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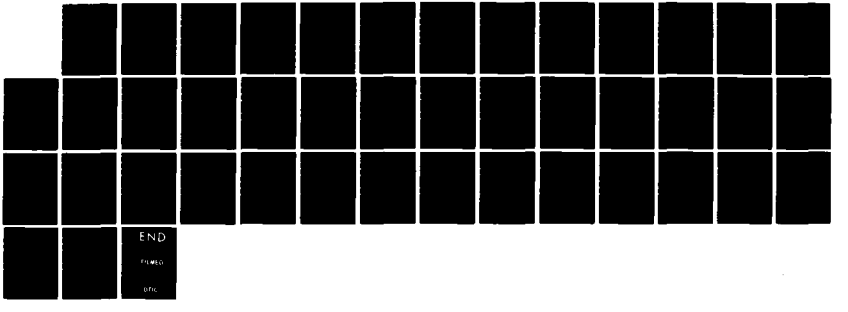

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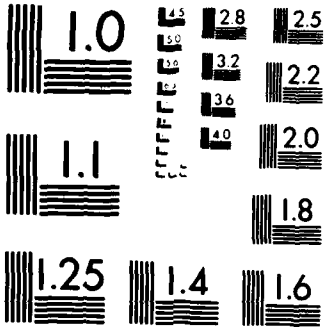

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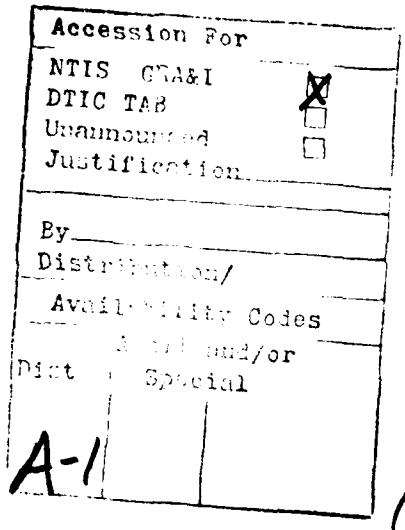

An Examination of the Use of Wave Packets for the Calculation of Atom Diffraction by Surfaces.

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ABSTRACT

We use analytic models, valid for neutron scattering, and numerical calulcations to examine a method proposed by Drolshagen and Heller for computing atom diffraction from surfaces. Our main concern is the manner in which the use of narrow packets, causing a partial coherence of the incident beam, might affect the diffracted intensity. We find that the demands of representing beam coherence correctly conflict with the requirements for the validity of the propagation scheme. We suggest some improvements that should increase the reliability of the method without affecting greatly its remarkable computational and conceptual advantages.

I. INTRODUCTION

In several recent papers[1] Drolshagen and Heller have presented a reformulation of the quantum theory of atom scattering by surfaces which seems to have great numerical and conceptual advantages over the traditional basis set expansion method. The key idea, taken over from Heller's prior work,[2] is to write the wave function of the incident particle as a sum of Gaussian wave packets, to propagate them independently by using the time dependent Schrodinger equation, and to reconstruct the post-collision wave function by adding the scattered packets. If the width of each packet is narrower than the length scale over which the potential varies, the center of the packet moves according to classical mechanics. The calculation of the scattering of one packet is thus reduced to the calculation of a classical trajectory, plus four other first order differential equations giving the complex width and the phase of the packet. In what follows we call this the simplest Heller method, or SHM. Even if hundreds of packets are needed to construct the wave function SHM requires less computer time than the traditional quantum methods.

While the resulting theory has a strong resemblance with classical mechanics it contains all the important quantum effects: interference - which is crucial in a study of diffraction - is preserved since the post-collision packet amplitudes are added and then squared; Heisenberg principle is intact since the packets have a width so that both the position and the momentum are allowed to fluctuate; finally the observables are computed by the rules of quantum mechanics (i.e. by using operators and matrix elements, rather than the classical definitions). Thus the theory must be viewed as a fully quantum theory designed to resemble classical mechanics and acquire thus the computational advantages of the latter.

Such a theory holds great promise for several reasons. (a) There is no conceptual difficulty in extending the theory to partly disordered surfaces[1] and dealing with scattering by

surfaces with short correlation length will not strain the capability of existing computers. By comparison a traditional quantum scattering method[3] encounters severe difficulties when translational symmetry is lost. (b) The theory is easily extended to the case when some degrees of freedom are to be treated classically, while the translation of the projectile is quantized.[4] This is very important since it permits us to calculate, non-perturbatively, how the thermal motion of the lattice affects diffraction.[5] Once such developments are completed and tested, they will augment substantially the usefulness of atom diffraction as a sensitive surface probe.

While the Drolshagen-Heller papers justify high hopes, their use of the simplest version of Heller's theory is cause for some concern. As is well known the signal produced by interference effects depends on the degree of coherence of both the probing beam and the target; scattering of a partially coherent beam from a perfectly ordered surface gives broad peaks, as if the surface is disordered. Intuitively it is clear that the coherence in the direction parallel to the surface is more important than that in the direction perpendicular to it, since that is the plane in which the target is ordered. The Drolshagen-Heller theory does a good job in this regard, since they use a sum of wave packets to build a piece of a two dimensional planar wave (i.e. full coherence) over the unit lattice, scatter it from the unit cell and then construct the final wave function from it by using Bloch's theorem. However, the beam is partially coherent in the z-direction since it resembles a planar wave only on a length scale equal to the width of the packet (which plays the role of a coherence length). Existing experience with interference suggests that if this width does not exceed some of the important length scales of the target, the partial coherence of the beam will broaden the diffraction peak; the use of wave packets would then affect the diffraction results. One cannot avoid this difficulty by using broad packets since the dynamic scheme used for packet

propagation (i.e. SHM) requires them to be narrower than the length over which the potential changes.

The purpose of this article is to examine more closely the conflicting demands imposed by the need for adequate coherence (i.e. broad packets) and for computational simplicity (i.e. narrow packets). We do this by comparing the analytic expressions obtained for the diffraction of partially coherent (wave packets) and fully coherent (plane waves) neutron beams by a bulk lattice, a lattice of ordered scattering centers located on a hard wall, and a set of scattering centers located on a wall and affected by static or thermal disorder. In all cases we find that the use of wave packets can be justified if their width exceeds certain length scales describing the properties of the target, such as lattice spacing, potential range and coherence length (i.e. the decay length of the correlations in the target density fluctuations).

However, since neutron scattering can only provide, at best, qualitative guidance for what would happen in the case of atom scattering, we also undertake a numerical study of He diffraction by using the SHM (as applied to diffraction by Drolshagen and Heller). We find that no matter how we chose the initial width of the packet the interaction with the surface broadens the packet to the extent that the requirements for the validity of the SHM propagation equations are not satisfied. A detailed comparison of the results obtained by the DH method with those given by the usual quantum theory shows a good agreement between the two.[1] This seems to suggest that SHM works well--at least in the case examined--outside its stated range of validity. While this is fortunate one cannot help being slightly uncomfortable in regards to the reliability of the results for situations in which "exact" quantum calculations are not available (or obtainable) for testing those produced by SHM. Methods that increase the reliability of wave packet calculations are available and their application to diffraction will be discussed in a future article.[6]

II. AN ANALYSIS OF WAVE PACKET DIFFRACTION BY USING SIMPLE ANALYTICALLY SOLVABLE MODELS.

II.A Introductory remarks.

We examine several simple models to clarify how the diffraction peaks are affected by the use of particle states which are defined to maintain a Gaussian dependence on the z variable throughout the collision process. We find that this practice modifies the intensity of the diffraction peaks in a manner which depends on the relationship between various length scales: the width of the packet, the lattice spacing, the range of the potential and the correlation length of the scatterers.

