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How to measure the wavefunction of an adatom: the semiclassical theory of desorbtive scattering

K N Trohidou† and J M F Gunn
Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

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Abstract. It is argued that, when an adatom has several bound states on a substrate, then its ground-state wavefunction can be measured by scattering in which it is desorbed. The requirement is for weak scattering and a short-range interaction with the probe, both conditions being met by a neutron beam. A simple semiclassical picture of the process is presented.

1. Introduction

Several experimental probes measure the position of adsorbed atoms on a surface, e.g. LEED (Pendry 1976) or scanning tunnelling microscopy (Binnig and Rohrer 1987). However, to get detailed information about the ground-state wavefunction of the atoms in its entirety (as against the mean position), is much harder. In this paper we will describe a technique that uses neutrons to measure directly the Fourier transform of the ground-state wavefunction, from which the wavefunction itself is readily extracted.

The physical idea, in classical terms, is that if one particle (the 'target' particle) is struck by another sufficiently hard, the 'environment' of the struck particle (e.g. other target particles) is irrelevant and the collision occurs as though it were in free space. In that case the only variable associated with the struck particle in the problem is its momentum. Thus the scattering will be characteristic of that momentum, and hence is a method of determining momentum distributions (as long as multiple scattering of the probe particle may be neglected). In quantum terms, for single particles, these are the modulus squared or the Fourier transform of the wavefunction. This procedure is particularly simple if the interaction is of a 'contact' form (vanishing range); neutron scattering complies with this requirement and also is a weak probe, so that there are no problems with multiple scattering.

In quantum terms it is a little mysterious how to translate the above idea (see for instance Newton (1982)). In a previous paper (Gunn *et al* 1986) it was shown that, for high-energy transfers, one could treat the final states in a violent collision in a semiclassical manner. In the vicinity of the ground-state wavefunction, ϕ_0, (i.e. near the bottom of the potential well that the struck particle resides in) the final-state wavefunctions look like plane waves, which leads to the matrix elements involved in the cross section becoming Fourier transforms of ϕ_0. This allows the determination of ϕ_0 itself. In this paper we develop a similar argument for the case where the struck

† Present address: Department of Physics, University of Reading, Whiteknights, Reading RG6 2AF, UK

particle can break free from the potential well, and in particular when this occurs at a surface. This entails several new features compared to the previously treated one, where the particles were permanently confined to a potential well.

The plan of the paper is as follows. We first construct the appropriate semiclassical wavefunctions and discuss the validity of the semiclassical approximation; then we calculate the 'desorbtive' cross section in the Born approximation and finally discuss the limitations and extensions of our work.

2. Adsorbate wavefunctions

One aim of the present calculation is to show how one may deduce the ground-state wavefunction, $\phi_0(z)$, associated with motion normal to the substrate (the z direction), from desorbtive scattering. The feature of the scattering which allows us to work backwards, to $\phi_0(z)$, is the assumption that sufficient energy is transferred to the desorbed atom so that its motion is semiclassical. In that case, given the potential $V(z)$, we may immediately write down the wavefunction associated with the desorbed atom, $\psi_\epsilon(z)$, using the WKB approximation (e.g. Dicke and Wittke 1960):

$$\psi_\epsilon(z) = \left(\frac{2}{L}\right)^{1/2}\left(\frac{1-V(z)}{\epsilon^z}\right)^{-1/4}\sin\left(\int_{z_c}^{z_0}\left[(2m/\hbar^2)(\epsilon^z - V(z'))\right]^{1/2}\mathrm{d}z' - \pi/4\right) \tag{2.1}$$

where we have assumed that we are in the 'classically allowed' region, $\epsilon_z > V(z)$, where ϵ_z is the part of the energy not associated with kinetic energy parallel to the substrate. z_c is the classical turning point, where $\epsilon_z = V(z_c)$. Under what conditions is the WKB approximation valid? Basically (Dicke and Wittke 1960) the change in the phase $\eta(z)$:

$$\eta(z) = \int_{z_c}^{z}\left[(2m/\hbar^2)(\epsilon_z - V(z'))\right]^{1/2}\mathrm{d}z' \tag{2.2}$$

must be small compared to $\eta(z)$. That is:

$$\left|\frac{\eta''(z)}{(\eta'(z))^2}\right| = \left|\frac{(\hbar^2/2m)^{1/2}(-1/2)V'(z)}{(\epsilon_z - V(z))^{3/2}}\right| \ll 1. \tag{2.3}$$

