show any such dependence).

Overall, the present work provides a very convenient and instructive model for the gas-surface collision problem. Although in principle the formalism allows one to treat all possible n -phonon inelastic scattering processes, it has been shown that it is possible to obtain a good qualitative agreement with experiment even if one chooses to examine only the one-phonon effect. It is furthermore encouraging that such results are obtainable from a simple one-dimensional surface model, even though it seems reasonable to expect that an extension of the method to the treatment of a two-dimensional lattice could be made with little difficulty. One should also feel that the absence of the commonly used flat-surface assumption provides a definite advantage in that the treatment of a wider range of structured surfaces become feasible.

Appendix A: Summation Over Unit Cells

The coordinate integrals over the interval $[-\infty, \infty]$ may be transformed to integrals over the interval $[0, a]$, where a is the unit cell length, via the identity

$$\int_{-\infty}^{\infty} dx f(x) = \sum_n \int_0^a dx f(x+na)$$

where the integer n numbers the unit cells. For example, by using this formula the elastic contribution to the intensity may be written

$$I_0 = \delta(\Delta E) \left| \sum_n \int_0^a dx e^{-i\Delta k_x(x+na)} e^{-i\Delta k_z Z(x+na)} e^{-W(x+na)} \right|^2. \quad (\text{A.1})$$

But since $Z(x) = Z(x+na)$ by assumption and since presumably $W(x) = W(x+na)$ inasmuch as functions of x only must exhibit the periodicity of the lattice (obviously any model for these functions must bear out this assumption),

Eq. (A.1) becomes

$$\begin{aligned} I_0 &= \delta(\Delta E) \left| \int_0^a dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} e^{-W(x)} \sum_n e^{-i\Delta k_x na} \right|^2 \\ &= \delta(\Delta E) \left| \int_0^a dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} e^{-W(x)} \right|^2 \sum_n \sum_{n'} e^{-i\Delta k_x a(n-n')} \end{aligned}$$

Defining $\bar{n} = \frac{n+n'}{2}$ and $\Delta n = n-n'$ and then resummng (noting that the sum over \bar{n} just gives N , the total number of unit cells within the physical limits of the experiment),

$$I_0 = N\delta(\Delta E) \left| \int_0^a dx e^{-i\Delta k_x x} e^{-i\Delta k_z Z(x)} e^{-W(x)} \right|^2 \sum_{\Delta n} e^{-i\Delta k_x a \Delta n}$$

Then, by using the Poisson sum rule one finally obtains

$$I_0 = N\delta(\Delta E) \sum_{\ell} \delta\left(\ell - \frac{\Delta k a}{2\pi}\right) \left| \int_0^a dx e^{-i\Delta k x} e^{-i\Delta k Z(x)} e^{-W(x)} \right|^2 .$$

Appendix B: Debye-Waller Integrals

From Eq. (3.11a) we need to calculate

$$|S_{\ell}^0|^2 = \left| \frac{1}{a} \int_0^a dx e^{-\frac{2\pi i \ell}{a} x} e^{-i\Delta k_z Z(x)} e^{-W(x)} \right|^2$$

Linearizing the Debye-Waller exponential,

$$\begin{aligned} |S_{\ell}^0|^2 &\cong \left| \frac{1}{a} \int_0^a dx e^{-\frac{2\pi i \ell}{a} x} e^{-i\Delta k_z Z(x)} - \frac{1}{a} \int_0^a dx e^{-\frac{2\pi i \ell}{a} x} e^{-i\Delta k_z Z(x)} W(x) \right|^2 \\ &\cong |S_{\ell(s)}^0 - \Delta S_{\ell}^0|^2 \\ &\cong |S_{\ell(s)}^0 \left(1 - \frac{\Delta S_{\ell}^0}{S_{\ell(s)}^0} \right)|^2 \end{aligned}$$

Then by resumming, with the hope of recovering some of the higher order contributions lost in the linearization, $|S_{\ell}^0|^2$ may be written in terms of $|S_{\ell(s)}^0|^2$, the result for the static surface limit, as

$$|S_{\ell}^0|^2 \cong |S_{\ell(s)}^0|^2 e^{-2 \operatorname{Re} \frac{\Delta S_{\ell}^0}{S_{\ell(s)}^0}} \quad (\text{B.1})$$

Substituting Eqs. (3.15) and (3.17) for $Z(x)$ and $W(x)$,

$$S_{\ell(s)}^0 = \frac{1}{a} e^{-i\Delta k_z Z_0} \int_0^a dx e^{-\frac{2\pi i \ell}{a} x} e^{-i\ell \cos \frac{2\pi x}{a}} = e^{-i\Delta k_z Z_0} e^{-i \frac{\pi}{2} \ell} J_{\ell}(\lambda)$$

and

$$\Delta S_{\ell}^0 = \frac{\sqrt{\alpha}}{4\pi} \Delta k_z^2 \langle q_z^2 \rangle e^{-i\Delta k_z Z_0} \int_0^a dx e^{-\frac{2\pi i \ell}{a} x} e^{-i\lambda \cos \frac{2\pi x}{a}} \frac{1 + 2\mu \cos \frac{2\pi x}{a}}{(1 + 2\mu^2 \cos^2 \frac{2\pi x}{a})^2}$$

Assuming μ to be small (at constant surface amplitude, ha), one then expands the quotient above in a Taylor series and integrates term by term to obtain

$$\Delta S_{\ell}^0 = \bar{w} e^{-i\Delta k_z Z_0} e^{-i \frac{\pi}{2} \ell} [J_{\ell}(\lambda) + i(2\mu - 4\mu^2) J'_{\ell}(\lambda)]$$

to order μ^2 .

Thus, to this order in μ , Eq. (B.1) may be evaluated as

$$|S_{\ell}^0|^2 \approx J_{\ell}(\lambda)^2 e^{-2\bar{w}}$$

This same approximation procedure is then used for the calculation of the integrals in Eq. (3.18), still retaining only the terms through μ^2 . By this method, the integrals S_{ℓ} and C_{ℓ} in Eq. (3.19) are found to be of the form

$$S_{\ell} = \frac{1}{\pi} \int_0^{\pi} d\theta \sin \ell \theta \sin \frac{\theta}{2} e^{i\lambda \cos \theta}$$

$$C_{\ell} = \frac{1}{\pi} \int_0^{\pi} d\theta \cos \ell \theta \cos \frac{\theta}{2} e^{i\lambda \cos \theta}$$

An expansion of the exponential followed by term-by-term integration yields the series solutions given in Section C.

IV. Selective Adsorption on a Solid Surface.

The previous chapter has treated two of the three possible physical events which may occur when a gas atom collides with a solid surface, namely elastic diffraction and inelastic energy transfer. In the present section the remaining phenomenon, the adsorption of the gas atom, shall be considered, with particular attention being given to the identification of those situations for which adsorption is most probable. Of course, interest in the theory of such a process has for many years stimulated considerable activity in this field. Even as early as 1936, Lennard-Jones and Devonshire⁴⁴ coined the term "selective adsorption" to describe the event whereby an atom in an unbound continuum state undergoes a transition into a surface state which is bound in the direction perpendicular to the plane of the surface. Such a transition has more recently been viewed in terms of conventional resonance models^{25,45-50}--it is such a view which shall be adopted here.

An important difference between this study and the bulk of previous work is that herein the emphasis shall be placed not upon the identification of resonance structure in the gas-surface scattering intensity but rather upon the dynamics of the adsorption process. Since the primary goal of this work is the clarification of the physical picture of the adsorption event, one seems likely to benefit from an investigation of the lifetime of the adsorbed state and of the dependence of that lifetime upon the way in which the energy of the state is partitioned between motion parallel and motion perpendicular to the surface plane. Furthermore, inasmuch as one would wish to be able eventually to relate the results of this study to experimental findings, the corrections to the zeroth-order model

arising from a consideration of the inherent dynamic nature of the surface contour also warrant examination. In any case the present research shall be predicated upon the assumptions that the positions of the resonances are already known and that the potential function which gives rise to these observed resonances is sufficiently well characterized.

It must be admitted, however, that selective adsorption is quite difficult to treat in complete generality due to the multitude of processes which can lead to the atom being bound to the surface. An easy way to overcome this difficulty involves the neglect of any scattering into a resonant state via an inelastic event. As a matter of fact, the extent to which elastic coupled-channel calculations have successfully reproduced the general features of the resonance structure has been cited⁵⁰ as being indicative of the presence of only rather minor inelastic contributions to the overall scattering. By making such a restriction, one need therefore only consider transitions from elastically scattered (i.e., diffractive) states into the bound surface energy levels; presumably this limitation will not be severe if the system parameters are such that elastic effects dominate the scattering intensity. In the present work this zeroth order static approximation [recall that the absence of inelastic scattering events is characteristic of a motionless surface contour (see Chapter III, Section C)] shall be used in order to obtain approximate values for the resonance widths. Since, however, there may certainly be a non-negligible inelastic perturbation of these calculated elastic widths, in Section C a correction factor shall be derived which within the impulsive collision model of Chapter III yields the first-order effect of the motion of the surface atoms.

