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1996 J. Phys.: Condens. Matter 8 8733

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Quantum one-phonon-assisted adsorption of light atoms on cold solid surfaces

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Received 27 March 1996

Abstract. Quantum-mechanical one-phonon-assisted sticking of ^4He on LiF and NaF is considered under **T**-matrix formalism. The bound-state energies, lifetimes and corresponding surface temperatures at which the sticking takes place are evaluated and compared with the experimental results. The exact **T**-matrix approach is found to give better results even for Morse-potential parameters.

1. Introduction

The process of adsorption and desorption of a gas at a solid surface is primarily controlled by the molecular interactions between the particles making up the gas and the solid phases. In adsorption experiments [1, 2] a clean solid surface is suddenly exposed to a gas, and the build-up of the adsorbate, i.e. of those gas particles that are bound to the solid, is followed as a function of time and characterized by an adsorption time τ_s [3].

For low-energy incoming particles, the inelastic processes become very important and responsible for sticking. Normally, if the coupling to the surface degrees of freedom is considerable, the first-order perturbation theory may not give the correct results as the successive phonon scattering may affect the particle wavefunction. The quantum reflection effects which reduce the adsorption coefficient to zero in the limit of zero energy could very well be destroyed by successive phonon interaction, and coupling to low-energy modes may allow the exchange of the energy between the incoming particle and the surface, leading to possible physisorption and inelastic scattering [4].

We therefore, conjecture that, for phonon-assisted scattering of a gas–solid interaction, the lower-order distorted-wave Born approximation (DWBA) calculations may not be adequate to explain the total inelastic component of the gas–solid interaction.

The purpose of the present work is therefore to take into account the proper corrections to inelastic scattering and consequently to evaluate the sticking by taking the higher-order terms in the scattering **T** matrix of the system. We calculate the probability that the particle ends up in a bound state (BS) after interaction with the surface, leading to emission of one phonon. For phonon-assisted adsorption in which the one-phonon process is taking part, the controlled adsorption process is completed after an equilibrium adsorbate has been built up with the gas temperature T_g equal to the initial solid temperature and then suddenly lowered by the emission of one phonon to a new solid temperature T_s , leading to the formation of BS.

We concentrate on phonon-mediated physisorption of gas particles at normal incidence for low coverages at localized adsorption sites, assuming that interaction between the adsorption sites is negligible.

We have proposed a Hamiltonian in terms of a localized and a phonon basis and changed the phonon basis into the localized basis by a canonical transformation. Hence we obtain the general theory for the temperature-dependent BS energy for the adsorbed system. The theory developed can then be used to calculate the sticking and inelastically scattered intensities for different BS of the systems.

The variation in BS energies with temperature obtained from the \mathbf{T} -matrix pole has already been reported earlier [5]. In the present case the problem has been extended to study the sticking coefficient and the transient time τ_s obtained from the imaginary part of the \mathbf{T} matrix. The transient time is much shorter than the quantum-mechanical time of interaction for maximum sticking, as reported earlier [6]. The model potential chosen in our calculation is the Morse potential which facilitates the comparison of our results with the earlier reported values obtained using the same potential model. Model calculations are carried out which include not only the DWBA but also the higher-order single-phonon processes.

2. Theoretical model

The model Hamiltonian for the gas–solid system with localized and non-localized basis may be written

$$H = H_g + H_s + H_{dyn} \quad (1)$$

where H_g is the Hamiltonian of the non-interacting gas system in a box. For just one shallow BS the three-dimensional theory can be reduced to one-dimensional theory. In terms of the wavefunction $\psi(x)$ of the gas we can write

$$H_g = -\frac{\hbar^2}{2m} \int \left(\psi_k^\dagger(x) \frac{d^2}{dx^2} \psi_k(x) \right) dx. \quad (2)$$