As we will see in the next section, we shall be interested in the validity of (2.1) for z the minimum of $V(z)$, where (2.3) vanishes identically. 'Near' means within the extent, l_0, of the ground-state wavefunction. Let us rewrite (2.3), roughly, in terms of the depth of the potential well V_0 and the zero-point energy of the ground state, $\tilde{\epsilon}$, defined by $V_0 - \epsilon_0$, where ϵ_0 is the binding energy of the ground state. Write

$$V'(z_0 + l_0) \simeq l_0 V''(z_0) \simeq \tilde{\epsilon}/l_0. \tag{2.4}$$

Then using $(\hbar^2/2ml_0^2)^{1/2} \sim \tilde{\epsilon}^{1/2}$, we find that the criterion for the validity of (2.1) near the minimum of $V(z)$ is:

$$\left[\tilde{\epsilon}/(\epsilon_z - V(z_0))\right]^{3/2} \ll 1. \tag{2.5}$$

Therefore, as long as the zero-point energy is a small fraction of the well depth, WKB will be applicable.

Alternatively, if we use the definition

$$p = \left[2m(\epsilon_z - V(z))\right]^{1/2} \tag{2.6}$$

for the particle momentum, we can write the equality (2.3) in a different form:

$$p^3 \gg m\hbar\left|\frac{\mathrm{d}V(z)}{\mathrm{d}z}\right|. \tag{2.7}$$

It follows from (2.7) that the WKB approximation is applicable for the motion of particles with large momenta in a potential field with a small gradient (Davydov 1976).

3. Desorbtive cross section

In this section we will define the desorbtive cross section and calculate it in the limit of weak scattering (Born approximation) for the particular case of neutron scattering. Given our aim of deriving information on the ground-state wavefunction of the absorbate, we will assume that we may use the semiclassical results of section 2.

If $\mathrm{d}\sigma(\theta, \phi; \theta_t, \phi_t; E')$ is the part of the total cross section associated with final motion of the scattered particles in the direction θ, ϕ, with energy E' and of the target particle in direction θ_t, ϕ_t, then we may define the 'desorbtive cross section', $\mathrm{d}^3\sigma/\mathrm{d}\Omega\,\mathrm{d}\Omega_t\,\mathrm{d}E'$, by

$$\mathrm{d}\sigma = \frac{\mathrm{d}^3\sigma}{\mathrm{d}\Omega\,\mathrm{d}\Omega_t\,\mathrm{d}E'}\mathrm{d}\Omega\,\mathrm{d}\Omega_t\,\mathrm{d}E'. \tag{3.1}$$

In fact we will find that for kinematic reasons we end up with the partial differential cross section.

As stated above, for neutron scattering, the Born approximation is quite sufficient (using the Fermi pseudopotential $V(\boldsymbol{r}) = 4\pi(\hbar^2/2m)b\delta(\boldsymbol{r})$, b being the s wave scattering length and m is the mass of the neutron) and we may trivially generalise the usual treatment of the partial differential cross section (Lovesey 1986) to the desorbtive cross section.