As a means of characterizing the resonant continuum-bound transition (or conversely but equivalently, the decay of the metastable adsorbed state), use shall be made of the particularly convenient "golden rule" formalism described previously by Miller.^{51,52} Inasmuch as this method has already been shown to yield quite reasonable results for other resonance processes such as, for example, atomic⁵² and molecular⁵³ autoionization, one would anticipate that such an approach should at least provide a semi-quantitative picture of the resonance effects expected for the gas-surface scattering model. Indeed, this particular methodology has been employed in a recent paper by Wolfe and Weare,⁴⁹ who were concerned with analyzing the He-Li(001) data obtained by Frankl.⁵⁴ Whereas that work was primarily interested in confirming peak positions and in determining whether intensity minima or maxima are to be observed for a given resonance, here the main goal will be an investigation of surface residence lifetimes. Consequently, the straightforward calculations using the golden rule formula may be seen to provide a distinctly advantageous means of obtaining the desired widths in that they may be performed quite easily and rapidly for a variety of initial parameters.

A. Review of the Theory

Because the expressions yielding resonance energies and widths have been previously reported in considerable detail,^{51,55} only the essential features of the derivation need be indicated here. This derivation, which is based on Feshbach's more general prescription for characterizing scattering resonances, employs the projection operators P and Q , defined such that

$$\lim_{R \rightarrow \infty} Q\Psi = 0$$

$$P = 1 - Q$$

where Ψ is the total wavefunction for the scattering system and R is some general separation coordinate (in the present case $R \rightarrow \infty$ simply means that the incident particle is sufficiently far from the surface that there is effectively no interaction).

One then adopts Miller's⁵¹ particular choice for Q

$$Q = |\phi\rangle\langle\phi| \quad (4.1)$$

where $|\phi\rangle$ is the particular eigenstate, normalized to unity, which describes the metastable resonant state (in this case, the adsorbed atom state) in the absence of an interaction. In short, Q projects out the specific state which is responsible for the observed resonance, while P projects onto all other possible quantum states, namely the continuum states within which the quasibound state is embedded.

Substituting these projection operators, Eq. (4.1), into the formal results given by O'Malley and Geltman,⁵⁵ one may obtain an exact expression for the resonance width (in atomic units)

$$\Gamma_s = 2\pi\rho |\langle\phi|H-E_s|\chi\rangle|^2, \quad (4.2)$$

where the resonance energy E_s is given, save for a presumably negligible shift, by

$$E_s = \langle\phi|H|\phi\rangle \quad (4.3)$$

and furthermore where the continuum function χ is defined via the

eigenequation

$$P(H-E_s)P\chi = 0 \quad (4.4)$$

and is characterized by a density of states ρ . [Note that Eqs. (4.3) and (4.4) explicitly indicate the energy degeneracy of the bound and continuum states.] Eq. (4.2) may be seen to be formally analogous to the conventional "golden rule" from time-dependent perturbation theory;⁵⁷ consequently, one is lead to interpret the matrix element $\langle\phi|H-E_s|\chi\rangle$ as just being a term which expresses the coupling between the bound and continuum states via some interaction. To show this interpretation explicitly, Eq. (4.2) may be rewritten as

$$\begin{aligned} \Gamma_s &= 2\pi\rho|\langle\phi|V^{\text{int}}|\chi\rangle|^2 \\ &= 2\pi\rho|V_{f\leftarrow i}^{\text{int}}|^2 \end{aligned} \quad (4.5)$$

where V^{int} is the interaction potential which produces transitions from the initial to the final states. Hence, if one is able to characterize to a good approximation the bound and continuum states and the interaction, it is then a relatively simple matter to obtain reliable estimates⁵⁸ of the resonance widths with the above formalism.

B. Elastic Gas-Surface Resonances

In this section the general resonance formalism which was outlined in Section A is applied to the specific problem of the adsorption of a gas atom on a rigid solid surface. Actually, however, the process of interest is the desorption of the atom from the surface rather than the reverse

transition. If the resonance width is very large, then the residence time of the atom on the surface is quite short, which implies that desorption occurs almost spontaneously with adsorption. On the other hand, a very narrow resonance shape corresponds to a long-lived metastable adsorbed state. One should note, of course, that there is no absolute definition of "long" or "short" times, but roughly one may say that if the metastable state does not survive longer than a time equal to the vibrational period of the gas-surface bound species, then for all practical purposes no adsorption has occurred. Conversely, if the predicted residence time does exceed this characteristic vibrational period, and in particular if the state lifetime is an order of magnitude or so in excess of the period of oscillation, one may confidently expect that surface adsorption will produce a significant effect on the overall scattering behavior at certain energies.

1. Potential Energy

Prior to construction of the expressions for the initial and final quantum states, it is necessary to examine the potential function which describes both the surface potential energy in the absence of colliding gas atoms and the gas-surface interaction [the gas atom is assumed to move as a free particle when outside the effective range of the surface potential]. A particularly convenient choice, albeit not necessarily the most accurate one,⁵⁴ for the total potential is that form which was proposed by Lennard-Jones and Devonshire⁴⁴ and which has been frequently used by other workers,^{46,59} namely

$$\begin{aligned}
 V(x, z) &= V_0(z) + V^{\text{int}}(x, z) \\
 &= D[e^{-2\alpha z} - 2e^{-\alpha z}] - 2\beta D e^{-2\alpha z} \cos \frac{2\pi x}{a} \quad (4.6)
 \end{aligned}$$

(here, as in Chapter III, x and z are respectively the coordinates parallel and perpendicular to the surface plane). In the above equation the parameters D and α are the usual Morse parameters,⁶⁰ β is a measure of the strength of the atom-surface interaction (an adjustable parameter), and a is the surface unit cell dimension. The "non-interacting" part of the total potential, V_0 , is just a conventional Morse oscillator potential and is a function of only the radial coordinate, i.e., the coordinate expressing the atom-surface separation, while the interaction term, V^{int} , is a simple exponential repulsion, the magnitude of which varies periodically along the surface. (Note that again as in the preceding chapter the problem has been reduced to one of scattering from a line of atoms; however, the formalism may be trivially extended to a two-dimensional surface in the event that translations along the two orthogonal surface directions are not coupled.)

Before passing to the consideration of the wavefunctions, one should recognize that Eq. (4.6) defines a potential well which can support bound levels in the z -direction but does not allow for the possibility that the surface contour impedes essentially free-particle motion parallel to the surface. However, for a surface which is not "too rough", it is likely that this omission will not be significant. For the canonical example of helium impinging on the (001) plane of lithium fluoride, the prototype system described in the calculations of Section D, there appears to be no reason for suggesting that such free motion is not appropriate. One might certainly envision, though, a system for which diffusive motion parallel to the surface could represent a superior characterization and hence for which the Lennard-Jones and Devonshire potential form would be seriously deficient.

2. Wavefunctions

Since the unperturbed (i.e., non-interacting) part of V is a Morse potential, one is led to the selection of a bound Morse wavefunction as a description of the z -component of the initial metastable quantum state, $\phi(x,z)$, of the adsorbed species. Such a description in fact represents the only reasonable choice inasmuch as the experimentally determined potential parameters appearing in Eq. (4.6) are actually obtained by fitting the observed resonance energies to the potential form. Thus, within the ability of a Morse potential function to model the true surface potential, this wavefunction will exactly mimic the behavior of the metastable state in the z -direction.

One then completes the construction of the adsorbed state wavefunction by assuming that the composite function is merely a product of x and z component terms. Since the x -component may, as indicated above, be described by a plane wave factor which exhibits the periodicity of the lattice, the total wavefunction may be written as

$$\phi_{n,m}(x,z) = A_m e^{i(k_x + \frac{2\pi n}{a})x} \psi_m^{\text{Morse}}(z) \quad , \quad (4.7)$$

where n and m are quantum numbers which take on only integral values, $\psi_m^{\text{Morse}}(z)$ is the bound-state Morse eigenfunction⁶⁰ described above, k_x is the projection of the momentum vector of the gas atom onto the surface plane, and A_m is an appropriate normalization factor (the determination of which is presented in the Appendix at the end of this chapter).

The generation of the continuum final state $\chi(x,z)$ proceeds along similar lines. Again, motion in the x -direction is described by a plane wave factor [note that the lattice periodicity restricts changes in the

momentum parallel to the surface as a result of the bound-continuum transition to a reciprocal lattice vector]. However, now the "radial" function in the z-direction must be such that the correct scattering boundary conditions are satisfied for large atom-surface separations. i.e., the z-component of $\chi(x,z)$ must asymptotically ($z \rightarrow \infty$) go as $\sin(k_z z + \eta_\epsilon)$, where k_z is the projection of the momentum vector perpendicular to the surface and η_ϵ is a phase shift which is dependent, in general, upon the energy. Obviously, the usual bound Morse oscillator eigenfunctions cannot satisfy this normalization criterion; still, it is possible to generate the corresponding continuum functions via only a simple modification of the bound-state functions. Recognizing that the solution of the Schrödinger equation for the Morse oscillator involves the solution of a confluent hypergeometric differential equation, one can easily show that by choosing the independent solution denoted by U (which is related to the generalized hypergeometric function ${}_2F_0$, see Reference 61 for details on notation) rather than the M-function (which is also written ${}_1F_1$), the resulting function does indeed have the requisite asymptotic form. Thus, the total continuum wavefunction may be expressed as

$$\chi_{n',v}(x,z) = B_{v(\epsilon)} e^{i(k_x x + \frac{2\pi n'}{a} z)} \psi_{v(\epsilon)}^{\text{Morse}}(z), \quad (4.8)$$

where n' is some integer, $v(\epsilon)$ is an energy-dependent complex quantity which plays the same role as does the quantum number for a bound system, and $\psi_{v(\epsilon)}^{\text{Morse}}(z)$ is the continuum Morse function. The normalization constant $B_{v(\epsilon)}$ may be determined by matching $\chi_{n',v}(x,z)$ to the boundary conditions, the details of that matching being given in the Appendix.