After describing briefly in Section II.B the model for the incident wave function and its propagation, we discuss in Section II.C elastic neutron scattering by a perfectly ordered bulk crystal. For this case the particle-lattice interaction can be adequately described by a potential consisting of sums of δ-functions and the scattering process treated by first order perturbation theory.. The only lengths in the problem are the width of the packet, the de Broglie wavelength, and the lattice constant. In Section II D we consider a disordered lattice (static or thermal disorder), which adds two new lengths to the problem: the correlation length and the mean amplitude of the deviations of the atom positions from the perfect lattice. In II.E we consider a model that simulates surface scattering by looking at a hard wall on which we place an ordered, two dimensional array of scattering centers. We allow the projectile to interact with these centers through an exponentially repulsive potential to study how the relationship between the coherence length of the packet and the range of the potential affects diffraction.

II.B. The Model

The initial wave function, at a time t_1 prior to the collision, is

$$\psi_i(\vec{r}) = (4\pi a^2)^{-1/2} \int_{-\infty}^{-\infty} d\kappa \exp\{-(\kappa-\kappa_1)^2/4a^2\}\exp\{-i\kappa_1 z_1\}\exp\{i\vec{k}\cdot\vec{r}\}$$

$$= \exp\{-a^2(z-z_1)^2\}\exp\{i\vec{K}\cdot\vec{R}\}\exp\{i\kappa_1(z-z_1)\} . \qquad (2.1)$$

Here $\vec{K} = (k_x, k_y)$ and $\vec{R} \equiv (x,y)$ are two dimensional vectors parallel to the surface, κ is the z-component of the wave vector and $\vec{k} \equiv (\vec{K},\kappa)$ is the total, three-dimensional wave vector.

The z dependence of ψ_i is a Gaussian centered at z_1 with a width $\sigma=a^{-1}$. This width defines the spatial scale on which the variation of ψ_i with z (at fixed x and y) resembles a planar wave: thus σ is the coherence length of the beam along the z direction. To simplify matters we have assumed perfect coherence in the x and y direction so that σ is the only coherence length in the problem. If $a \to 0$, ψ_i becomes a planar wave and the coherence length becomes infinite.

The initial state ψ_i is propagated with the Hamiltonian

$$H = H_o + V \equiv -(\hbar^2/2m)\nabla^2 + V(r) \qquad (2.2)$$

to some final time t_2 chosen such that at t_2 the packet has already passed through the lattice and stopped interacting with it. We want to compute the probability

$$P(\vec{k}') = \int d\vec{r} \exp\{-i\vec{k}'\cdot\vec{r}\}\ U(t_2-t_1)\ \psi_i(\vec{r})^2 \qquad (2.3)$$

that the scattered particle emerges from the solid with a wave vector $\vec{k}'$. The propagator $U(t_2-t_1)$ is computed by using time dependent perturbation theory:

$$U(t_2-t_1) = U_o(t_2-t_1) - (i/\hbar) \int_{t_1}^{t_2} d\tau\, U_o(t_2-\tau)\, V\, U_o(\tau-t_1); \tag{2.4}$$

here

$$U_o(t) = \exp\{-iH_o t/\hbar\}. \tag{2.5}$$

and V is the particle-surface interaction energy.

Since the wave packet is not a stationary state of H_o we use time dependent perturbation theory rather than the Golden Rule expression which is normally used[8] in the theory of neutron scattering.

II.C. Neutron scattering by a three-dimensional lattice.

Neutron scattering can be adequately described by using the neutron-lattice interaction

$$V(\vec{r}) = (V_o/N) \sum_{n,m,l=1}^{N_x,N_y,N_z} \delta(\vec{r}-\vec{r}_{n,m,l}) \quad . \qquad (2.6)$$

where the vectors $\vec{r}_{n,m,l} = c(n\hat{x}-m\hat{y}-l\hat{z})$ give the positions of the lattice atoms, c is the lattice constant, $\hat{x},\hat{y},\hat{z}$ are unit vectors along the coordinate axis (we consider a cubic lattice with the crystal axis along $\hat{x}$, $\hat{y}$, $\hat{z}$), n,m,l are integers, N_x, N_y, N_z are the number of atoms in the x,y and z directions, and N is the total number of lattice atoms. The crystal is located between z=0 and $z=N_z c$ and is infinite in the x and y directions. Since we take in Eq.(2.1) $z_1<0$ and $k_1>0$ the wave packet starts in the half space z<0 and moves towards the z=0 face of the crystal with the group velocity $v_1 = \hbar k_1/m$.

Using the Eqs. (2.1-2.6) we can calculate the probability $P(\vec{k}')$ that a neutron whose initial state is described by Eq. (2.1) will have, after the collision with the lattice, a final momentum $\vec{k}'$. The result is

$$P(\vec{k}') = \pi(V_o \hbar a v_1)^2 f(\Delta k_x) f(\Delta k_y) F \qquad (2.7)$$

with

$$f(\Delta k_\mu) = (\sin(c\Delta k_\mu N_\mu/2)/N_\mu \sin(c\Delta k_\mu/2))^2, \quad \mu = x \text{ or } y. \qquad (2.8)$$

and

$$F = N_z^{-2} \exp(-(1/2)(\Delta\epsilon/\hbar a v_1)^2) \sum_l \sum_{l'} \{\exp[-i\Delta\kappa(l-l')c] \cdot \exp[i\Delta\epsilon(l-l')c/\hbar v_1]\} \qquad (2.9)$$

$\Delta\kappa \equiv \kappa' - \kappa_1$ is the difference between the z-components of the final momentum and the initial mean momentum of the packet; $\Delta k_\mu = k_\mu - k_\mu$, $\mu = x,y$, is the momentum transfer in the x or y direction; and $\Delta\epsilon = (\hbar^2/2m)(k'^2 - k_1^2)$, with $k'^2 = (k_x)^2 - (k_y)^2 - \kappa^2$ and $k_1^2 = k_x^2 - k_y^2 - \kappa_1^2$, is the energy transfer. Since we do perturbation theory the packet maintains the velocity v_z as it goes through the lattice. In carrying out the integrals over time we have assumed that the width of the packet remains constant in time. This is not quite correct since, in perturbation theory, the packet width has its free space variation given by $a(t) = a[1 - 2\hbar a^2 t/m]^{-1/2}$. The neglect of this time dependence allows us to get a simple result, hopefully without altering substantially the physics of the problem.

In order to better understand the modifications introduced by the use of a wave packet we compare Eqs (2.7-2.9) to the diffraction formula for neutrons whose initial state is a planar wave. The transition rate for the latter case is

$$W(\vec{k}') = V_o^2 (2\pi/\hbar)^2 f(\Delta k_x) f(\Delta k_y) f(\Delta k_z) \delta(\omega(k') - \omega(k)) \qquad (2.10)$$

As N_x, N_y, N_z go to infinity $f(\Delta k_\mu) \to \delta(k_\mu - \kappa_\mu - 2\pi n_\mu)$ where $n = 0, \pm 1, \pm 2, \ldots$ and $\mu = x, y$ or z; thus, the product $f(\Delta k_x) f(\Delta k_y) f(\Delta k_z)$ generates Bragg's diffraction condition. Furthermore, since we consider elastic scattering, a δ-function enforcing energy conservation appears in Eq.(2.10).

The essential difference between a wave packet and a planar wave initial state is that the term $h \equiv \delta(\kappa' - \kappa_1 - 2\pi n_z)\delta(\Delta\epsilon)$, appearing in the planar state case and representing the conservation of the z-component of momentum and of the energy is replaced by F. Since the wave packet is not an eigenvalue of the zero order Hamiltonian, or of the momentum operator, it is not surprising that the simple conservation conditions expressed by

h, for planar wave initial condition, are no longer valid. Note that as $a \to \infty$, $F \to h$, as it should.

