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Richard I. Masel, Robert P. Merrill, and William H. Miller

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ON ATOM SCATTERING FROM SOLID SURFACES

by

Richard I. Masel, Robert P. Merrill

Department of Chemical Engineering
University of California
Berkeley, California 94720

and

William H. Miller

Department of Chemistry, and Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

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ABSTRACT

The boundary conditions for elastic atom scattering at a sinusoidal hardwall are considered. The wave function must vanish on and below the surface and be outward-going only. Specifically, solutions of the Rayleigh form such as Beeby has presented are not outward-going only and fail to treat the closed channel properly.

In a previous paper (Masel et al.) in order to model atom scattering from solid surfaces we presented a solution of the Schrödinger equation for scattering of an incident plane wave from a sinusoidal hardwall. The derivation began with the Lippmann-Schwinger (1950) integral equation for the wavefunction

$$\psi(x,z) = \Phi(x,z) + \int dx' \int dz' \; Go^{+}(x,z;x',z') \; V(x',z') \; \psi(x',z') \quad , \quad (1)$$

where

ψ = the wavefunction

Φ = the incident plane wave

V = the scattering potential

G_o^+ = the free particle green's function with outgoing boundary conditions.

The wavefunction ψ determined by Eq. (1) is also a solution to the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V-E\right)\psi = 0 \quad , \quad (2)$$

but the integral equation is a more useful starting point since the correct scattering boundary conditions (incident plane wave plus purely outgoing radial waves) are explicitly contained in it and need not be supplied at some later stage of the calculation.

In our previous paper (Masel et al.) we show that for a hardwall potential defined by

$$V(x,z) = \begin{cases} 0, & z > D(x) \\ +\infty, & z < D(x) \end{cases} \quad , \quad (3)$$

where x = distance along the surface which is structureless in the y direction and z = distance perpendicular to the surface, the quantity $V\psi$ is given by

$$V(x,z)\ \psi(x,z) = f(x)\ \delta[z-D(x)] \quad , \tag{4}$$

where $\delta[z-D(x)]$ is the Dirac delta function and f(x) is a function yet to be determined; Eq. (4) is easily deduced from Eq. (2). Substituting Eq. (4) into Eq. (1) (and performing the integration over z') gives wavefunction as

$$\psi(x,z) = \Phi(x,z) + \int dx'\ Go^{+}(x,z;x',D(x'))f(x') \quad . \tag{5}$$

The function f(x) is then determined by the requirement that $\psi(x,z) \equiv 0$ below the surface. Applying this condition for the special case

$$D(x) = ah\ \sin(2\pi x/a) \tag{6}$$

yields (Masel <u>et al.</u>) a solution that we will label ψ_1. ψ_1 is given explicitly by

$$\psi_1(x,z) = \phi(x,z) - \sum_{n=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} C_n \frac{e^{ik\sin\theta_\ell}}{\cos\theta_\ell} \times$$

$$\frac{1}{a} \int_{-1/2}^{1/2} dx'\ e^{i[2\pi(n-\ell)(x'/a) + k\cos\theta_\ell|z-D(x')|]} \quad , \tag{7}$$

where the constants C_n are determined by the linear equations

$$\cos\theta_I\ \delta_{\ell,0} = \sum_{n=-\infty}^{\infty} C_n\ J_{n-\ell}(hka\cos\theta_\ell) \quad . \tag{8}$$

See our previous paper (Masel et al.) for the definitions of the various quantities in Eqs. (7)-(8), more details of the derivation, and explicit formulae for the scattering cross sections.