3. Construction of the Widths

One now substitutes Eq. (4.6), (4.7), and (4.8) into (4.5) and in doing so obtains the expression to be solved for the widths. [Nothing has been said as yet about the density of final continuum states, but it is not too difficult to show that for the radial asymptotic form indicated above, $\rho = 2\mu/\pi k_z$ in atomic units (here μ is the atom mass).] However, before continuing on to the actual solution, one should note the similarity between the formalism thusfar described and that which was proposed by Strachan⁶² many years ago. That early work also involved the calculation of bound-continuum interaction matrix elements, but there do exist definite differences between the two approaches. Specifically, Strachan's treatment did not include a consideration of the effects on desorption arising as a consequence of lattice periodicity. As shall be seen below, such periodicity imposes additional constraints on the energy redistribution which accompanies the transition to an unbound state. Neglect of the nature of the surface contour thus constitutes a rather severe limitation on the accuracy of the overall method.

Inasmuch as the actual calculation of the widths is straightforward, only the important features of the method used herein shall be indicated. First, the expression for the matrix element appearing in Eq. (4.5) may be written explicitly as

$$V_{n', \nu(\epsilon) \leftarrow 0, m}^{\text{int}} = -2\beta D A_m^* B_{\nu(\epsilon)} \int dz \int dx e^{-ik_x x} e^{i(k_x + \frac{2\pi n'}{a})x} \cdot \psi_m^{\text{Morse}*}(z) \psi_{\nu(\epsilon)}^{\text{Morse}}(z) e^{-2\alpha z} \cos \frac{2\pi x}{a}, \quad (4.9)$$

where the quantum number n has been set to zero (only a single bound

level is considered). The x-integral is then easily done analytically by transforming the integral $(-\infty, \infty)$ to a sum of integrals over unit cells of length a, with the result being

$$\int dx e^{2\pi i n' x/a} \cos \frac{2\pi x}{a} = M \frac{a}{2} \delta_{n', -1} \quad (4.10)$$

where M is the number of unit cells within the experimentally defined region of interest. Note that the lattice periodicity has linked desorption to a first-order diffractive scattering event. [The formal solution of the integral in Eq. (4.10) also permits the transition whereby $n' = +1$, however it is clear that such a process does not conserve total energy.]

In the remaining z-integral it is convenient to make the change of variables defined by the equation

$$\xi = \frac{2\sqrt{2\mu D}}{\alpha} e^{-\alpha z} \quad .$$

Thus one finds that Eq. (4.9) may be reduced to

$$v_{-1, v(\epsilon)+0, m}^{\text{int}} = -\frac{\alpha \beta a M}{8\mu} A_m^* B_{v(\epsilon)} \int_0^\infty d\xi \xi \psi_m^{*\text{Morse}}(\xi) \psi_{v(\epsilon)}^{\text{Morse}}(\xi) \quad ,$$

this integral being easily calculated via Gaussian quadrature.

4. Energy Conservation

In order that there be no net energy loss or gain accompanying desorption, one finds that at resonance

$$k_z^2 + \left(k_x - \frac{2\pi}{a}\right)^2 = 2\mu\epsilon_m + k_x^2 = E \quad , \quad (4.11)$$

($h = 1$) where the momentum vectors are those for the unbound atom, ϵ_m is the energy of the m^{th} bound surface state, and the transition is such that $n' = -1$ (see above). Rearranging and solving the quadratic equation, one obtains equivalently

$$k_z = [2\mu\epsilon_m + 2k_x \left(\frac{2\pi}{a}\right) - \left(\frac{2\pi}{a}\right)^2]^{1/2} .$$

Furthermore, if one defines the angle from the surface normal to \vec{k} to be θ , then

$$\theta = \sin^{-1} \left[\sqrt{1 - \frac{2\mu\epsilon_m}{k^2} - \frac{2\pi}{ka}} \right] , \quad (4.12)$$

$k = |\vec{k}|$. These last two expressions make clearer the fact that there are infinitely many ways in which the resonance condition, Eq. (4.11), may be satisfied. Physically these different resonant states correspond to having varying amounts of energy placed into the motion in the x-direction. Since each of these situations corresponds to a unique energy configuration, each should also be characterized by a particular resonance width and hence a particular lifetime. Thus the calculations described in Section D are performed for a wide range of initial conditions.

From Eq. (4.11) one may also determine energy "cutoff" values below which desorption cannot occur. In such cases the total energy of the system is such that when the bound-continuum transition is made, the energy appearing as motion perpendicular to the surface is less than zero and consequently the atom cannot escape. These cutoffs are obtained by setting k_z to zero in the resonance condition and solving for the total energy in terms of the bound state energy, with the result being (in a.u.)

$$E_m^{\text{cutoff}} = \frac{1}{8\mu} \left[\left(\frac{2\pi}{a} \right)^2 + \frac{a}{2\pi} (2\mu\epsilon_m) \right]^2 . \quad (4.13)$$

No transitions are possible for a system in the m^{th} bound level with a total energy less than E_m^{cutoff} unless by chance a higher bound level exists (say, m') which exactly differs in energy from the m^{th} level by

$$|\epsilon_m - \epsilon_{m'}| = \Delta\epsilon = \frac{1}{2\mu} \left[\left(\frac{2\pi}{a} \right)^2 - 2 \left(\frac{2\pi}{a} \right) \sqrt{2\mu(E - \epsilon_m)} \right] .$$

Since in general such specific level spacings are very unlikely to be encountered, any desorption from these low energy states must proceed via an inelastic mechanism which cannot be treated within the present model.

C. Inclusion of Inelastic Effects

The inherent difficulty faced when one attempts to incorporate atom-surface energy transfer processes into the static-surface framework thus far proposed arises as a result of the sheer size of the problem. For example, the longer a particle is bound to the surface, the more likely it is that collisions with phonons will impart enough energy so that desorption may occur. Furthermore, it is also possible that adsorption of energy will kick the atom into a higher (but still bound) energy level, which may then decay either via the "elastic" transition of Section B or by some inelastic process. Not only would such a complex situation clearly be cumbersome to handle exactly, but also one could by no means be sure that the customary simplifications, e.g., the one-phonon approximation, have any

relevance to the actual dynamics. Still, it is desirable to obtain in some way a rough estimate of the effect of inelasticity on the predicted static-surface widths. To this end, some of the same methods used in Chapter III for inelastic surface scattering have been applied to the problem at hand in order that a first-order correction to the results of the previous section might be constructed.

It shall be assumed that the resonant state may be characterized by a simple product state, namely

$$|r\rangle = |k_x^r\rangle |k_z^r\rangle |\tilde{n}^r\rangle, \quad ,$$

where $|k_x\rangle$ and $|k_z\rangle$ are respectively the parallel and perpendicular momentum states and $|\tilde{n}\rangle$ is the product of individual solid phonon states (note that in the static-surface limit, $|r\rangle = |k_x^r\rangle |k_z^r\rangle$, which is just Eq. (4.7)). Similarly, the final continuum states may be written as

$$|f\rangle = |k_x^f\rangle |k_z^f\rangle |\tilde{n}^f\rangle, \quad ,$$

the result being that for a particular resonant state $|r\rangle$, the width is just the sum of partial widths

$$\Gamma_r = \sum_{\tilde{n}_f} 2\pi\rho_f |\langle r|V^{\text{int}}|f\rangle|^2, \quad (4.14)$$

each partial width corresponding to decay into a particular distribution of phonon modes. However, since the mode distribution $|\tilde{n}^r\rangle$ cannot be experimentally identified, a more useful quantity is an average width defined as follows:

$$\begin{aligned}\bar{\Gamma} &= \sum_{\substack{\tilde{n}_r \\ \tilde{r}}} \rho_{\tilde{n}_r} \Gamma_r \\ &= 2\pi \sum_{\substack{\tilde{n}_r \\ \tilde{r}}} \sum_{\substack{\tilde{n}_f \\ \tilde{f}}} \rho_{\tilde{n}_r} \rho_{\tilde{n}_f} |V_{r,f}^{\text{int}}|^2, \quad (4.15)\end{aligned}$$

where here a sum is performed over the various resonant phonon states and is weighted by some normalized mode distribution function $\rho_{\tilde{n}_r}$.