The manner in which the use of a wave packet affects diffraction can be understood by examining F. Carrying out the double sum and taking $N_z \to \infty$ we obtain

$$F = \exp\{-2(\Delta\epsilon/\hbar a v_1)^2\}\ \delta(\Delta\kappa - 2\pi n/c - \Delta\epsilon/\hbar v_1) \quad . \qquad (2.11)$$

In the case of a planar wave the permissible final momenta can be found by specifying n_x and n_y since the restriction imposed by the energy conservation term $\delta(\Delta\epsilon)$ fixes n_z and thus the permisible values of κ'. Since the latter restriction disappears when a wave packet is used, a larger number of values for κ' are allowed for a given pair (n_x, n_y). Thus, what used to be a sharp Bragg spot, when the initial state was a planar wave, may degrade into a large number of spots having the same azimuthal angle, but different polar angles. If the detector does not resolve these spots they form a strip whose intensity $I(\theta)$ varies with the polar angle θ. The spots are determined from Eq. (2.11) through the condition

$$\Delta\kappa_n = 2\pi n/c - \Delta\epsilon_n/\hbar v, \qquad n = (n_x, n_y) \quad . \qquad (2.12)$$

where n_x and n_y are fixed. The intensity of the spot corresponding to $\Delta\kappa_n$ is determined by the magnitude of the Gaussian $\exp\{-2(\Delta\epsilon_n/\hbar a v_1)^2\}$. Since $\Delta\epsilon_n = (\hbar^2/2m)(K_n'^2 - K^2) - (\hbar^2/2m)(\kappa_n'^2 - \kappa^2)$, the only part of $\Delta\epsilon_n$ depending on $\Delta\kappa_n$ is $\alpha_n \equiv (\hbar^2/2m)(2\Delta\kappa_n\kappa - \Delta\kappa_n^2)$. The variation of the intensity with $\Delta\kappa_n$ is then given by $\exp\{-2(\alpha_n/\hbar a v_1)^2\}$. Since κ is of order of the de Broglie wave vector k_d and in diffraction studies we use a de Broglie wave length of order of the lattice spacing, we find that the exponential cuts off the values of $\Delta\kappa_n$ which are larger than $(k_d a)^{1/2} \sim (2\pi a/c)^{1/2}$. The wave packet gives the same result as a planar wave when $k_d a$ is very small. This means that a^{-1} must

be larger than the de Broglie wave length and lattice spacing.

Note that besides turning a spot into a strip along the polar angle, the use of a wave packet also changes the intensity of the spots as (n_x, n_y) are changed, through the Gaussian term appearing in F. This effect is negligible for those peaks for which $\Delta\epsilon_n/\hbar a v_1$ is very small. Since $\Delta\epsilon_n$ is less than the incident energy we have an upper bound for $\Delta\epsilon_n$ leading to the condition $\hbar^2 k_1^2/2m\hbar a v_1 << 1$ which gives $a^{-1} << k_d/k_1^2$. If k_i is of order of k_d, if $a^{-1} << k_d^{-1}$ the effect of the use of a wave packet on the spot intensity is negligible .

The manner in which the use of the wave packet affects diffraction can be understood by examining what happens in the double sum in Eq. (2.9). If the exponential $\exp(-i\Delta\epsilon(l-l')c/\hbar v_1)$ was absent, the double sum would give-because of constructive and destructive interference-the Bragg condition for $\Delta\kappa$. The presence of that exponential alters the perfect interference However, since the packet looks like a planar wave over the length a^{-1} this alteration does not lead to a complete destruction of the interference pattern. To see this let us divide the values of $(l-l')$ into two sets. One set contains those values of $l-l'$ for which $\exp(-i(l-l')\Delta\epsilon c\ \hbar v_1)\sim 1$, i.e. those satisfying $(l-l')\Delta\epsilon c/\hbar v_1 < 1$. The other set contains the remaining values of $l-l'$. Thus if we denote $(\hbar v_1/c\Delta\epsilon) \equiv \Delta l$, the first set is defined by $l-l' \leq \Delta l$. Now we can write the double sum appearing in F as

$$\alpha \sum_{l=0}^{N_z} \sum_{l-l'=0}^{\Delta l} \exp(-i\Delta\kappa(l-l')c) - \text{remaining terms.}$$

In the remaining terms the phase $\Delta\epsilon(l-l')c\ \hbar v_1$ is larger than 2π and thus acts as a random phase leading to cancellations in the double sum and destroying interference. Thus interference is present in the first term only and we have

$$\alpha \sum_{l=0}^{N_z} \sum_{l-l'=0}^{\Delta l} \exp(-i\Delta\kappa(l-l')c)\exp(-2(\Delta\epsilon\cdot\hbar a v_l)^2)$$

$$- \text{background}.$$

The double sum is proportional to $(\sin(\Delta\kappa c\Delta l/2)\cdot\Delta l\sin(\Delta\kappa c\cdot 2))^2$ which has a central peak at $\Delta\kappa=0$, having a width Δl^{-1}. Now since $\Delta l\sim\hbar v_l/c\Delta\epsilon$ and the Gaussian cuts $\Delta\epsilon$ off at $\hbar a v_l$, the width of the function $F(\Delta\kappa)$ is $(\Delta l)^{-1} \sim c\hbar a v_l/\hbar v_l = ca$. If ca is very small (i.e. if $\sigma >> c$) the packet scattering resembles that of a planar wave.

This example was used here only because it is the simplest possible situation in which we can examine the effect of using wave packets on diffraction. Since in atom surface scattering, which is the phenomenon in which we are interested, the atom does not pass through the solid, the effects discussed above are not directly relevant to atom surface scattering. However, the mathematical machinery through which these effects are generated is the same. A model which mimics the physical conditions of surface scattering is discussed in Section II.E.

II D The effect of wave packets on diffraction by a partly disordered lattice.

It is intuitively clear that the presence of partial disorder in the position of the scattering centers must affect the diffraction pattern in a manner similar to the partial coherence of the beam. Since one of the hopes opened up by the Drolshagen-Heller paper is the possibility of interpreting atom scattering from partly ordered surfaces[1], it is important to use simple models in order to try to understand how the use of wave packets might influence the results of such a computation. The key practical matter is to find under what conditions the use of a wave packet for the z dependence of the initial state leads to the same results as the use of a planar wave.

We consider here lattice disorder that can be described by a small displacement $\vec{U}_B$ (in what follows we use $B\equiv(n,m,l)$ and $B'\equiv(n',m',l')$) of each solid atom relative to the lattice point $\vec{r}^{\,o}_B$. (i.e. the position of the atom located near the site B is $\vec{r}_B = \vec{r}^{\,o}_B - \vec{U}_B$). Such disorder could be caused either by thermal motion or by poor crystallization when the solid was formed (i.e. static disorder). We assume that in both cases $\vec{U}_B$ is a Gaussian variable, and therefore it can be completely characterized by the correlation function $D(B-B';t) \equiv \langle U_B(t)\, U_{B'}(0)\rangle$ and the condition $\langle U_B(t)\rangle = 0$. In the case of thermal disorder U_B is a Gaussian variable if the solid is harmonic. For static disorder (in which case the displacement is time independent) we postulate the Gaussian property: the true statistical properties of $\vec{U}_B$ depend on the mechanism of crystallization.

The disorder introduces two new length scales: the amplitude $A=\langle U_B U_B\rangle^{1/2}$ and the correlation length l_c defined as the distance beyond which the density-density correlation function equals the density squared (i.e. $\langle\rho(\vec{r})\rho(0)\rangle \cong \langle\rho(\vec{r})\rangle\langle\rho(0)\rangle$ for $\vec{r} \geq l_c$). Here $\langle\rangle$ is either a thermal average or an average

over the distribution function characterizing the static disorder.