Beeby (1971, 1972, 1973, 1974, and personal communication, 1974, 1975) has suggested an alternate procedure for calculating the wavefunction. In his formulation the position of the "emitter surface"--the function $D(x')$ in Eq. (5)--is deemed to be irrelevant (provided it is on or below the actual surface). The boundary conditions are $\psi(x,z) = 0$ on the surface and specification of the incident wave at large distances from the surface. The trouble with this approach is that the resulting wavefunction is not zero in all regions below the surface and thus is not a solution to the Schrödinger equation; this is easy to see from Eq. (2) because the term $V\psi$ will be infinite if ψ is not zero when V is infinite. In our previous paper (Masel et al.), for example, we showed that if the "emitter surface" were taken to be a plane below the surface, then a different wavefunction ψ_2 is obtained:

$$\psi_2(x,z) = \Phi(x,z) + \sum_{n=-\infty}^{\infty} \frac{C_n^{\,b}}{\cos\theta_n} e^{i(k_n^{\,x} x - k_n^{\,z}|z-y| + k_n^{\,z} y)} , \qquad (9)$$

where $y < -ha$ and where the coefficients $C_n^{\,b}$ are determined by

$$J_\ell(ak_z^0 h) = \sum_{n=-\infty}^{\infty} \frac{C_n^{\,b}}{\cos\theta_n} J_{n-\ell}(akh\cos\theta_n) . \qquad (10)$$

Since ψ_2 is not zero below the surface, Beeby (1971) has in effect suggested that a new wavefunction ψ_3 is the correct wavefunction:

$$\psi_3(x,z) = \psi_2(x,z)\, q[z-D(x)] \quad , \tag{11}$$

where $q[z-D(z)]$ is the step function,

$$q(y) = \begin{cases} 1, & y > 0 \\ 0, & y < 0 \end{cases} \quad .$$

Although one can readily verify that ψ_3 does satisfy the Schrödinger equation above and below the surface, it does not satisfy the Lippmann-Schwinger equation, Eq. (1), and therefore is not the <u>particular</u> solution of the Schrödinger which has the correct scattering boundary conditions.

To show this, we start with the Schrödinger equation

$$V\psi = \left(E + \frac{\hbar^2\nabla^2}{2\mu}\right)\psi \tag{12}$$

and apply it to ψ_3 (setting $\hbar = 1$ for simplicity)

$$V\psi_3 = \left(E + \frac{\nabla^2}{2\mu}\right)\psi_3 \quad . \tag{13}$$

Direct evaluation gives, for $\psi_2 \equiv 0$ at $z = D(x)$,

$$V\psi_3 = \frac{1}{2\mu}\,\delta[z-D(x)]\left[\frac{\partial\psi_2}{\partial z} - \frac{\partial\psi_2}{\partial x}\,\frac{\partial D(x)}{\partial x}\right] \quad . \tag{14}$$

Defining $\widehat{\psi_3}$ by

$$\widehat{\psi_3} = \Phi_I + \int G_o^+\, V\psi_3 \quad , \tag{15}$$

this expression can be evaluated using the methods in our previous paper; the result is, for $z \geqslant ha$,

$$\overline{\psi_3} = \Phi_I + \sum_{\ell} \frac{\Phi_\ell}{2} \Big\{ J_\ell[(\cos\theta_I + \cos\theta_\ell)hka] +$$

$$\pi h \tan \Phi_I \Big[J_{\ell-1}[(\cos\theta_I + \cos\theta_\ell)hka] +$$

$$J_{\ell+1}[(\cos\theta_I + \cos\theta_\ell)kha] \Big] +$$

$$\sum_n C_n^b \Big\{ J_{n-\ell}[(\cos\theta_n - \cos\theta_\ell)hka]$$

$$+ \pi h \tan \theta_n \Big[J_{n-\ell-1}[(\cos\theta_n - \cos\theta_\ell)hka] +$$

$$J_{n-\ell+1}[(\cos\theta_n - \cos\theta_\ell)hka] \Big] \Big\} \Big\} \qquad (16)$$

unless $h \equiv 0$ ψ_3 and $\overline{\psi_3}$ are not the same. This means that in the general case ψ_3 does not satisfy the Lippmann Schwinger Equation, i.e., the condition that the scattered wave is outward going only, and so it is not a valid wavefunction for the scattering problem. The possibility exists, however, that due to an unobvious cancellation of errors this formulation of the Beeby solution could yield the correct scattering distribution far above the surface. Eq. (10) is identical to Rayleigh's equation (1907) for an analogous problem in optics. There is a wealth of literature discussing its validity (for a review see Millar, 1973). Petit and Cadilhac (1966) have demonstrated that if one attempts to solve the equation by only considering the C_n's that satisfy

$$|n| \leq N$$

the results for $h > .0714$ do not converge with increasing N, which supports our contention that Beeby's method is not correct.