Of course, the interaction potential appearing in Eqs. (4.14) and (4.15) is no longer that given by Eq. (4.6), but rather is properly a generalization of the static interaction to the case of a moving surface contour. In determining that generalized potential, one is guided by the repulsive model proposed in Section C of the preceding chapter. Specifically, by subtracting from Eq. (3.12) the overall radial repulsion and by using the surface displacement coordinates defined by Eq. (3.13) (that is to say, by adopting the modified Einstein model for the surface), one finds that

$$\begin{aligned}v^{\text{int}} &= v_0 \sum_j e^{-\gamma(z-q_j^z)} e^{-\lambda(x-ja-q_j^x)^2} - v_0 \sigma \sum_j e^{-\gamma(z-q_j^z)} \\ &= v_0 \sum_j e^{-\gamma(z-q_j^z)} (e^{-\lambda(x-ja-q_j^x)^2} - \sigma), \quad (4.16)\end{aligned}$$

where γ , λ and σ are parameters which must be fit to the particular surface of interest.

It is possible, though, to describe γ and σ in terms of the "known" parameters of Section B. Consider the static limit of Eq. (4.16),

$$\begin{aligned}
 v_{q=0}^{\text{int}} &= v_0 \sum_j e^{-\gamma z} (e^{-\lambda(x-ja)^2} - \sigma) \\
 &= e^{-\gamma z} v_0 \left(\sum_j e^{-\lambda(x-ja)^2} - \sigma M \right) ,
 \end{aligned}$$

there being M terms in the summation over the unit cells within the experimentally defined region of interest. Then by using the Poisson sum rule and keeping only the first harmonic terms (again, see the manipulations appearing in Chapter III, Section C),

$$v_{q=0}^{\text{int}} \cong e^{-\gamma z} v_0 \left[\frac{\sqrt{\pi}}{a\sqrt{\lambda}} \left(1 + 2e^{-\pi^2/\lambda a^2} \cos \frac{2\pi x}{a} \right) - \sigma M \right] ,$$

which is transformed into the canonical Lennard-Jones and Devonshire form⁴⁴ (see Eq. (4.6)) with the identifications

$$\begin{aligned}
 \sigma &= \frac{\sqrt{\pi}}{Ma\sqrt{\lambda}} \\
 v_0 &= -\frac{a\sqrt{\lambda}}{\sqrt{\pi}} \beta D e^{\pi^2/\lambda a^2} \\
 \gamma &= 2\alpha .
 \end{aligned} \tag{4.17}$$

Therefore, the present work adopts the mode-dependent interaction potential which is found by substituting Eqs. (4.17) into (4.16), namely

$$v^{\text{int}} = \beta D e^{\pi^2/\lambda a^2} \sum_j e^{-2\alpha(z-q_j^z)} \left(\frac{1}{M} - \frac{a\sqrt{\lambda}}{\sqrt{\pi}} e^{-\lambda(x-ja-q_j^x)^2} \right) .$$

(Note that the parameter λ is as yet undetermined; but because further manipulations will reveal that λ does not enter into the lowest-order correction term, one need not worry about its evaluation.)

It is now possible to construct the dynamical analogue of the matrix element of Eq. (4.9) using the above potential,

$$V_{r,f}^{int} = A_m^* B_{v(\epsilon)} \beta D e^{\pi^2/\lambda a^2} \int dz \int dx \int dq e^{2\pi i n' x/a} \psi_m^{*Morse}(z) \psi_{v(\epsilon)}^{Morse}(z) \\ \cdot \phi_{n_r}^*(q) \phi_{n_f}(q) e^{-2\alpha z} \sum_j e^{2\alpha q_j^z} \left(\frac{1}{M} - \frac{\epsilon \sqrt{\lambda}}{\sqrt{\pi}} e^{-\lambda(x-j a - q_j^x)^2} \right),$$

where $\phi_{\underline{n}}(q) = \langle q | \underline{n} \rangle$. The x -integral may be done analytically (the details shall not be given here), thereby permitting simplification of the matrix element to

$$V_{r,f}^{int} = A_m^* B_{v(\epsilon)} \beta D e^{\pi^2/\lambda a^2} a \int dq \phi_{n_r}^*(q) \phi_{n_f}(q) \int dz e^{-2\alpha z} \psi_m^{*Morse}(z) \\ \cdot \psi_{v(\epsilon)}^{Morse}(z) \sum_j e^{2\alpha q_j^z} (\delta_{n',0} - e^{-\pi^2 n'^2/\lambda a^2} e^{2\pi i n' q_j^x/a}).$$

Now, if $n' = 0$ one sees immediately that $V_{r,f}^{int}$ vanishes. Thus, even for the non-static surface, the desorption process must be accompanied by diffraction. One therefore may write the non-vanishing contribution as

$$V_{r,f}^{int} = - A_m^* B_{v(\epsilon)} \beta D e^{\pi^2(1-n'^2)/\lambda a^2} a \int dq \phi_{n_r}^*(q) \phi_{n_f}(q) \sum_j e^{2\alpha q_j^z} \\ \cdot e^{2\pi i n' q_j^x/a} \int dz e^{-2\alpha z} \psi_m^{*Morse}(z) \psi_{v(\epsilon)}^{Morse}(z) \\ = e^{\pi^2(1-n'^2)/\lambda a^2} V_{n',v(\epsilon)+0,m} \cdot \frac{1}{M} \int dq \phi_{n_r}^*(q) \phi_{n_f}(q) \sum_j e^{2\alpha q_j^z} \\ \cdot e^{2\pi i n' q_j^x/a},$$

where $V_{n', \nu(\epsilon)+0, m}$ is a static-surface matrix element as defined in Section B. At this point, n' will be taken to have the value -1 inasmuch as the primary goal of this work is to obtain a correction for the static results. Also, it is useful to examine more closely the remaining summation over j . First, recognize that by assumption $q_j^x/a \ll 1$ (i.e., the surface distortions are small compared with a unit cell dimension). Therefore, one may to a very good approximation linearize the second exponential and obtain

$$e^{-2\pi i q_j^x/a} \cong 1 - 2\pi i \frac{q_j^x}{a}$$

In fact, it is not unreasonable to drop the imaginary term altogether since when the square modulus of the matrix element is taken that term will contribute only to order $(q_j^x/a)^2$. Hence,

$$\begin{aligned} \sum_j e^{2\alpha q_j^z} e^{-2\pi i q_j^x/a} &+ \sum_j e^{2\alpha q_j^z} \\ &= \sum_j (1 + 2\alpha q_j^z + 2\alpha^2 q_j^z{}^2 + \dots) \\ &= M + 0 + 2\alpha^2 M \langle q_z^2 \rangle + \dots \\ &= M (1 + 2\alpha^2 \langle q_z^2 \rangle) \end{aligned}$$

through first order in $\langle q_z^2 \rangle$ (note that $\langle q_z \rangle = 0$ for harmonic displacements).

The above simplifications lead to a particularly simple form for the matrix element, specifically

$$V_{r, f(n'=-1)}^{\text{int}} = V_{-1, \nu(\epsilon)+0, m} (1 + 2\alpha^2 \langle q_z^2 \rangle) \langle n_r | n_f \rangle$$

With this expression one is finally in a position to calculate an average resonance width as given by Eq. (4.15).

$$\begin{aligned}
 \bar{\Gamma} &= 2\pi \sum_{\vec{n}_f} \sum_{\vec{n}_r} p_{\vec{n}_r} \rho_f |V_{-1, \nu(\epsilon)+0, m}|^2 (1 + 2\alpha^2 \langle q_z^2 \rangle)^2 |\langle \vec{n}_r | \vec{n}_f \rangle|^2 \\
 &= 2\pi \rho_f |V_{-1, \nu(\epsilon)+0, m}|^2 (1 + 2\alpha^2 \langle q_z^2 \rangle)^2 \sum_{\vec{n}_r} p_{\vec{n}_r} \langle \vec{n}_r | \vec{n}_r \rangle \\
 &= 2\pi \rho_f |V_{-1, \nu(\epsilon)+0, m}|^2 (1 + 2\alpha^2 \langle q_z^2 \rangle)^2 \\
 &= \Gamma_s (1 + 2\alpha^2 \langle q_z^2 \rangle)^2 \tag{4.18}
 \end{aligned}$$

(here Γ_s is the static-surface width). So, within the present model it is possible to obtain an extremely simple modification of the computed static widths which affords some first estimate of the effect of inelasticity on the gas-surface resonance process.

D. Results and Observations

Calculations have been performed using parameters corresponding to the prototype He-LiF(001) system as given by Goodman.⁶³ Both widths and lifetimes were obtained (the lifetime in atomic units being just the reciprocal of the width) for each of the three bound Morse states at a range of total energies extending from just above the energy cutoff to 30 meV. Some of these results, along with the corresponding angles given by Eq. (4.12), are displayed in Table 5. Also listed there are values of a lifetime factor, T_r , which is defined via the expression

$$T_r = \log \frac{\tau}{\tau^0} \quad (4.19)$$

where τ is the calculated lifetime and τ^0 is the period of oscillation for a particle in the Morse potential. Thus, for example, a value of $T_r = 2$ represents an adsorbed atom remaining on the surface for 100 vibrations. In Figure 4 curves showing the variations in T_r with total energy (and hence with the amount of energy parallel to the surface) are plotted in order that one might get a better feeling for how the energy partitioning affects the adsorption lifetime. [The displayed results are for the case $\beta = 0.1$. If, say, one takes $\beta = 0.04$, then the calculated T_r -values are increased uniformly by roughly 0.8, i.e., the lifetime is lengthened by nearly an order of magnitude.]