$$\frac{\mathrm{d}^3\sigma}{\mathrm{d}\Omega\,\mathrm{d}\Omega_t\,\mathrm{d}E'} = \sum_{\boldsymbol{k}',\boldsymbol{\kappa}'}\frac{(\mathrm{d}/\mathrm{d}t)(|a_{\boldsymbol{k}',\boldsymbol{\kappa}'}(t)|^2)N\delta(\Omega_{k'}-\Omega)\delta(\Omega_{\kappa'}-\Omega_t)\delta[(\hbar^2k'^2/2m)-E']}{L^{-3}N(\hbar k/m)}. \tag{3.2}$$

Here N is the total number of neutrons in volume L^3, $\boldsymbol{k}'$ and $\boldsymbol{k}$ are their final and incident wavevectors and $\boldsymbol{\kappa}'$ is the final wavevector of the target particle. $a_{\boldsymbol{k}',\boldsymbol{\kappa}'}(t)$ is the amplitude for the neutron and target particle to have wavevectors $\boldsymbol{k}'$ and $\boldsymbol{\kappa}'$. The delta functions select the values of $\boldsymbol{k}'$ and $\boldsymbol{\kappa}'$ consistent with the neutron emerging in direction $\Omega = (\theta, \phi)$ with energy E' and the desorbed particle in $\Omega_t = (\theta_t, \phi_t)$.

Now use the Fermi's golden rule expression for $(\mathrm{d}/\mathrm{d}t)|a_{\boldsymbol{k}',\boldsymbol{\kappa}'}(t)|^2$ (where $\boldsymbol{Q}^{\parallel} = \boldsymbol{\kappa}' - \boldsymbol{\kappa}$, $\boldsymbol{q}^{\parallel} = \boldsymbol{k}' - \boldsymbol{k}$ and $\boldsymbol{r}^{\parallel}$ is the component of the position vector parallel to the surface):

$$\begin{aligned}(\mathrm{d}/\mathrm{d}t)|a_{\boldsymbol{k}',\boldsymbol{\kappa}'}(t)|^2 &= (2\pi/\hbar)(2/L^{11})[4\pi(\hbar^2/2m)b]^2 \\ &\quad\times\left|\int \mathrm{d}\boldsymbol{r}^{\parallel}\,\exp(\mathrm{i}\boldsymbol{q}^{\parallel}\cdot\boldsymbol{r}^{\parallel})\exp(-\mathrm{i}\boldsymbol{Q}^{\parallel}\cdot\boldsymbol{r}^{\parallel})\int \mathrm{d}z\,\phi_0(z)\psi_\epsilon(z)\exp(\mathrm{i}q^z z)\right|^2 \\ &\quad\times\delta(E'+\epsilon-E-\epsilon_0).\end{aligned} \tag{3.3}$$

Here ϵ is the total final energy of the target particle and E is the incident neutron energy. We may perform the $\boldsymbol{r}^{\parallel}$ integration to yield:

$$\left|\int \mathrm{d}\boldsymbol{r}^{\parallel} \exp(\mathrm{i}(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel}) \cdot \boldsymbol{r}^{\parallel})\right|^2 = (2\pi)^2 L^2 \delta(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel}) \tag{3.4}$$

expressing conservation of momentum parallel to the substrate.

The deduction of $\phi_0(z)$ from the desorbtion cross section depends on the simplification of the integral over z in (3.3) in the semiclassical limit. The physical simplification is that (Gunn *et al* 1986) in the region that the ground-state wavefunction, $\phi_0(z)$, is significantly non-zero, the kinetic energy of the final state changes little since the potential energy varies insignificantly compared to the total energy. Mathematically this implies that we may replace the WKB wavefunction $\psi_\epsilon(z)$ by a plane wave of the wavevector corresponding to the centre of the ground state, z_0, with a phase shift η.

$$\psi_\epsilon(z) \simeq (2/L)^{1/2}(1 - V(z_0)/\epsilon_z)^{-1/4} \sin(\eta + (z - z_0)\kappa'^z) \tag{3.5}$$

where

$$\kappa'^z = [(2m/\hbar^2)(\epsilon_z - V(z_0))]^{1/2} \qquad \eta = \int_{z_c}^{z_0} [(2m/\hbar^2)(\epsilon_z - V(z'))]^{1/2} \mathrm{d}z' - \pi/4. \tag{3.6}$$