Now we introduce the second quantized creation operator c_k^\dagger annihilation operators c_k in the state $|k\rangle$ through the expressions

$$\psi_k(x) = \sum_k \phi_k(x) c_k$$

and

$$\psi_k^\dagger(x) = \sum_k \phi_k^*(x) c_k^\dagger$$

where the free-gas-particle wavefunction is

$$\phi_k(x) = \sqrt{\frac{2}{L}} \sin(kx). \quad (3)$$

The free-gas-particle wavefunction is taken as a real function normalized in a one-dimensional box of length L and assumed to vanish at the solid surface $x = 0$; hence

$$H_g = \sum_k \epsilon_k c_k^\dagger c_k \quad (4)$$

where $\epsilon_k = \hbar^2 k^2 / 2m$ is the kinetic energy of the free gas particle. The second part of Hamiltonian (1) is that of the solid which in the harmonic approximation may be written as

$$H_s = \sum_p \hbar \omega_p b_p^\dagger b_p \quad (5)$$

with b_p^\dagger the creation operator and b_p the annihilation operator of longitudinal acoustic phonons of frequency ω_p in the absence of gas.

The third term in equation (1) gives the gas–solid interaction. It consists of two parts: a static part and a dynamic part. For small displacements, u is given by

$$u = (M_s N_s)^{-1/2} \sum_p \left(\frac{\hbar}{2\omega_p} (b_p^\dagger + b_p) \right) \quad (6)$$

with solid particle mass M_s and number N_s of particles in a normalized box of length L . The first part of the gas–solid interaction potential leads to the static part H_{gs}^{st} of H_{gs} and the second part gives the dynamic part H_{gs}^{dyn} . Using the transformation by creation and annihilation operators as before we have

$$H_{gs}^{st} = \sum_p \epsilon_q c_q^\dagger c_q \quad (7)$$

and hence

$$H_{st} = H_g + H_{gs}^{st} = \sum_k \epsilon_k c_k^\dagger c_k + \sum_q \epsilon_q c_q^\dagger c_q. \quad (8)$$

The Hamiltonian (8) is diagonalized by using the linear transformation $c_k = \sum_q \phi_q(k) c_q$. Here $q = 0$ gives the localized BS and $q > 0$ gives the continuum state. With this transformation we have

$$H_{st} = \sum_q E_q c_q^\dagger c_q \quad (9)$$

where E_q is the eigenvalue of the free-particle state and BS energy E_n with $n = 0, 1, 2, 3, \dots$

In fact the phonon-mediated gas–solid interaction is accounted for by the dynamic part of the Hamiltonian which in the lowest-order harmonic approximation is given by

$$H_{dyn} = \sum_{q, q-p} \chi_{q, q-p} c_{q-p}^\dagger \sum_p \omega_p^{-1/2} (b_p^\dagger + b_p) c_q \quad (10)$$

where for a local surface potential we have

$$\chi(q, q-p) = \left(\frac{\hbar}{2M_s N_s} \right)^{-1/2} \int \phi_{q-p}^*(x) \frac{dV_0(x)}{dx} \phi_q(x) dx. \quad (11)$$

Here the $\phi_q(x)$ are the eigenfunctions of H_{st} denoted by the eigenvalue equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0(x) \right) \phi_q(x) = E_q \phi_q(x). \quad (12)$$

Now with the help of equations (5), (8) and (9) the Hamiltonian H in equation (1) takes the form

$$H = \sum_q E_q c_q^\dagger c_q + \sum_p \hbar \omega_p b_p^\dagger b_p + \sum_{q, q-p} \chi(q-p, q) c_{q-p}^\dagger \sum_p \omega_p^{-1/2} (b_p^\dagger + b_{-p}) c_q. \quad (13)$$

Now we use the similarity transformation $H_s = \exp(-s)H \exp s$ with the generating function S given by [7]

$$\langle n|s|m\rangle = \frac{\langle n|H_{dyn}|m\rangle}{E_m - E_n} \quad (14)$$

where $E_m \neq E_n$. This reduces the Hamiltonian (13) to

$$H = \sum_q E_q c_q^\dagger c_q + \sum_p \hbar\omega_p b_p^\dagger b_p + \frac{1}{2} \sum_{q,q'} \chi(q-p, q) \chi(q'+p, q') \lambda_p^2 c_{q'+p}^\dagger c_{q-p} c_q \\ \times \left(\frac{1}{(E_q - E_{q-p} - \hbar\omega_p)} - \frac{1}{E_{q'} - E_{q'+p} + \hbar\omega_p} \right) \quad (15)$$

where $\lambda_p^2 = 1/\omega_p$.