Two obvious trends may be seen in the curves of Figure 4. First, at a given total energy, the lower the bound energy level from which desorption occurs, the longer the lifetime of the adsorbed metastable state. Such a result is, of course, to be expected--when a state which is just barely bound undergoes a diffractive transition to an energetically degenerate continuum state, the continuum level which is produced has more translational energy in the z-direction than would be found in an unbound state derived from a transition from a deeply bound level. This extra velocity of the departing atom perpendicular to the surface decreases the time spent by the particle in the vicinity of the surface and thereby leads to the smaller calculated lifetime values.

The second general trend which is discernible is that the lifetimes increase with increasing translational energy parallel to the surface. Note here the particular limit in which the total energy of the adsorbed atom is allowed to become very large. If the resonance condition, Eq. (4.11),

is still to be satisfied, one finds from Eq. (4.12) that the angle at which the desorbed atom leaves the surface must approach 90° . But clearly such a limiting case corresponds to motion only along the surface and not away from it and therefore to a lifetime which approaches infinity. On the other hand, if the total energy is such that the transition to the continuum leaves very little energy in the x-direction, the atom departs quickly from the surface interaction region, and consequently the lifetime of the metastable state appears short. The monotonic increase in T_p with total energy which is seen in Figure 4 bears out this expected behavior. [For total energies less than the cutoff values, which are displayed in Table 6, the lifetimes are again infinite inasmuch as there is insufficient energy to excite the bound atom to the continuum; however, the present analysis breaks down for such a case since a desorptive transition is not possible.] Physically, then, one expects a very sharp onset of desorption at the cutoff energy, with the shortest lifetimes (and hence the largest widths) being obtained for total energies just slightly greater than the cutoff.

Having thus obtained a description of the basic phenomenology, one needs to see whether or not the first order inelastic correction to the static widths which was derived in Section C significantly alters the quantitative results calculated above. A useful estimate of the inelastic effect may be constructed by considering various values of the root-mean-square displacement of a surface atom, those values being expressed as percentages of a unit cell dimension. Table 7 lists representative values of the width correction factor for a variety of r.m.s. displacements. One can easily conclude from those computed factors that inelasticity has a strong effect on the adsorption lifetimes even within the low order of

approximation considered herein. For example, the lifetime of the metastable level is nearly cut in half if the r.m.s. surface displacements are equal to ten percent of a cell length, i.e., about 0.3 \AA . One caveat, of course, that even though such an inelastic mechanism predicts that the widths may be made arbitrarily large by simply increasing the surface temperature (and hence the r.m.s. displacements), this limitless increase in the resonance widths does not correspond to a physically realizable objective since melting of the solid must surely occur at some point. Nevertheless, inelasticity can make a non-negligible contribution to the widths at temperatures below the melting point.

Before going further, one should recognize that any inferences drawn from the aforementioned formalism must be qualified somewhat due to the fact that certain very real effects have been omitted entirely. One of these omissions concerns the means by which the interaction of the adsorbed state with solid phonons has been introduced into the theory. The present work accounts for the distortions of the surface resulting from random thermal vibrations but gives no direct prescription for the inclusion of purely inelastic transitions. Certainly the longer the atom remains in the proximity of the surface, the more likely it is that phonon annihilation (or creation) will excite (or de-excite) the atom into another bound state or into the continuum. Although beyond the scope of the present work, the consideration of a more detailed energy transfer mechanism is probably necessary if one is to derive reliable information about long-term adsorption effects.

The second caveat is in regard to the transferability of any conclusions obtained herein to the adsorption of an arbitrary species

on a crystal face. In particular, one must realize that the above treatment has concerned only physical adsorption--no mention has been made of the potentially more interesting and certainly more complicated contribution of chemisorption. If some sort of chemical interaction, however weak it might be, is possible for the particular system of interest, then that interaction could be expected to lengthen dramatically the residence times. However, it may also be true that the analysis pursued here will be of some utility even in this more complicated situation if the chemical forces are of shorter range than is the attractive part of the gas-surface potential and the number of binding sites is small. Under that circumstance the initial interaction may result in a bound state being formed which may be treated via the proposed model, with the adsorbed species undergoing free translation along the crystal face, until at some point a chemisorption site is encountered. There the present analysis breaks down, of course, but note that prior to some average time for the attainment of the chemically bound state, one may still employ the formalism of Section A. Nonetheless, any long-time physical adsorption results must be viewed somewhat sceptically if the system being studied affords the possibility of chemical binding to the solid.

At this juncture one would like to be able to compare the calculated resonance widths with experimentally measured ones, but unfortunately such a comparison is not in general possible. The obvious reason for this difficulty is to be seen in the results presented in Table 5; in short, the widths are so very narrow that they are experimentally unresolvable. An experimental study by Meyers and Frankl⁵⁴ of the He-LiF(001) system indeed indicates that any lifetime broadening of the observed resonance peak

structure is completely negligible as compared with the unavoidable helium beam widths. The computations performed here suggest that if resolvable widths are to be obtained at all, then they would be seen at conditions under which not only are the total energies just above the energy cutoff values but also surface temperatures are sufficiently high that appreciable inelastic broadening of the widths would be anticipated. Certainly such exacting conditions are at best very difficult to produce.

Prior to concluding, it is useful to note in more detail the structure of the inelastic correction factor which was constructed in the previous section. For example, by using the definition of the space-independent phenomenological Debye-Waller factor,⁶⁴

$$W = \frac{1}{2} \Delta k_z^2 \langle q_z^2 \rangle$$

(note that this W differs from the "effective" Debye-Waller factor defined in Eq. (3.20) by a multiplicative constant, $a\sqrt{\alpha}/2\pi$), Eq. (4.18) may be written as

$$\bar{\Gamma} = \Gamma_s \left(1 + \frac{4\alpha^2 W}{\Delta k_z^2} \right)^2, \quad (4.20)$$

where here Δk_z is the change in the perpendicular component of the momentum vector [there are conflicting opinions in the literature as to how Δk_z should be defined--see Reference 64 for a discussion of this controversy]. Presumably, if one were able to create the specific conditions required in order that a width might be experimentally measured, then by taking data at various surface temperatures it would be possible for someone to calculate Debye-Waller factors to reasonable accuracy (in principle such

a procedure would yield more accuracy than the conventional intensity comparison methods). It is also interesting to note that the truncated series in Eq. (4.20) may be approximately resummed (the same trick used in Appendix B of Chapter III) to give

$$\bar{\Gamma} \approx \Gamma_g e^{-8\alpha_w^2 / \Delta k^2 z^2}$$

which is of the canonical form, namely the static surface result multiplied by an exponential which involves a Debye-Waller factor.

Overall, the application of the golden rule resonance width formalism to the problem of the adsorption of a gas atom onto a solid surface (or equivalently, the desorption of the atom from the surface) seems to provide a useful method for analyzing the various dynamical features of that process. Even more important is the effect which the normally neglected motion of the surface contour has on the preliminary results obtained from a static surface model. It has been shown that the inclusion of just lowest-order inelastic contributions can easily decrease adsorption lifetimes by 20-50%. Although the present work cannot claim to have considered all possible energy transfer processes, it does strongly suggest that in general such mechanisms should not be ignored.

Appendix: Wavelfunction Normalization[†]

A. Free-Particle States

Both the bound and continuum functions exhibit free-particle motion parallel to the surface (the x-direction), i.e., each has a factor of the form

$$u_n(x) = c_x e^{i(k_x + \frac{2\pi n}{a})x},$$

c_x being the normalization constant. Such functions are box-normalized over a unit cell:

$$\begin{aligned} |c_x|^2 \int_0^a dx u_{n'}^*(x) u_n(x) &= |c_x|^2 \sum_m \int_0^a dx u_{n'}^*(x+ma) u_n(x+ma) \\ &= |c_x|^2 \sum_m \int_0^a dx e^{2\pi i(n-n')x/a} e^{2\pi i(n-n')m} \\ &= |c_x|^2 M \int_0^a dx e^{2\pi i(n-n')x/a} \\ &= |c_x|^2 M a \delta_{n,n'}, \end{aligned}$$

where M is the number of unit cells within some experimentally defined region. Thus,

$$c_x = [aM]^{-1/2}$$

B. Bound Morse state

A bound state must, of course, be normalized to unity. Conventional Morse functions⁶⁰ are of the form

$$\psi_m^{\text{Morse}}(z) = c_m e^{-\xi(z)/2} \xi(z)^s F(-m, 2s+1, \xi(z)) ,$$

where

$$\xi \equiv \frac{2\sqrt{2\mu D}}{\alpha} e^{-\alpha z} ,$$

$$s \equiv \frac{\sqrt{-2\mu E}}{\alpha} = \frac{ik}{\alpha} ,$$

F is the appropriate confluent hypergeometric function (denoted M in Reference 61), and c_m is the normalization constant (which is dependent on the quantum number m).