To understand how the use of a wave packet in the z variable affects the diffraction by a disordered lattice we consider neutron scattering by a bulk crystal. We use the potential defined by Eq.(2.6) and write

$$\vec{r}_B = \vec{r}_B^{\,o} - \vec{U}_B \tag{2.18}$$

Using the methods described earlier in this article combined with standard neutron scattering methods[8] we find

$$P(\vec{k}',\omega) = (V_o/\hbar N)^2 \int_o^\infty dt \int_o^\infty dt' \exp\{i\Delta\epsilon(t-t')/\hbar\} \cdot \sum_B \sum_{B'} \exp\{-i\Delta\vec{k}\cdot(\vec{r}_B-\vec{r}_{B'})\} S(B,B';t,t') \tag{2.19a}$$

with

$$S(B,B';t-t') = \langle \exp\{i\Delta\vec{k}\cdot\vec{U}_{B'}(t')\} \exp\{-a^2(lc-\vec{U}_{B'}(t')\cdot\hat{z}-z(t'))^2\} \exp\{-i\Delta\vec{k}\cdot\vec{U}_B(t)\} \exp\{-a^2(lc-\vec{U}_B(t)\cdot\hat{z}-z(t))^2\} \rangle . \tag{2.19b}$$

Here $\Delta\vec{k}\equiv\vec{k}'-\vec{k}_1$, $z(t)=z_1-\hbar\kappa_1 t/m$ and $\vec{U}_B(t)\cdot\hat{z}$ is the projection of the displacement vector at site B along the z direction. The type of average depends on whether we deal with static or thermal disorder. If we use a planar wave in the z direction S becomes the structure factor of the lattice (essentially the density-density correlation factor).[8,9] Note that because of the use of the Gaussian wave packet, the displacement amplitude $\vec{U}_B$ appeares squared in some of the exponents present between the averaging brackets. This makes the evaluation of the averages cumbersome. For this reason we neglect the terms containing the square of the displacement, and then compute the average by standard methods. It can be shown that this does not introduce substantial errors

We can thus compute $S(B,B';t,t')$ and obtain

$$S(B,B':t,t') = \exp\{-a^2[(lc+z(t))^2-(l'c-z(t'))^2]\}\cdot$$

$$\exp\{[-2(\Delta\vec{k})^2-4a^4(l'c-z(t'))^2-4a^4(lc-z(t))^2-4i(\Delta\vec{k})a^2$$

$$((l-l')c+z(t')-z(t))]\ D(B,B';0)/2\}\cdot$$

$$\exp\{[2(\Delta\vec{k})^2+8a^2(l'c-z(t'))(lc-z(t))\ -$$

$$4i(\Delta\vec{k}\cdot\hat{z})a^2(c(l'-l)+z(t)-z(t'))]\ D(B,B':t-t':)/2\}\ . \qquad (2.20)$$

In the case of thermal disorder, the correlation function D is given by

$$D(B,B';t) = \langle\vec{U}_B(t)\vec{U}_{B'}(0)\rangle$$

$$= (\hbar/12NM)\sum_{\vec{q}}\omega(\vec{q})^{-1}\{\exp[i\vec{q}\cdot(\vec{r}_{B'}-\vec{r}_B)-i\omega(q)t]$$

$$(n(q)+1)+\exp[-i\vec{q}\cdot(\vec{r}_{B'}-\vec{r}_B)-i\omega(q)t]n(q)\}\ . \qquad (2.21)$$

where $\vec{q}$ and $\omega(q)$ are the phonon wave vector and frequency, respectively, M is the mass of the lattice atom and $n(q)=[1-\exp(-\hbar\omega(q)/kT)]^{-1}$ is the thermal phonon population.

The exponential in Eq.(2.20) containing $D(B,B':0)$ is the analog of the Debye-Waller (DW) factor. If a planar wave is used, instead of a wave packet, that term reduces to the usual DW factor $\exp(-2W) \equiv \exp(-2(\Delta\vec{k})^2\ D(B,B;0))$ (we assume a simple Bravais lattice). The exponential, in Eq. (2.20), containing $D(B,B':t-t')$ represents the effect of the inelastic collisions. For the purpose of analyzing what happens to the DW factor when a wave packet is used we can consider the elastic term only; this is done[8,9] by taking $D(B,B':t)=0$.

We can now compute $P(\vec{k}')$ for an elastic collision and obtain

$$P(\vec{k}') = \pi(V_o \hbar a v_1)^2 (1-4a^2D)^{-1} \exp(-2W(1-4a^2D)^{-1})$$

$$\exp(-[2(1-4a^2D)]^{-1}(\Delta\epsilon.\hbar a v_1)^2)$$

$$\exp(2\,\Delta\vec{k}\,(\Delta\epsilon)D[v_1\hbar(1-4a^2D)]^{-1})\; f(\Delta k_x) f(\Delta k_y) \qquad (2.22)$$

$$N_z^{-2} \sum_{l,l'} \exp(-i[\kappa'-\kappa_1)-(\Delta\epsilon\,\hbar v_1)])(1-l') \; c$$

The above equation is valid, due to some approximations we made, only if

$$4a^2D(B.B;0) < 1. \qquad (2.23)$$

We see that the use of a packet results in the replacement of the customary DW factor $\exp(-2W)$ with $\exp[-2W(1-4a^2D)^{-1}]$. Thus the partial coherence in the beam leads to greater reduction of the intensity. Intuitively this is not surprising since we can think of the scattering of a planar wave by a perfectly ordered solid, as the scattering of a fully coherent probe by a fully coherent object. Introducing disorder in the object is equivalent to turning it into a partially coherent target. The use of a wave packet causes some partial destruction of the probe coherence, which is equivalent to a "disorder" in the beam. We expect that the scattering event will convolute the incoherence of the beam with that of the target; thus the intensity decrease associated with the lattice disorder is accentuated by the "disorder" of the beam. If $4a^2D(B.B;0)$ approaches 1, the scattering probability is strongly diminished. This indicates that unless $A \sigma \ll 1$ the Debye-Waller factor obtained by a calculation using a wave packet in the z-direction is substantially larger than the one obtained when a planar wave is used. If the lattice temperature is several hundred degrees Kelvin a beam coherence length of only one Å will lead to noticeable changes in the Debye-Waller factor

Since the form of the potential is such that SHM propagation requires a packet width of about 1/4 Å, the use of the wave packets could lead to either errors in propagation (when a large width is used) or in the DW factor (when a small width is used). We will come back to this in the next section.

As in the zero temperature case we get in Eq. (2.22) a Gaussian in $\Delta\epsilon$ reflecting the effect of the energy spread in the initial wave function ψ_i: the width of this Gaussian has been however modified by disorder and decreases as the fluctuation amplitude A increases. There is also a new term which raises or lowers the intensity of various peaks depending upon the sign of $\Delta\vec{K}$ and $\Delta\epsilon$. For small a, $\Delta\epsilon$ is almost 0 and this term is small compared to the one modifying the Debye-Waller factor. The Bragg conditions are modified as in the zero temperature case.

In summary, the use of a wave packet in the z-direction has the effect of increasing the Debye Waller factor, and generating a new term which further modifies the amplitudes for $\Delta\epsilon\neq 0$. As in the zero temperature case the restrictions concerning conservation of energy and z-momentum are loosened, resulting in peak broadening along the polar angle Θ. The peaks are centered at positions specified by $\epsilon(\kappa') = \epsilon(\kappa)$.

Before proceeding further we make a few remarks concerning some of the practical problems encountered in computations. We have so far concentrated on the role of the partial coherence along the z-direction; however, when numerical calculations are carried out, some difficulties appear in treating fully the parallel (i.e., x,y direction) coherence if the lattice is disordered or it undergoes thermal motion. For a perfectly ordered target we can build up the wave function of the scattered neutrons by writing the "parallel" planar wave $\exp(i\vec{K}\cdot\vec{R})$ as a sum of wave packets and propagating only those packets that hit a given unit cell: Bloch's theorem allows us to construct the

different name from this information. The same procedure can be used [illegible] the calculation of the Debye-Waller factor which is (within perturbation theory) the square of the Fourier transform of the expectation value of the density operator

$$\langle \rho(\vec{r}) \rangle = \mathrm{Tr}\{e^{-\beta H} Z^{-1} \sum_B \delta(\vec{r}-\vec{r}_B)\} .$$

One can easily show that $\langle \rho(\vec{r}) \rangle$ is a periodic function consisting of sums of Gaussains centered around the lattice points. Therefore one can construct the Debye-Waller effect by calculating scattering by a unit cell whose atoms are allowed to move thermally, and using Bloch's theorem. If we select only the elastic events this calculation will give the effect of the temperature on the peak intensity, but not on its width.