We may now readily perform the z integration in (3.3) to arrive at

$$\begin{aligned}(\mathrm{d}/\mathrm{d}t)|a_{\boldsymbol{k}',\boldsymbol{\kappa}'}(t)|^2 &= [(2\pi)^3/\hbar](2/L^9)[4\pi(\hbar^2/2m)b]^2 \delta(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel})[1 - (V(z_0)/\epsilon_z)]^{-1/2} \\ &\quad \times (1/4)\delta(E' + \epsilon - E - \epsilon_0) \\ &\quad \times |\exp(\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z + \kappa'^z) - \exp(-\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z - \kappa'^z)|^2. \end{aligned} \tag{3.7}$$

(where $\tilde{\phi}_0(k)$ is the Fourier transform of $\phi_0(z)$).

Substituting this into (3.2), and letting the sums become integrals, we find:

$$\begin{aligned}\frac{\mathrm{d}^3\sigma}{\mathrm{d}\Omega\, \mathrm{d}\Omega_t\, \mathrm{d}E'} &= \frac{b^2}{2\pi}\frac{1}{2k}(\hbar^2/m) \int\int \delta(E' + \epsilon - E - \epsilon_0)\delta(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel})[1 - (V(z_0)/\epsilon_z)]^{-1/2} \\ &\quad \times \mathrm{d}\boldsymbol{k}'\mathrm{d}\boldsymbol{\kappa}' |\exp(\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z + \kappa'^z) - \exp(-\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z - \kappa'^z)|^2 \\ &\quad \times \delta(\Omega_{k'} - \Omega)\delta(\Omega_{\kappa'} - \Omega_t)\, \delta[(\hbar^2 k'^2/2m) - E']. \end{aligned} \tag{3.8}$$

Now changing variables to polar coordinates for $\boldsymbol{k}'$ and $\boldsymbol{\kappa}'$ we find:

$$\begin{aligned}\frac{\mathrm{d}^3\sigma}{\mathrm{d}\Omega\, \mathrm{d}\Omega_t\, \mathrm{d}E'} &= \frac{b^2}{2\pi}\frac{k'}{k}\delta(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel})[1 - (V(z_0)/\epsilon_z)]^{-1/2}\kappa'^2(2M/[\hbar^2\kappa'^2])(1/4\kappa') \\ &\quad \times |\exp(\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z + \kappa'^z) - \exp(-\mathrm{i}(\eta - z_0\kappa'^z))\tilde{\phi}_0(q^z - \kappa'^z)|^2 \end{aligned} \tag{3.9}$$

where now $\boldsymbol{q}$ and $\boldsymbol{Q}$ are implicit functions of $\Omega_{k'}$ and $\Omega_{\kappa'}$.

The interpretation of the first two terms is conventional (Lovesey 1986). Turning to the other terms, the inverse of the recoil energy, $2M\hbar^2\kappa'^2$, indicates the approximate spread of the allowed energy transfers for momentum transfer to the desorbed particle of about $\hbar\boldsymbol{\kappa}'$. Thus this factor is associated with the 'd/dE'' of the left-hand side. The term $\kappa'^2\delta(\boldsymbol{q}^{\parallel} - \boldsymbol{Q}^{\parallel})$ implies the kinematic constraint linking $\Omega_{k'}$ and $\Omega_{\kappa'}$. The final term is the interesting one in terms of deducing $\phi_0(z)$. If one can ignore interference between the two constituent terms inside the modulus squared, then one finds

$$\frac{d^3\sigma}{d\Omega\, d\Omega_t\, dE'} \propto |\tilde{\phi}_0(q^z + \kappa'^z)|^2 \tag{3.10}$$

that is the momentum distribution of the state $\phi_0(z)$. Fourier transformation of (3.10) immediately yields $\phi_0(z)$. The condition for the lack of interference is that the wavevector, κ'^z, of the final state should be much larger than the momentum spread of the initial state.