Since when m is a positive integer F is just an m^{th} degree polynomial, it is a simple matter to obtain ψ_m^{Morse} for the first few values of m and to calculate the corresponding c_m 's analytically. For example, if $m = 0$, $F(0, 2s+1, \xi) = 1$; thus

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} dz \psi_m^{*\text{Morse}}(z) \psi_m^{\text{Morse}}(z) \\ &= |c_0|^2 \frac{1}{\alpha} \int_0^{\infty} d\xi e^{-\xi} \xi^{2s-1} \\ &= |c_0|^2 \frac{1}{\alpha} \Gamma(2s) \end{aligned}$$

$$c_0 = \left[\frac{\alpha}{\Gamma(2s)} \right]^{1/2}$$

where here Γ is an ordinary gamma function.⁶⁵ One may similarly construct the other functions and normalization constants:

$$\begin{aligned} m = 1: \quad F(-1, 2s+1, \xi) &= 1 - \frac{\xi}{2s+1} , & c_1 &= \left[\frac{\alpha(2s+1)}{\Gamma(2s)} \right]^{1/2} \\ m = 2: \quad F(-2, 2s+1, \xi) &= 1 - \frac{2\xi}{2s+1} + \frac{\xi^2}{(2s+2)(2s+1)} , & c_2 &= \left[\frac{\alpha(2s+1)(2s+2)}{\Gamma(2s)} \right]^{1/2} . \end{aligned}$$

Therefore, the overall normalization constant for the m^{th} bound state is

$$\Lambda_m = \frac{c_m}{\sqrt{aM}}$$

C. Continuum Morse State

As indicated in Section B, since the z -component of the continuum functions must go asymptotically as $\sin(k_z z + \eta_c)$, the complete function is taken to have the form

$$\psi_{\nu(\epsilon)}^{\text{Morse}}(z) = c_{\nu(\epsilon)} e^{-\xi(z)/2} \xi(z) U(-\nu, 2s+1, \xi(z)) ,$$

where, in addition to the parameters previously defined (note that for this case s is imaginary),

$$\nu(\epsilon) = \frac{\sqrt{2\mu D}}{\alpha} - \frac{1}{2} - s ,$$

and

U is the independent solution of the confluent hypergeometric equation described within the text.

In the limit $z \rightarrow \infty$ it can be seen that

$$\begin{aligned} \psi_{\nu(\epsilon)}^{\text{Morse}}(z) \sim c_{\nu(\epsilon)} \frac{i\pi}{\sinh \frac{2\pi k}{\alpha}} \left\{ \left(\frac{2\sqrt{2\mu D}}{\alpha} e^{-\alpha z} \right)^{ik/\alpha} \frac{1}{\Gamma(-\nu)^* \Gamma(2s+1)} \right. \\ \left. - \left(\frac{2\sqrt{2\mu D}}{\alpha} e^{-\alpha z} \right)^{-ik/\alpha} \frac{1}{\Gamma(-\nu) \Gamma(2s+1)^*} \right\} . \end{aligned}$$

Then, by defining η_c such that

$$e^{i\eta_c} = \left[\frac{\Gamma(-\nu)^* \Gamma(2s+1)}{\Gamma(-\nu) \Gamma(2s+1)^*} \right]^{1/2} \left(\frac{2\sqrt{2\mu D}}{\alpha} \right)^{-ik/\alpha} ,$$

one finds that

$$\psi_{\nu(\epsilon)}^{\text{Morse}}(z) \sim c_{\nu(\epsilon)} \frac{i\pi}{\sinh \frac{2\pi k}{\alpha}} [|\Gamma(-\nu)|^2 |\Gamma(2s+1)|^2]^{-1/2} \{e^{-ikz} e^{-i\eta_{\epsilon}} e^{ikz} e^{i\eta_{\epsilon}}\}$$

$$\sim c_{\nu(\epsilon)} \frac{2\pi}{\sinh \frac{2\pi k}{\alpha}} [|\Gamma(-\nu)|^2 |\Gamma(2s+1)|^2]^{-1/2} \sin(kz + \eta_{\epsilon})$$

$$\sim \sin(kz + \eta_{\epsilon})$$

if

$$c_{\nu(\epsilon)} \equiv \frac{\sinh \frac{2\pi k}{\alpha}}{2\pi} |\Gamma(-\nu)| |\Gamma(2s+1)| \quad .$$

So, the full normalization constant for this unbound state is just

$$B_{\nu(\epsilon)} = \frac{\sinh \frac{2\pi k}{\alpha}}{2\pi \sqrt{aM}} |\Gamma(-\nu)| |\Gamma(2s+1)| \quad .$$

[†]All quantities discussed herein are expressed in atomic units ($\hbar = 1$).

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Table 1: Eigenvalues for $V(x) = 0$ ^a

<u>Quantum Number</u>	<u>WKB^b</u>	<u>Modified WKB^c</u>	<u>Ratio</u>
0	0.125	.5	4.00
1	1.125	2.0	1.78
2	3.125	4.5	1.44
3	6.125	8.0	1.31
4	10.125	12.5	1.23
5	15.125	18.0	1.19
10	55.125	60.5	1.10
15	120.125	128.0	1.07
20	210.125	220.5	1.05

^aParameters as defined in Chapter I, Section C(1).

^bOrdinary WKB eigenvalues given by Eq. (1.13).

^cModified WKB eigenvalues from Eq. (1.10) (same as quantum mechanical values).

Table 2: Eigenvalues for a Harmonic Oscillator in a Box.^a

<u>Quantum Number</u>	<u>L/√2</u>	<u>WKB</u> ^b	<u>Quantum</u> ^c	<u>Modified WKB</u> ^d
0	0.5	2.47	9.87	9.88
0	1	0.64	2.48	2.48
0	2	0.25	0.65	0.67
0	3	0.25	0.34	0.38
0	4	0.25	0.27	0.30
1	0.5	22.21	39.48	39.55
1	1	5.57	9.89	9.90
1	2	1.47	2.54	2.54
1	3	0.82	1.25	1.26
1	4	0.75	0.88	0.90

^aPotential parameters as defined in Chapter I, Section C(2).

^bResults of the ordinary (i.e., un-modified) WKB quantum condition, Eq. (1.3) with $\Delta V = 0$.

^cResults of Reference 10.

^dResults of the modified WKB quantum condition, Eqs. (1.3) and (1.14).

Table 3: Open-Channel Reaction Probabilities for Collinear H + H₂(inner projection expansion of V_{ex}).

<u>Number of</u> <u>expansion functions</u> ^{a,b}	<u>Width parameter,</u> ^b β^2						
	<u>24.0</u>	<u>20.0</u>	<u>16.0</u>	<u>12.0</u>	<u>7.0</u>	<u>4.0</u>	<u>1.0</u>
2	.0001	.0000	.0008	.0130	.0938	.1736	.0006
4	.0082	.0441	.1407	.7078	.1294	.1139	.1134
6	.2613	.1501	.1163	.1064	.1082	.1124	.1138
8	.1055	.1026	.1029	.1043	.1147	.1137	.1154
10	.1010	.1016	.0958	.1159	.1137	.1137	.1171
12	.0966	.1365	.1149	.1138	.1137	.1137	.1120
14	.1176	.1143	.1138	.1137	.1137	.1144	.0790
16	.1140	.1137	.1137	.1140	.1137	.1137	.1266
18	.1137	.1137	.1137	.1137	.1137	.1141	.0818
20	.1137	.1137	.1137	.1137	.1137	.1139	.1033

^aThe number of functions $\{u_i\}$ used in the inner projection expansion of Eq. (2.10).

^bThe functions $\{u_i(R)\}$ are given by $u_i(R) = \sqrt{\beta} \phi_i[\beta(R-R_0)]$, with $R_0 = 2.1 a_0$, where $\phi_i(x)$ are the standard harmonic oscillator eigenfunctions of Reference 18 (for $\hbar = m = \omega = 1$).

Table 5: Open-Channel Reaction Probabilities for Collinear H + H₂
(outer projection expansion of V_{ex}).

<u>Number of</u> <u>expansion functions</u> ^{a,b}	<u>Width parameter,</u> ^b β^2	
	<u>24.0</u>	<u>7.0</u>
10	.0511	.0500
12	.0773	.1074
14	.0942	.0735
16	.1039	.0761
18	.1090	.0935
20	.1115	.1067
22	.1127	.1125
24	.1133	.1134
26	.1135	.1128
28	.1137	.1122
30	.1137	.1124
32	.1137	.1128
34	.1137	.1134

^aThe number of functions $\{u_i\}$ used in the outer projection expansion of Eq. (2.9).