3. Sticking coefficient and lifetime

We have solved the Hamiltonian (15) for the He–NaF and He–LiF systems by the Green function technique and obtained the \mathbf{T} matrix for the systems. For just one shallow BS we take the static surface potential as

$$V_0(x) = U_0 \{ \exp[-2\gamma(x-x_0)] - 2 \exp[-\gamma(x-x_0)] \}. \quad (16)$$

Now in order to obtain the Dyson equation for the scattering \mathbf{T} matrix we write the single-particle Green function as

$$G_{km}(t) = \langle \langle \alpha_k(t), \alpha_m^\dagger(0) \rangle \rangle \quad (17)$$

where α_m^\dagger and α_k are the dummy operators for the creation and annihilation, respectively, of localized particles.

The Green function may be written in the form of Dyson equation using the Hamiltonian (15) and taking the Fourier transformation as

$$G_{kk}(E) = G_k(0) + G_k(0) \mathbf{T} G_{kn}(E) \quad (18)$$

which on iteration leads to

$$G_{kk}(E) = G_0(E) + G_0(E) \mathbf{T} G_0(E) \quad (19)$$

where

$$G_0(E) = \frac{1}{2\pi(E-E_k)} \quad \mathbf{T} = 2\pi \Delta_k / \left(1 - \sum_q \frac{\Delta_q}{(E-E_q)} \right) \\ \Delta_q = \sum_p \frac{|\chi(q, q-p)|^2 \lambda_p^2 n_{q-p}}{E_q - E_{q-p} - \hbar\omega_p}. \quad (20)$$

Here q is the momentum of the gas particle in the localized state and $q-p$ is that in the BS. E is the effective final energy with transformed BS energy $E_{n'}$ due to gas–solid interaction plus the phonon energy.

The relative gas atom occupation number in the substrate maintained at temperature T is

$$n_{q-p} = \exp[\beta(E_{n'} - \mu)] \ll 1 \quad (21)$$

with $\beta = 1/k_B T$ and μ the chemical potential of the gas which consists of N particles in a one-dimensional box of length L and is defined as

$$\exp(-\beta\mu) = \frac{L}{N} \left(\frac{2\pi k_B T m}{h^2} \right)^{1/2}. \quad (22)$$

Now, while evaluating $|\chi(q, p)|^2$, we consider the dimensionless parameters as [8]

$$\sigma_0^2 = \frac{2mU_0}{\hbar^2\gamma^2} \quad S_n^2 = \frac{2m|E_n|}{\hbar^2\gamma^2} \quad r = \frac{2m\omega_d}{\hbar\gamma^2} \quad \xi = \gamma x \quad \xi_0 = \gamma_0 x_0$$

and we get the normalized BS wavefunction as $\phi_n(x) = \sqrt{\gamma} \text{fn}(\xi)$ with

$$\begin{aligned} \text{fn}(\xi) = & (2\sigma_0)^{S_n} \Gamma^{(-1/2)}(2S_n) \binom{2S_n + n}{n}^{-1/2} \exp\{-\alpha_0 \exp[-(\xi - \xi_0)]\} \\ & \times \exp[-S_n(\xi - \xi_0)] L_n^{2S_n}\{2\sigma_0 \exp[-(\xi - \xi_0)]\} \end{aligned} \quad (23)$$

where $S_n = \sigma_0 - n - \frac{1}{2}$, with $n = 0, 1, 2, \dots$, and $L_n^{2S_n}(u)$ is a Laguerre polynomial.