Some difficulty appears when inelastic effects are included to compute the effect of the temperature on the width of the diffraction peaks. In a simple perturbation theory such effects appear in the cross section through the Fourier transform of $\langle \rho(\vec{r},t)\rho(0,0) \rangle$ with respect to time and space. The projectile samples now the <u>correlated</u> motion of <u>all</u> the particles within the density-density correlation length l_c. Therefore we must scatter a two dimensional planar wave from a surface of area l_c^2 and this requires the propagation of a very large number of Gaussians, and simultaneously the generation of the correlated motion of all the lattice atoms within l_c^2. This is a rather expensive calculation which will provide a great incentive for finding a way to circumvent it by incorporating the inelastic processes through perturbation theory: this should work for light scatterers and heavy lattice atoms.

II.E. Surface scattering

In this section we examine the effect of the beam coherence σ on scattering from a surface consisting of a hard wall on which we superimpose a potential $V(x,y,z)$ which is periodic in a direction parallel to the surface and decays exponentially in the direction of the vacuum. To compute the scattering probability we use the distorted wave approximation: the hard wall is treated exactly and $V(x,y,z)$ is considered a small perturbation. This model allows us to gain some insight into the relationship which the coherence length in the z direction σ must have with the potential range λ^{-1} and the lattice constant c. in order that scattering of the wave packet by the surface mimics the case of a planar wave. We find that unless σ exceeds both λ^{-1} and c the calculated diffraction intensity is strongly affected by the use of a wave packet.

A zeroth order Hamiltonian which describes surface scattering is obtained by adding a term $V'(z)$ to H_o in Equation (2.2), where

$$V'(z) = \infty \quad z \leq 0$$

and (2.12)

$$V'(z) = 0 \quad z > 0 \ .$$

The eigenstates of $H_o + V'(z)$ are

$$\psi_i(\vec{r}) = e^{i\vec{K}\vec{R}} (e^{i\kappa z} - e^{-i\kappa z}) \quad z > 0$$

and (2.13)

$$\psi_i(\vec{r}) = 0 \ . \quad z \leq 0 \ .$$

The initial state is

$$\psi_i(\vec{r}) = (4\pi a^2)^{-1/2} \int_{-\infty}^{\infty} d\kappa \exp\{-[(\kappa-\kappa_1)/2a]^2\}$$

$$e^{-i(\kappa_1 \cdot z_1)} e^{i\vec{K}\cdot\vec{R}} (e^{i\kappa z} - e^{-i\kappa z}), \quad \text{for } z>0. \tag{2.14}$$

and

$$\psi_i(\vec{r}) = 0, \quad \text{for} \quad z \leq 0.$$

The wave function $\psi_i(r)$ consists of two wave packets, one in the vacuum and the other one inside the solid, symmetrically located with respect to the surface. When $\psi_i(\vec{r})$ is propagated in time, both packets move towards the surface and overlap there. Then the packets separate again and there is only one in the vacuum. Since by definition, $\psi_i(\vec{r})=0$ for $z \leq 0$, the sum of the two packets has no meaning for $z \leq 0$; only the values of ψ_i for $z > 0$ contribute to the wave function of the system.

To the zeroth order Hamiltonian described above we add

$$V(r) = \sum_{n,m}^{N_x,N_y} V_{xy}(\vec{r}-\vec{R}_{nm})\, e^{-\gamma z} \tag{2.15}$$

where $\vec{R}_{nm} = nc\hat{x} + mc\hat{y}$

This potential introduces an interaction length γ^{-1} in the z-direction and a lattice parameter c in the x,y plane.

By using the methods described in the preceding sections we find

$$P(\vec{k}') = \frac{\pi}{\hbar^2 a^2 v_1^2} |\tilde{V}_{xy}(\Delta\vec{K})|^2 f(\Delta k_x)\, f(\Delta k_y) \exp\{-(\Delta\epsilon/a\hbar v_1)^2/2\} \tag{2.16}$$

$$\frac{4(k_1 - \epsilon)^2}{[\gamma^2 - (\kappa' - \kappa_1 - \epsilon)^2][\gamma^2 - (\kappa_1 + \kappa' - \epsilon)^2]}$$

where $\epsilon = \Delta\epsilon\, \hbar v_1$, and $\tilde{V}_{xy}(\Delta\vec{K})$ is the Fourier transform of the x,y part of the potential. Note that the Laue conditions for scattering in k_x and k_y, i.e. $f(\Delta k_x)f(\Delta k_y)$, factor out. This happens because we have separated the x,y part of the potential from the z part (i.e. because v(x,y,z) has the form f(x,y) g(z)) and because $\psi_i(\vec{r})$ is a plane wave in the direction parallel to the surface. However, similarly to the case of bulk scattering, the use of a wave packet in the variable z causes a broadening of the diffraction peaks in the variable κ' (which is equivalent to the polar angle θ).

For the case of an infinite surface we can rewrite Eq. (2.16) as a sum over diffraction peaks

$$P(k^1) = (\pi/\hbar^2 a^2 v_1^2) \sum_{n,m} |\tilde{V}_{xy}(\Delta\vec{K}_{nm})|^2 \exp\{-\epsilon_{nm}^2/2a^2\} \tag{2.17}$$

$$\frac{4(k_1 - \epsilon_{nm})^2}{[\gamma^2 - (\kappa' - \kappa_1 - \epsilon_{nm})^2]\,[\gamma^2 - (\kappa' + \kappa_1 - \epsilon_{nm})^2]}$$

where

$$\epsilon_{nm} = (1/2\kappa_1)[\Delta_{nm} - \kappa_1^2 - (\kappa')^2]$$

$$\Delta_{nm} = K^2 - (K'_{nm})^2$$

and

$$\vec{K}_{nm} = \vec{K} - [2\pi n/c]\hat{(x)} - [2\pi m/c]\hat{y}$$

In the coherent limit, a goes to 0 and the Gaussian term in Eq.

(2.17) dominates the diffraction structure along κ', becoming a delta function which enforces energy conservation for each peak. The probability peaks sharply at $\epsilon_{nm} = 0$, and the Lorentzian term, which results from the Fourier transform of the exponential repulsion, partially determines the intensity at each peak.

For the case of a finite coherence length, both the Gaussian and the Lorentzian terms in (2.17) can contribute to the diffraction structure. Which term dominates, and under what conditions we reach the coherent limit depends not only upon the packet width a^{-1} and the interaction length γ^{-1}, but also on Δ_{nm} and κ_1. The requirements for reaching this limit (where we have a single peak at $\epsilon_{nm} = 0$ for each n,m) are in general complicated, but a few observations can be made.

The Lorentzian term, which has a width γ, peaks when the perpendicular final momentum κ' satisfies

$$\kappa' = |\kappa_1| \pm \Delta_{nm}^{1/2} \quad .$$

We have assumed that the uncertainty in κ, which is equal to $\sqrt{2} = \sqrt{2}/\sigma$, is less than κ_1, such that ($\epsilon_{nm} < \kappa_1$ and) only the second term in the denominator of Eq. (2.17) gives peaks. The Gaussian term has a width $\sqrt{2}\, a = \sqrt{2}/\sigma$ and peaks at

$$\kappa' = [\kappa_1^2 - \Delta_{nm}]^{1/2}$$

where $\epsilon_{nm} = 0$. We see that these three peaks only overlap for the specular case, where $\Delta_{nm} = 0$ and $\kappa' = -\kappa_1$. If the packet width is too narrow, (making a too large) such that the Gaussian term is broad enough to overlap significantly with the Lorentzian peaks, than these peaks can dominate. In this case we would see two maxima as we scan along Θ, one on each side of the expected (for planar wave) $\epsilon_{nm} = 0$ position. Consider the case of some

low order diffraction peak where Δ_{nm} is small and positive, such that $\Delta_{nm}^{1/2} << |\kappa_1|$. If $\gamma < |\kappa_1|$, we recover the coherent limit when the width of the Gaussian is less than the spacing between the Gaussian and Lorentzian peaks, i.e. $\sigma > [2/\Delta_{nm}]^{1/2}$. Thus, when the packet width is larger than $(2/\Delta_{nm})^{1/2}$ we get a single narrow peak at the $\epsilon_{nm} = 0$ position. For larger Δ_{nm}'s where $\gamma < \Delta_{nm}/2\ \kappa_1$, the interaction length γ^{-1} becomes an important factor. In this limit the Lorentzian peaks are proportional to γ^{-2}. Thus, for a longer interaction length, we generally need a broader σ so that the Gaussian is narrow enough to dominate the scattering and produce a single coherent peak.