^bThe functions $\{u_i(R)\}$ are given by $u_i(R) = \sqrt{\beta} \phi_i[\beta(R-R_0)]$, with $R_0 = 2.1 a_0$, where $\phi_i(x)$ are the standard harmonic oscillator eigenfunctions of Reference 18 (for $h = m = \omega = 1$).

Table 5: Calculated Resonance Widths and Lifetimes for He-Li(001).

<u>m</u>	<u>E (meV)</u>	<u>θ (deg)</u>	<u>Γ_s (10^{-8} meV)</u>	<u>τ (nsec)</u>	<u>Γ_r^a</u>
0	1.0	75.7	25.8	.0936	2.00
0	2.0	54.9	14.3	.169	2.25
0	5.0	47.8	6.57	.368	2.59
0	10.0	48.0	2.43	.995	3.02
0	15.0	49.4	1.11	2.18	3.37
0	20.0	50.7	.573	4.22	3.65
0	25.0	51.9	.323	7.48	3.90
0	30.0	52.9	.194	12.5	4.12
1	1.0	15.2	141.	.0172	1.26
1	2.0	21.3	103.	.0234	1.39
1	5.0	30.5	49.9	.0485	1.71
1	10.0	37.7	20.4	.118	2.10
1	15.0	41.8	10.2	.237	2.40
1	20.0	44.6	5.74	.421	2.65
1	25.0	46.8	3.48	.694	2.87
1	30.0	48.4	2.23	1.08	3.06
2	1.0	19.5	281.	.00860	.960
2	2.0	.565	216.	.0112	1.07
2	5.0	20.1	117.	.0207	1.34
2	10.0	31.6	55.6	.0435	1.66
2	15.0	37.4	31.1	.0778	1.92
2	20.0	41.1	19.1	.127	2.13
2	25.0	43.8	12.5	.194	2.31
2	30.0	45.9	8.54	.283	2.48

Reference for Table 5:

${}^a T_r$ is calculated from Eq. (4.19), where $\tau^0 = 9.42 \times 10^{-4}$ nsec.

Table 6: Energy Cutoff Values.

<u>m</u> ^a	<u>E_m^{cutoff}</u> (meV) ^b
0	0.9018
1	8.151 x 10 ⁻⁴
2	0.3739

^aQuantum number of bound Morse state.

^bCutoff energy calculated from Eq. (4.13).

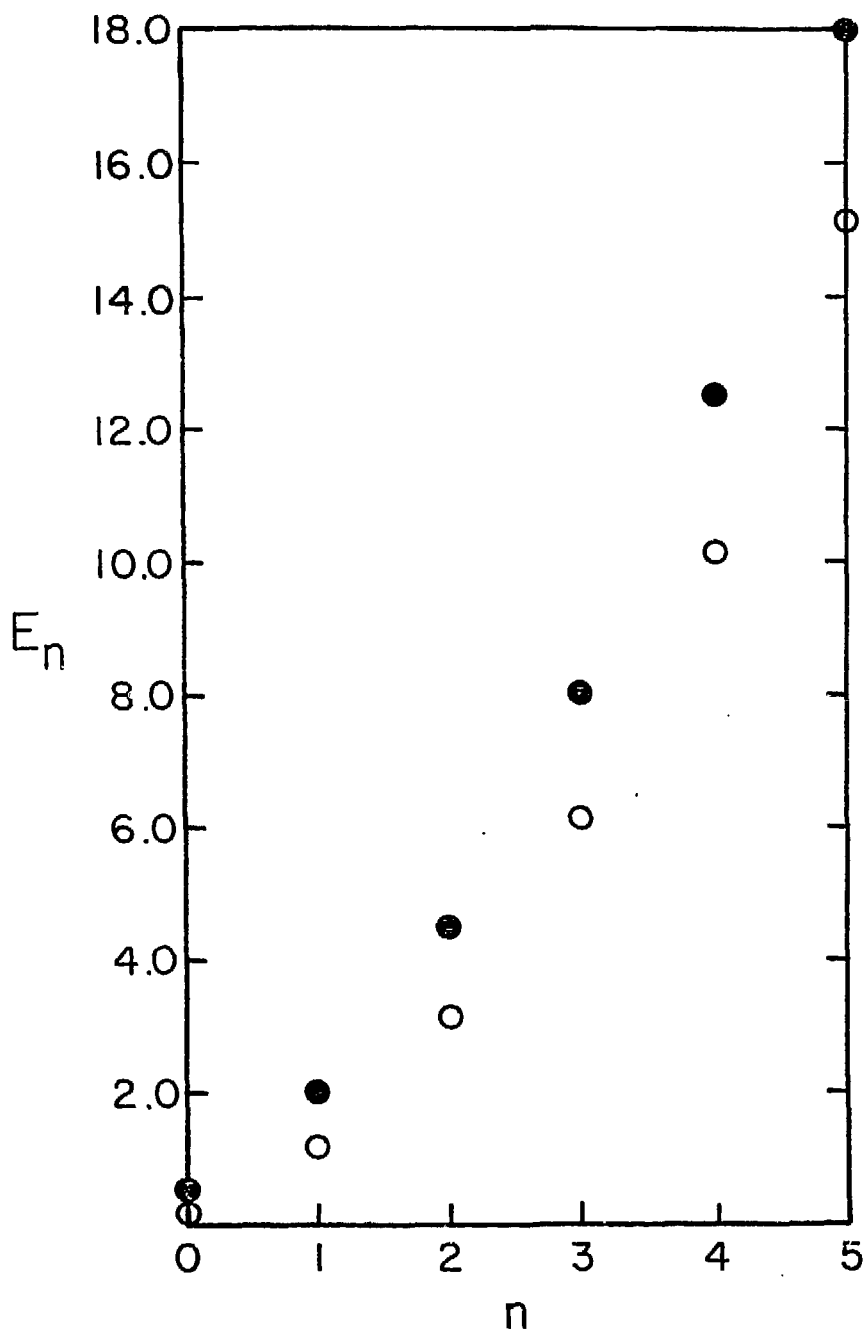
Table 7: Inelasticity Correction Factors.

$\frac{\langle q_z^2 \rangle^{1/2}}{a}$	$\frac{\bar{\Gamma}}{\Gamma_s}^a$
.01	1.00
.02	1.02
.05	1.10
.07	1.16
.10	1.43
.12	1.52
.15	1.86

^aAverage width calculated from Eq. (4.18).