Finally, an explicit demonstration that our boundary conditions and Beeby's give different scattering can be seen by constructing the matrix expressions for the S-matrices that result from the two approaches. Applying our boundary condition one finds the S-matrix to be

$$\underline{\underline{S}}_1 = \underline{\underline{N}} \cdot \underline{\underline{M}}^{-1} \quad , \tag{17}$$

where $\underline{\underline{M}}$ and $\underline{\underline{N}}$ are the matrices

$$M_{\ell,n} = J_{n-\ell}(akh \cos\theta_\ell) / \; k \cos\theta_\ell \tag{18}$$

$$N_{\ell,n} = J_{\ell-n}(akh \cos\theta_\ell) / \; k \cos\theta_\ell \quad , \tag{19}$$

while Beeby's boundary condition gives the S-matrix as

$$\underline{\underline{S}}_2^{tr} = \underline{\underline{M}} \cdot \underline{\underline{N}}^{-1} \quad , \tag{20}$$

$$tr \equiv \text{transpose} \quad .$$

At first glance it appears from Eqs. (17) and (20) that $\underline{\underline{S}}_2^{tr} = \underline{\underline{S}}_1^{-1}$, and since by unitarity $\underline{\underline{S}}_1^{-1} = \underline{\underline{S}}_1^{+} = (\underline{\underline{S}}_1^{tr})^*$, it would follow that $\underline{\underline{S}}_2 = \underline{\underline{S}}_1^{*}$, so that the two approaches would give the same diffraction probabilities. The trouble is that $\underline{\underline{M}}$ and $\underline{\underline{N}}$ are <u>infinite</u> matrices, whereas the S-matrix is finite, and the meaning of Eqs. (17) and (20) is that $\underline{\underline{S}}_1$ and $\underline{\underline{S}}_2^{tr}$ are the finite, open-channel block of the infinite matrices $\underline{\underline{N}} \cdot \underline{\underline{M}}^{-1}$ and $\underline{\underline{M}} \cdot \underline{\underline{N}}^{-1}$, respectively. It is well-known, however, that if $\underline{\underline{A}}_{1,1}$ is a finite block of the infinite matrix $\underline{\underline{A}}$--i.e.,

$$\underline{\underline{A}} = \begin{bmatrix} \underline{\underline{A}}_{1,1} & \longrightarrow \\ \downarrow & \searrow \end{bmatrix}$$

--then

$$(\underline{\underline{A}}_{1,1})^{-1} \neq (\underline{\underline{A}}^{-1})_{1,1} \quad ;$$

i.e., the inverse of the finite matrix $\underline{\underline{A}}_{1,1}$ is not equal to the 1-1 block of the infinite matrix A^{-1}. Eqs. (17) and (20) therefore do not imply that $\underline{\underline{S}}_1^{-1} = \underline{\underline{S}}_2^{tr}$.

Eqs. (17) and (20) do show, however, that if $\underline{\underline{N}}$ and $\underline{\underline{M}}$ are approximated by finite matrices that retain only the open channels ($\underline{\underline{M}}$ and $\underline{\underline{N}}$ are then of the same dimension as $\underline{\underline{S}}$), then it does follow that $\underline{\underline{S}}_2 = \underline{\underline{S}}_1$. This is consistent with our view that Beeby's formulation fails in the way it includes the closed channels, i.e., higher order multiple scattering. As in any inelastic scattering problem, closed channel terms in the wavefunction die out exponentially when one is far from the interaction region (i.e., the surface), but they are present in the interaction region (i.e., near the surface) and they must be included correctly in order to describe the scattering correctly.

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