For various parameter values, the exact requirements vary. However, for the typical case of a thermal molecular beam hitting a surface with c=2.5Å at a 30^0 angle, with γ^{-1}=2Å, we recover the coherent case for most diffraction peaks when σ is larger than a few Å or so. That is, in this limit we only get a single peak along Θ centered at the κ' value given by $\epsilon_{nm} = 0$. For a larger γ, or shorter interaction length, this limit is reached for smaller values of the packet width.

Note, however, that the peak heights, at their $\epsilon_{nm} = 0$ locations are proportional to a^{-2} and all other dependence on a drops out. Thus the relative peak amplitudes for $\epsilon_{nm} = 0$ are independent of the packet width. This is a result of the assumption that a(t) is a constant. If we make the simple but reasonable assumption that the incoming and scattered packet have different widths, a^{-1} and a'^{-1} respectively, then for $\epsilon_{nm} = 0$

$$P(\vec{\kappa}') \alpha \{[\gamma(a'-a)/a'a]^2 - [(\kappa'-\kappa_1/a - (\kappa'-\kappa_1)/a]^2\}$$
$$\{[\gamma^2-(\kappa'-\kappa_1)^2][\gamma^2-(\kappa'-\kappa_1)^2]\}^{-1} \qquad (2.17)$$

and the relative probabilities between different $\epsilon_{nm} = 0$ peaks is a function of the packet width. For a realistic a(t), this dependence is in general very complex. When a and a' are sufficiently large such that the Gaussian controls the scattering, this dependence goes away.

III. Numerical studies using SHM as implemented by Drolshagen and Heller.

The analysis of the neutron scattering model shows that the coherence length in the z-direction must exceed the lattice spacing, the de Broglie wave length, and the range of the potential. Otherwise the predicted diffraction intensities depend on detailed properties of the packet which are not physical properties of the beam.

Such requirements cannot be satisfied (within SHM) by using extremely broad wave packets since this approach would clash with the demand made by the method used to propagate the packets To describe the situation very briefly let us assume that the initial wave function has been written as a sum of Gaussians. SHM propagates each Gaussian in the sum independently: to do this it uses the time dependent Schrodinger equation with the potential expanded, to second order, in a Taylor series around the instantaneous position $\vec{r}_t$ of the packet. The expansion is legitimate only if the potential is almost constant around $\vec{r}_t$ on the length scale set by the packet width (in the coordinate representation) at the time t. Thus a correct treatment of beam coherence in the z direction requires broad packets in that direction, while the simple propagation scheme requires them to be narrow. The solution to these conflicting demands might be to construct the broad packets required to describe the incident wave function as sums of very narrow wave packets. The trouble with this idea is that once these packets interact with the surface we have no control over their width. In particular, a narrow packet may be broadened by the interaction with the surface more then the propagation scheme would safely permit. The simple models used in the previous section can not address such issues since they use perturbation theory and the packet width changes in time according to the free space dynamics. Therefore to find out whether our fears are founded we must turn

to numerical calculations.

The calculations used here were carried out like in the Drolshagen-Heller papers (DH)[1] which use SHM.

In representing the planar wave as a sum of Gaussians we use packets of the form

$$g(\vec{r},t) = \exp\{-\frac{i}{\hbar}[(\vec{r}-\vec{r}_t)\cdot\vec{A}(t)\cdot(\vec{r}-\vec{r}_t)-\vec{k}_t\cdot(\vec{r}-\vec{r}_t)-\gamma_t]\}$$

where $\vec{r}_t$, $\vec{k}_t$ are real functions of time representing the mean position and momentum of the packet; $\vec{A}(t)$ is a three dimensional matrix with time dependent complex elements; γ_t is a complex function of time. At a time prior to the collision with the surface such packets are added up to form a planar wave function in the x and y variables; a single packet is used in the z-variable. Since prior to the collision the x,y and z variables are decoupled the off-diagonal elements of the matrix A(t) are zero. The width of the packet (i.e. the coherence length) in the z-direction is $(\hbar/\mathrm{Im}A_{zz})^{1/2}$. By using the packets to construct the initial wave function at $t=t_o$ we fix γ_{t_o}, $\vec{r}_{t_o}$ and $\vec{k}_{t_o}$, but leave $A_{ij}(t_o)$, $i\equiv x,y$ or z, unspecified, except for the obvious requirement that if we fix the number of packets used for the fit, their width in the x and y directions should be large enough that they overlap. At first sight this feature is unpleasant, since we would prefer that the initial wave function-which carries all the information regarding how the beam was prepared-should fix the initial conditions for all the parameters in all the Gaussians. Since these parameters are propagated in time by first order differential equations, their final values depend on the initial ones. There is a danger that by making use of the existing flexibility in the choice of $A_{ij}(t_o)$ we can affect at will the final wave function (i.e. the diffraction results). However, Heller[1,2] has made an ingenious use of this freedom to optimize the calculation: he choses $A_{ii}(t_o)$ such that a freely

propagating packet starting at $\vec{r}_{t_o}$ will have a minimum uncertainty (i.e. $ReA_{ii}(t)=0$) at the surface and a very small width. Thus the packet should be narrow in the region where the potential varies fastest, satisfying the dynamic requirement of the SHM at the point where they matter most. The flexibility is thus greatly diminished but not eliminated. One wonders therefore whether the choice for ImA_{ii} affects the final results. Furthermore, it is not clear that by choosing the initial conditions in this way we can control the width in the collision region. These questions are answered in what follows by carrying out numerical calculations.

We consider the case of He scattered by a potential that mimics, very crudely, Pt(111). The interaction with the surface is taken to consist of two parts and is written as

$$V(r) = \sum_i \left[\frac{C_1}{|\vec{r}-\vec{R}_i|^{12}} - \frac{C_2}{|\vec{r}-\vec{R}_i|^{6}}\right] - \frac{C_3}{z^9} - \frac{C_4}{z^3}$$

where $\vec{R}_i$ denotes the position of the i-th surface atom. The first term is a sum of Lennard-Jones interactions of He with a small group of surface atoms. This term is responsible for the x-y variation of the potential and was chosen to give a corrugation of .19 A for a He beam energy of 1.2 kcal mole. The second is a bulk term which results from the pairwise summation of the Lennard-Jones interaction with all of the atoms in the solid. It is only a function of z, has the proper z^{-3} long range attractive part, and was made to produce a well depth of .125 kcal/mole. This particular form for the potential was chosen not to mimic the actual He/Pt(111) system, which has negligible off specular scattering,[10] but to provide a model system with a reasonable corrugation.

In Fig. 1 we plot the width of a packet in the z direction, σ, as a function of the distance from the surface for various

initial values of A(o) chosen such that, if we assume a free space propagation, the packet would be narrowest at the turning point. This can be achieved if we determine A(o) in the following manner. Since in free space there is no coupling between the x,y, and z coordinates, A(t) remains diagonal, and we can simply consider the propagation of some diagonal component A given by

$$A(t) = \frac{iA_T}{\frac{2i}{m} A_T(t-T) + 1} \quad .$$

At the turning point, t=T, $A(T) \equiv iA_T$, and the packet reaches its minimum width at the collision site. Thus A(o) is determined by using the time T and the chosen value for A_T in the above equation. In Fig. 1 we make all 3 diagonal elements in A(o) equal, and choose A_T = .01, 1, and 100, corresponding to free space Gaussian widths, at the classical turning point, of 2.5, .25, and .025 Å respectively. The units of a_T are amu (10^{-14} sec). The potential is plotted directly below in Fig. 2 for easy comparison. We observe a free space propagation up to 2 Å or so when the $\partial^2 V/\partial z^2$ term in the SHM equations starts modifying the width and gives it values differing from the free space ones. In all cases the broadening is out of control; note that in all the trajectories the dynamic effects, present (in SHM) through $\partial^2 V \partial z^2$, dominate the time evolution of the width and broaden it to about the same width, regardless of our choice for a_T: this width exceeds the values permitted by the validity condition of SHM. Thus due to these dynamic effects the interaction with the lattice increases the beam coherence; unfortunately the increase is so large that the validity of SHM, used in the propagation, is uncertain.