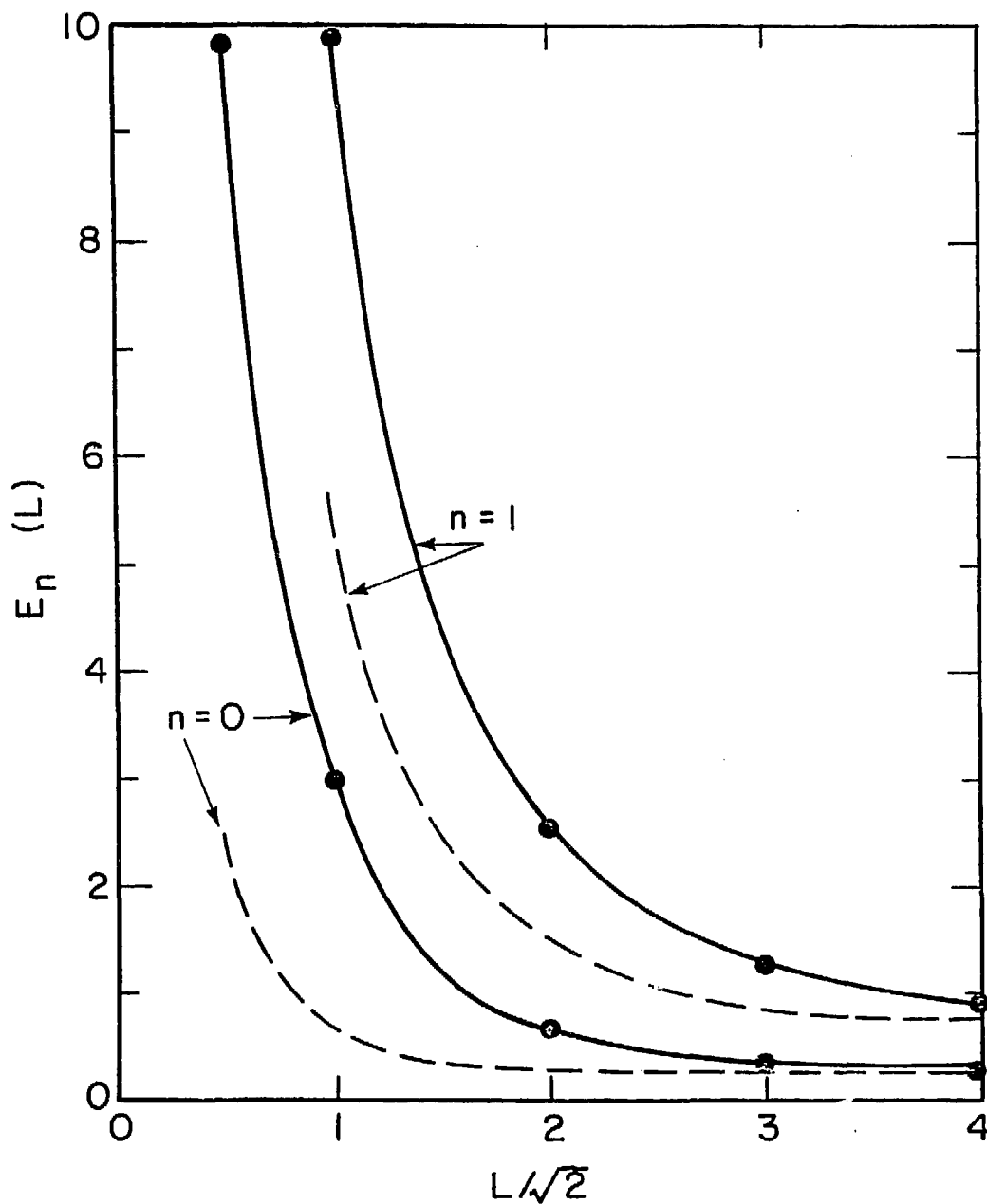
Figure Captions

- Figure 1. Particle-in-a-box eigenvalues for the parameters of Chapter 1, Section C(1). The open points are the ordinary unmodified WKB results, while the solid points are those obtained from the modified WKB formalism (and which are identical with the exact quantum eigenvalues).
- Figure 2. Eigenvalues of the ground ($n = 0$) and first excited state ($n = 1$) for a harmonic oscillator of frequency $\omega = \frac{1}{2}$ in a box of length L . The points represent the exact quantum mechanical values of Reference 10, the solid curves the values calculated via the modified WKB quantum condition, Eqs. (1.3) and (1.14), and the dashed lines the results given by the ordinary unmodified WKB quantum condition.
- Figure 3. Contour plot of the non-local exchange kernel $V_{ex}(R, R')$ for a total energy $E = 0.4898$ eV. R and R' are expressed in atomic units (a_0).
- Figure 4. Lifetime factors, T_r , predicted by Eq. (4.19) for the three metastable states of the He-LiF(001) adsorption at various total energies ($\beta = 0.1$). Higher values of E correspond to more energy appearing in translation parallel to the surface.



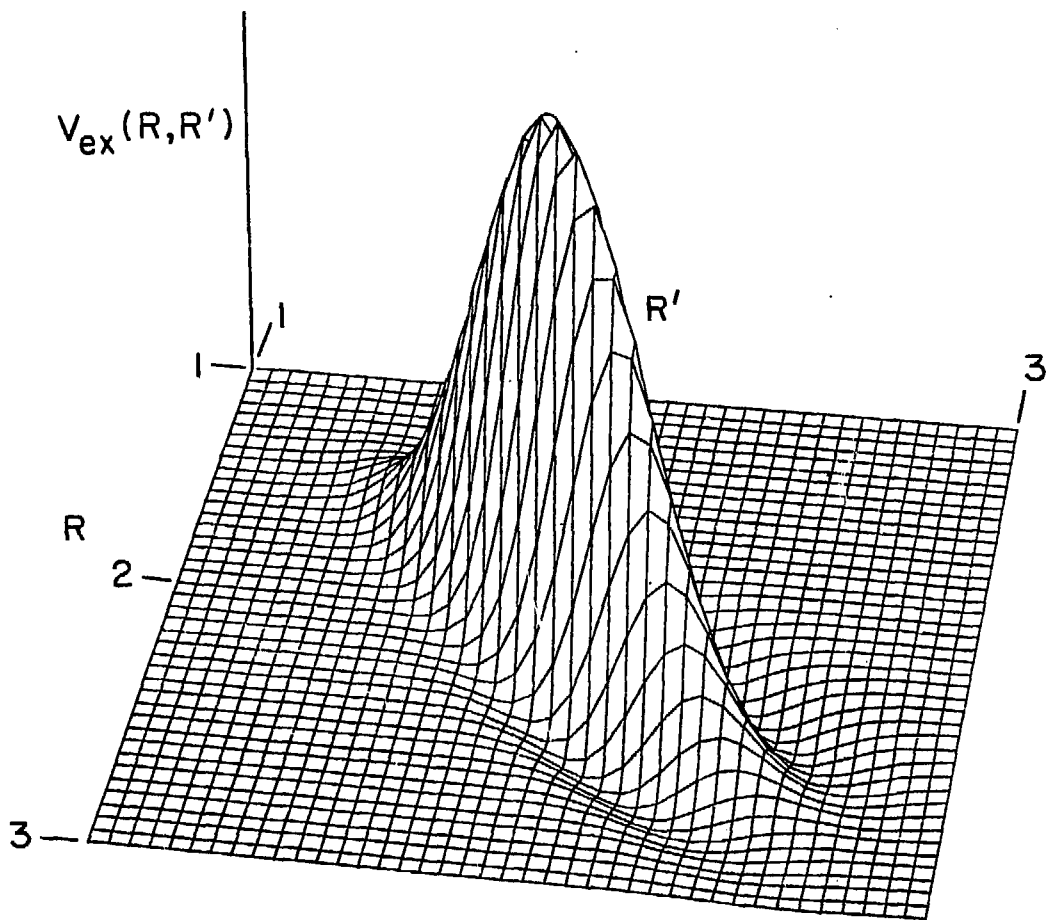
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Figure 1



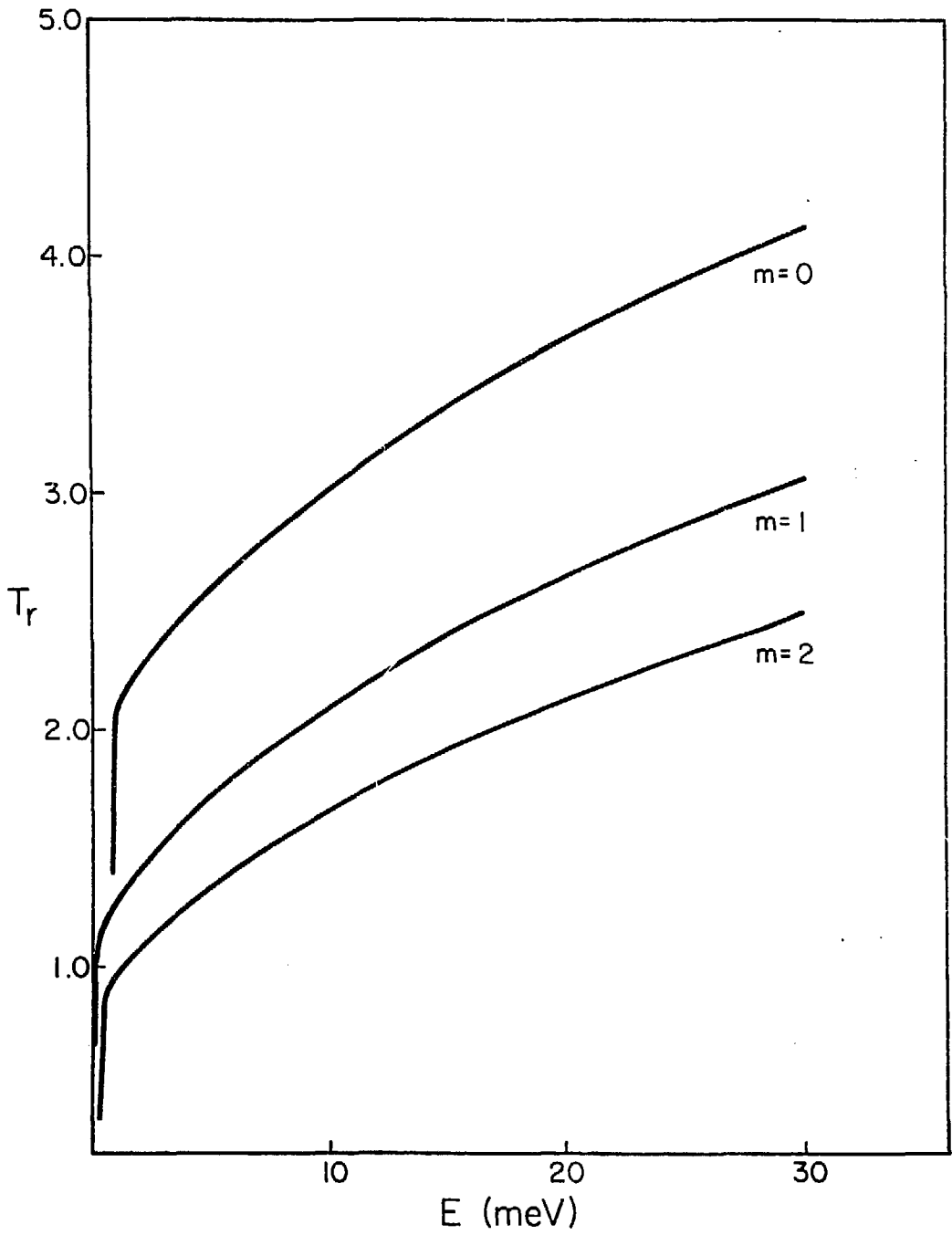
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Figure 2



XBL 7712-10943

Figure 3



XBL 793-9057

Figure 4