It is interesting to note the behaviour in the opposite limit, where both q^z and κ'^z are small compared to the momentum spread. In that case

$$\tilde{\phi}_0(q^z + \kappa'^z) \propto \exp(i(q^z + \kappa'^z)z_0) \tag{3.11}$$

thus yielding for the desorbtion cross section:

$$\frac{d^3\sigma}{d\Omega\, d\Omega_t\, dE'} \propto \sin^2\eta. \tag{3.12}$$

Equation (3.12) has an interpretation in terms of the 'geometric optics' of the classical trajectories of the desorbed particle, reflecting interference between the directly outgoing wave and the outgoing wave which has been reflected by the potential barrier of the substrate. This interpretation is clear, remembering the expression for η, (3.6). This result might suggest using desorbtive scattering as an 'interferometric' measure of the average separation of the absorbed atom and the substrate. However, the positional spread in $\phi_0(z)$ is usually of the same order as the separation, so implying that one wants to impose contradictory inequalities on κ'^z: that simultaneously it is smaller than the momentum spread but larger than the inverse separation.

One entertaining feature of the scattering process, now considered in three dimensions, is that as these outgoing particles move out of the potential well at the surface, they slow down, i.e. the momentum perpendicular to the surface decreases. This implies, since momentum is conserved parallel to the surface, that the particle trajectories 'refract' towards the substrate. In the limiting case when the final energy is zero, then the trajectories become asymptotically parallel to the surface. In general the scattering is predominantly away from the normal to the surface due to this reason.

4. Discussion and conclusions

We have shown that the ground-state wavefunction of an adsorbed particle may be determined by desorbtive scattering, as long as the scattering is sufficiently weak that one may use the Born approximation. For the case of neutrons, this is certainly true. Conversely one may worry that the interaction is *too* weak to detect any surface-specific scattering. However, as long as the surface area is sufficiently large (for example, for a powder) experiments on surfaces may be performed: see for instance section 9 of the review by Howard and Waddington (1980) and the recent example of a study of H on MoS_2 by Jones *et al* (1988). At present the technique that we are proposing would be most practicable for hydrogenous adsorbates, both for reasons of cross sections and kinematics, mentioned below. Another worry might be the need for high-energy neutrons (to allow the high-energy transfer); however, the recent development of spallation sources of neutrons has alleviated that difficulty.

One assumption that made the above analysis simple was that the substrate was 'inert' in the sense that it provided only a static potential and did not recoil when desorbing particles collided with it. To what extent is this a valid assumption? Basically it depends on the mass of atoms constituting the substrate, M_s, compared to the mass of the atoms being desorbed, M. If $M \ll M_s$, then the no-recoil assumption is sustainable, as the recoil energy $\propto (M/M_s)$.

Another assumption is that we could neglect neutrons being scattered from the *substrate* itself; which might complicate the interpretation of the cross section at the energies or momenta of interest. Again this neglect is reasonable if $M_s \gg M$. Then the recoil energy of the substrate (when the *neutron* strikes it) will be small compared to that of the desorbing particle, and hence well separated from it.

Finally we have assumed that the surface was smooth and not, for instance corrugated. This was merely for simplicity and such effects could be included for a detailed comparison with experimental data.

It is interesting to ask if the *above* treatment can be applied to other neutral particle beams, perhaps which are more surface-sensitive such as He-atom scattering. There are two difficulties here: firstly the scattering is strong, so that multiple scattering of the He atom may be a problem. Secondly the form of the interaction potential is more complicated than that for the case of neutrons. Thus probably our treatment is limited in applicability to neutron beams.

In conclusion we have shown how desorbtive neutron scattering allows the measurement of the ground-state wavefunction of an absorbed particle. This relies on there being several bound states in the surface potential well.

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