In Table 1 we list the peak heights for the specular and a few low order diffraction peaks, calculated using various initial values for A(t) as above. We choose A_T = .1, 1, 10, 100, 1000.

and normalize such that the height of the specular peak (0.0) is 1.0. As mentioned previously we see a non-negligible dependence on the parameter A_T. The results converge for $A_T > 50$ or so. In this regime σ is very broad over most of the trajectory, making a quadratic expansion of the potential invalid. The above analysis has also been applied to a similar system with a purely repulsive exponential gas surface interaction of the form

$$V(\vec{r}) = \sum_i C\, e^{-B|\vec{r}-\vec{R}_i|} \quad ,$$

where $\vec{R}_i$ again labels the position of the surface atom. We chose $B = 2.1\ \text{Å}^{-1}$ and selected c to give a corrugation similar to that of the previous example. This interaction is softer and of longer range than the Lennard-Jones potential used above but leads to similar results and conclusions.

IV. DISCUSSION

The analysis of the preceding section used the simple case of neutron scattering to establish a minimal set of requirements for the use of wave packets to construct diffracted wave functions. As expected the requirements on the dependence of the incident wave function on the "parallel" variable x and y are quite demanding. For the calculation of scattering by ordered systems at T=0 K, or for the calculation of the diffraction peak intensity decrease in elastic scattering from ordered lattices at finite temperature, or for scattering from disordered lattices lacking spatial correlations, the "parallel" coherence area of the beam must exceed the area of the unit lattice. Bloch's theorem can then be used to construct the scattered wave function for the whole lattice. Inelastic scattering from ordered lattices at finite temperature or from disordered lattices with spatial correlation require a parallel beam coherence area equal or larger than the coherence area of the density-density correlation function of the two dimensional scattering centers. These demands reflect the fact that if the beam is to be used to study the surface, its coherence must exceed the surface coherence. If this is not the case we end up using the surface to study the coherence properties of the beam, and this is not one of the aims of surface science.

The only existing comparison[1] between an SHM diffraction calculation and the corresponding "exact" quantum results (obtained by solving the Schroedinger equation numerically by using the standard eigenfunction expansion method) shows good agreement. The numerical experience (the use of the experimental data to test the reliability of the method is not possible since too little is known about the potentials) accumulated so far is too limited to allow us to say whether this is an accident or whether diffraction is peculiarly insensitive to the errors made by SHM. From a practical point of view we cannot be satisfied

with a new method whose reliability can only be established through a comparison with the results obtained with the method which it intends to replace; furthermore, for the most important applications, to disordered surfaces, we cannot benefit from such a comparison since the traditional methods are impractical for this case. It is therefore of importance to examine the fears raised by the use of SHM and the improvements that will alleviate them.

(1) The choice of the initial state. We find that (a) the use of a narrow wave packet for the z-dependence of the wave function is very likely to affect diffraction intensity. To prevent this the packet must be broader than the lattice spacing, de Broglie wave length of the atom and the range of the potential. This suggests that we should work with broad packets and therefore abandon the expansion of the potential (used in SHM) around the center of the packet which is valid only when the packet stays narrow throughout the collision. (b) Another troublesome feature is the choice of the width, to give a narrow minimum uncertainty wave packet at the wall, which is not unique, does not have the effect intended (since the interaction broadens the packet anyway) and it is not physically justifiable. Our application of SHM to curve crossing[11] or to the propagation of Morse states[12] reaches the same conclusion. Therefore we suggest the use of an initial state $\Psi_i(x,y,z)$ which is a two dimensional planar wave multiplied to a broad packet in the z-direction. This represents correctly the coherence of the beam used in experimental studies. We can then fit this state with a sum of Gaussians $\sum_\alpha G_\alpha(x,y,z;\{\lambda_\alpha\})$, where $\{\lambda_\alpha\}$ is a symbol for the set of parameters in the Gaussian α, by minimizing $\Psi_i - \sum G_\alpha$ with respect to all λ_α. Thus the initial values of all parameters are fixed by the physical conditions of the problem. We have found that this procedure improves dramatically[12] the results in another problem that is troublesome for SHM, that of the propagation of Morse eigenfunctions.[13]

(2) The propagation method. SHM can be replaced by a variational method[14] which generates coupled, non-linear first order differential equations for the parameters $\lambda_\alpha(t)$. Thus the parameters in the Gaussian α are affected by the motion of all other Gaussians β through coupling terms that become non-zero whenever α and β overlap. The presence of this coupling is clearly a necessary and important feature since if two Gaussians are present in the same spatial region $S(\vec{r})$ centered around $\vec{r}$ they construct the scattered wave function $\psi(\vec{r};t)$ for $\vec{r}\epsilon S(\vec{r})$ together: it is inconceivable that they can do this with any accuracy, if they propagate at all time independently of each other. This "intergaussian" coupling affects all the parameters, the width, the phase, the mean position and the mean momentum of the packets. It changes the physical picture from that of a set of indepenent Gaussians moving along classical trajectories to a "community" of Gaussians moving on non-classical trajectories that are coupled to each other.

Furthermore there is no need and no general physical or mathematical justification for expanding the potential around the center of the Gaussians. If the potential is fitted to exponentials, Gaussians or polynomials, or any combination of the above, all the integrals appearing in the theory can be done analytically and very little of the SHM simplicity is lost. One of the interesting consequences of giving up the expansion is that the force $\partial V(\vec{r}_t)/\partial \vec{r}_t$ appearing in SHM is replaced by the derivative of $W(\vec{r}_t) = \int G^*(\vec{r})V(\vec{r})G(\vec{r})d\vec{r}$ and this time dependent potential differs in interesting ways from $V(\vec{r}_t)$. For example[15] as the packet approaches the surface $W(\vec{r}_t)$ becomes non-zero as soon as the Gaussian overlaps with the potential. $W(\vec{r}_t;t)$ differs from the classical potential $V(\vec{r}_t)$, changes in time, and tends to come forward and meet the packet. The packet turns around earlier than in the classical case (i e. SHM). Since the motion of the center of the uncoupled packets takes place on

$W(\vec{r}_t,t)$ it is conceivable that this has a different corrugation than the true potential and thus affects diffraction.

We are currently pursuing these improvements of SHM. For the case of curve crossing[11] and of the Morse oscillator[12] they turn out to be essential. For diffraction we are not yet sure. The striking success of SHM[1,2] is partly due to Heller's excellent choice of problems, which involve very localized wave functions that need to be propagated for a very short time and or harmonic oscillator problems in which the Gaussians do not overlap. Diffraction deals with a very delocalized wave function in which the overlap between different Gaussians is very likely. Thus it is difficult to understand why SHM should work well in this case.[1] A conceivable reason might be that the process is dominated by interference, which SHM treats at a semi-classical level (since it gives each trajectory a phase equal to the classical action).