The continuum state wavefunctions of momentum q normalized in a box of length L ($-L < x < L$), are given by $\phi_q(x) = (2L)^{-1/2} f(\eta; \xi)$, $\eta = q/\gamma$ and

$$\begin{aligned} f(\eta; \xi) = & \left| \frac{\Gamma(\frac{1}{2} - \sigma_0 - i\eta)}{\Gamma(2i\eta)} \right| \exp\{-\sigma_0 \exp[-(\xi - \xi_0)] \exp[-i\eta(\xi - \xi_0)]\} \\ & \times \Psi\left(\frac{1}{2} - \sigma_0 + i\eta, 1 + 2i\eta, 2\sigma_0 \exp[-(\xi - \xi_0)]\right) \end{aligned} \quad (24)$$

where $\Psi(a, b, z)$ is a confluent hypergeometric function that vanishes at $z \rightarrow \infty$. Again while evaluating the sums we have to invoke the thermodynamic limit i.e. $\Sigma_k \rightarrow (L/\pi) \int_0^\infty dk$ and perform the sums over phonon states for a Debye model i.e. $\Sigma_p \rightarrow (3N_s/\omega_d^3) \int_0^{\omega_d} \omega_p^2 d\omega_p$. This leads to a real part and a imaginary part of the \mathbf{T} matrix. The transition probability from the initial continuum to final BS under the emission of phonon may be given by the golden rule

$$R_{cn} = \frac{2\pi}{\hbar} \langle \Psi_f | \text{Re } \mathbf{T} |^2 \Psi_i \rangle \delta(E_f - E_i) n_{eq} \quad (25)$$

where for the BS energy E_i

$$n_{eq} = \exp(\beta_g \mu - \beta_s E_i).$$

The real part of the \mathbf{T} matrix gives the transition probability R_{cn} and hence the sticking coefficient normalized by the flux of incoming particle τ_L defined by $\tau_L = 2Lm/\hbar k$, and the inverse of the imaginary part gives the lifetime τ_s of the scattering state. The flux of all incoming particles is given by $\sum_{q>0} (2Lm/\hbar q) R_{qn}$. Using equation (25) we have for the continuum to the BS transition the total sticking coefficient given by

$$S = 16\pi^4 r^2 \left[C / \left(\int_0^\infty F(x) dx \right) \right]^2 n_{eq} \quad (26)$$

where

$$C = \frac{\sinh(2\pi\sqrt{s^2})}{\sinh^2(\pi\sqrt{s^2}) + \cosh^2(\pi\sigma_0)} |\Gamma(\frac{1}{2} + \sigma_0 + i\sqrt{s^2})|^2 [s^2 + (\sigma_0 - n - \frac{1}{2})^2] s_n^2 s^2 \quad (27)$$

and

$$F(x) = \frac{\sinh(2\pi\sqrt{x})}{\sinh^2(\pi\sqrt{x}) + \cosh^2(\pi\sigma_0)} |\Gamma(\frac{1}{2} + \sigma_0 + i\sqrt{x})|^2 [x + (\sigma_0 - n - \frac{1}{2})^2] \frac{x - s_n^2 + s^2}{s^2} \quad (28)$$

with

$$n_{eq} = \exp|\beta_g \mu| \exp[-\delta s^2/r]$$

where $\delta = \beta_s \hbar \omega_d$ and $\beta_s = 1/k_B T_s$. The inverse of the imaginary part of the \mathbf{T} matrix given by equation (20) is used to obtain the lifetime τ_s as

$$\tau_s = \frac{h}{k_B T_g s^2} \left[\left(\int_0^\infty f(y) dy \right) / \left(\int_0^\infty f(x) dx \right) \right] \exp(\beta_s E_n - \beta_g \mu) \quad (29)$$