For problems in which the simplifying features mentioned above (i.e. localization and short time processes) are absent, more laborious versions of SHM might be needed. Our limited experience indicates that even with the computational effort added by these improvements Heller's method still has extremely good prospects to contribute substantially to surface science

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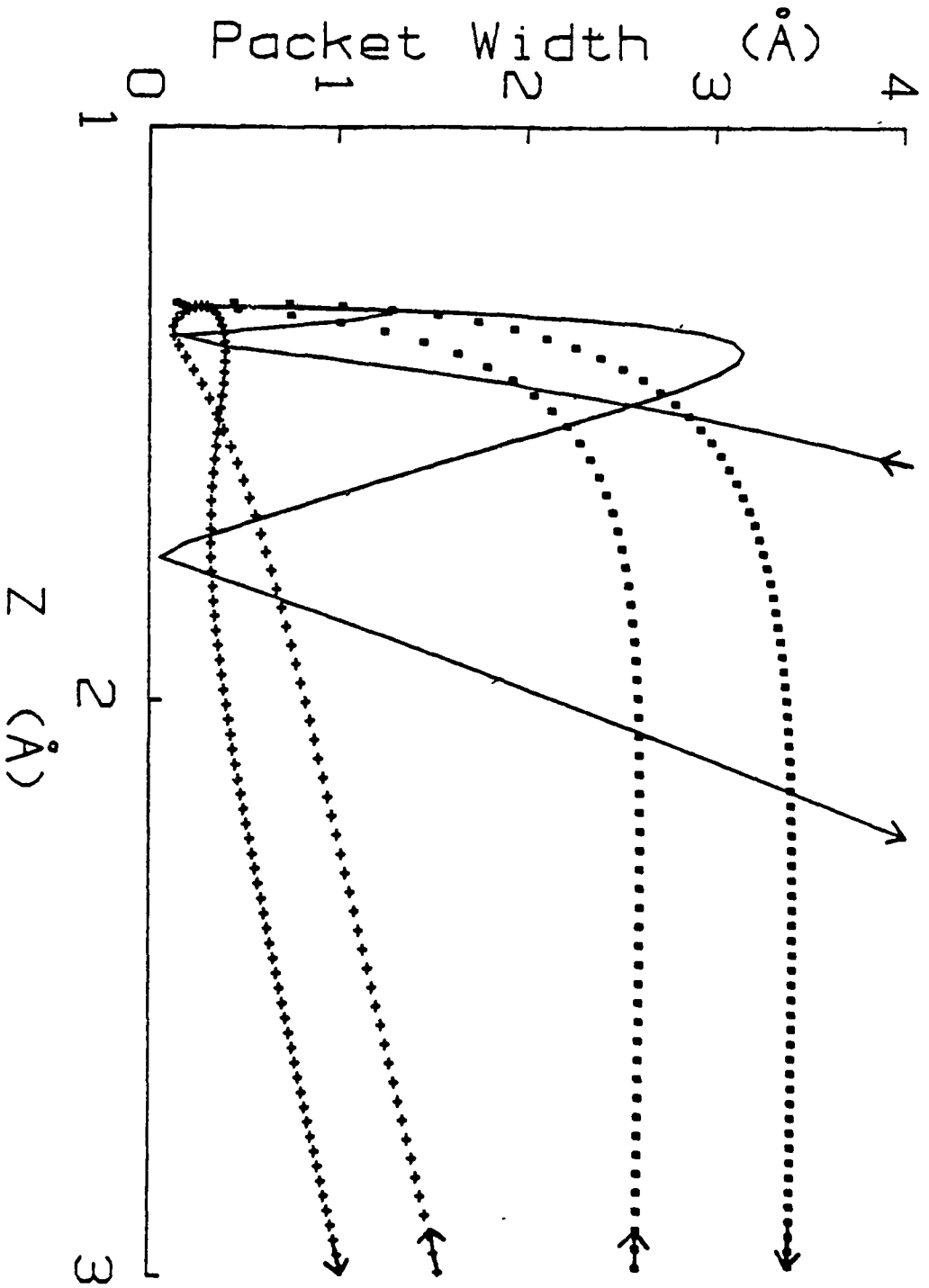
Table 1.

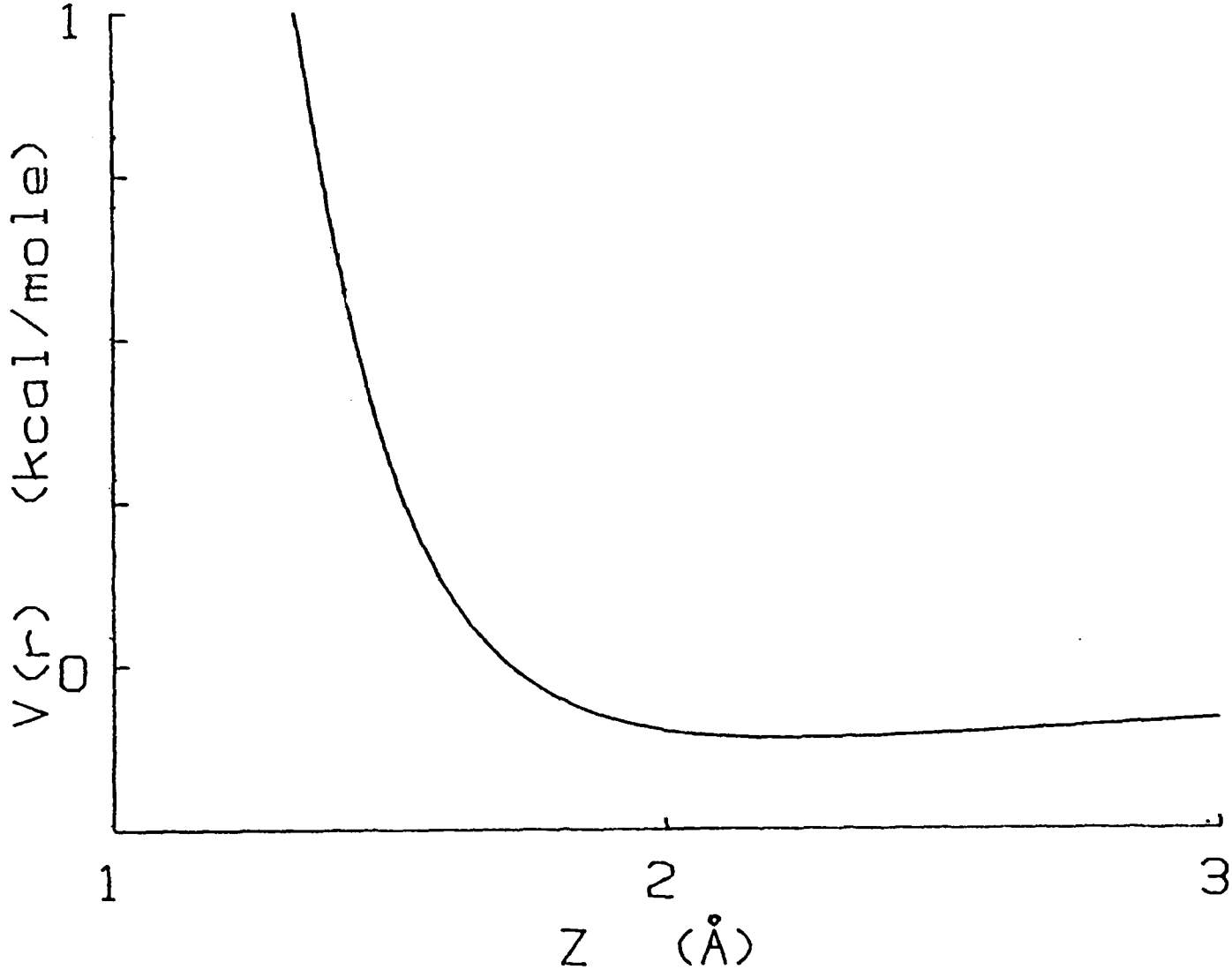
	P_{00}	P_{10}	P_{20}	P_{11}
$a_T = .1$	1.0	.2003	.0215	.0307
$a_T = 1.0$	1.0	.1978	.1388	.2402
$a_T = 10.0$	1.0	.1744	.1367	.3372
$a_T = 100.0$	1.0	.1548	.1472	.3428
$a_T = 1000.0$	1.0	.1528	.1459	.3431

FIGURE CAPTIONS

1. Packet width vs. distance from surface for a_T = .01 (.....), a_T = 1.0 (-----) and a_T = 100 (————). Arrows indicate direction of packet motion.

2. He surface potential for numerical example in text


Packet Width (Å)
0
1
2
3
4
Z (Å)
1
2
3


1
V(r) (kcal/mole)
0
1
2
3
Z (Å)

END

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5-85

DTIC