where

$$f(x) = \frac{\sinh(2\pi\sqrt{x})}{\sinh^2(\pi\sqrt{x}) + \cosh^2(\pi\sigma_0)} |\Gamma(\frac{1}{2} + \sigma_0 + i\sqrt{x})|^2 [x + (\sigma_0 - n - \frac{1}{2})^2]^2 \\ \times \left[r + \frac{s^2 - s_n^2 + x}{2} \ln \left| \frac{r}{x - s_n^2 + s^2} \right| \right] \quad (30)$$

and

$$f(y) = \frac{\sinh(2\pi\sqrt{y})}{\sinh^2(\pi\sqrt{y}) + \cosh^2(\pi\sigma_0)} |\Gamma(\frac{1}{2} + \sigma_0 + i\sqrt{y})|^2 [y + (\sigma_0 - n - \frac{1}{2})^2]^2 [x - s_n^2 + s^2]. \quad (31)$$

It may be noted that the BS lifetime τ_s given by equation (29) has been normalized by the time of interaction of the incident particle with the surface.

4. Numerical evaluation

The sticking coefficients of ^4He atoms on alkali-halide crystals in the quantum-mechanical regime has been evaluated under \mathbf{T} matrix formalism. It has already been pointed out that the lower-order DWBA on the phonon-mediated adsorption is inadequate for the calculation of sticking coefficients. In our earlier calculations [5] we have shown that the BS energy strongly depends on the substrate temperature T_s . The results obtained from our theoretical calculations for the BS energy and normalized transient time τ_s and the corresponding Morse parameters are given in tables 1 and 2.

Table 1. Morse potential parameters for He–LiF and He–NaF systems.

Systems	(γ^{-1}) (A^0)	U_0 (K)	$\hbar\omega_d/K_B$ (K)	σ_0	r	m/M_s
He–LiF	1.09	81.75	730	4.023	144.55	0.152
He–NaF	0.97	77.78	450	3.491	70.496	0.0952

We fit the experimental and Morse potential parameters listed in tables 1 and 2 to perform the numerical evaluations of the substrate temperatures and consequently the normalized low-temperature lifetimes of different BS for the He–LiF and He–NaF systems. The lifetimes evaluated for low substrate temperatures are found to be long, making the observation of BS possible within a typical experimental limit [9, 10] and are therefore important from an experimental standpoint. Our theoretical BS energies given in table 2 are compared with the experimental results, and corresponding substrate temperatures are also evaluated. The evaluations in the present case have been made numerically from the BS pole of the \mathbf{T} matrix. It has been found that the substrate temperatures T_s evaluated from our theoretical calculations are in good agreement with the findings reported earlier [8] for He–LiF and He–NaF systems. The calculations are then performed to evaluate the lifetimes τ_s by varying the substrate temperature (table 2) to match the experiment of interest [10–12],

Table 2. BS energies and transient times in a given temperature range.

Systems	Substrate temperature range (K)	n	Theoretical BS (K)	Experimental BS (K)	Transient time (t_s) (s)	Desorption time [8] (t_d^0) (s)
He–LiF	34	0	62.69	68.47	7.87×10^{-9}	1.53×10^{-8}
	8	1	32.16	28.55	2.17×10^{-8}	1.36×10^{-5}
	2	2	11.72	9.05	8.27×10^{-7}	2.62×10^{-4}
He–NaF	1	3	1.38	2.44	1.50×10^{-5}	0.97×10^{-3}
	18	0	57.10	57.10	1.92×10^{-9}	2.85×10^{-8}
	5	1	25.30	21.70	8.94×10^{-7}	2.89×10^{-6}
	1	2	6.27	6.27	7.11×10^{-3}	6.18×10^{-3}

e.g. the calculations of residence times in the BS at low surface temperatures. We assume that a particle is captured once it has been scattered into a BS. From an experimental standpoint the incident particle may be captured if the residence time in the BS is long compared with the collision time at low substrate temperatures which is of the order of the phonon vibration time, 10^{-13} s, for a phonon-mediated inelastic scattering system [13]. This happens at low substrate temperatures.

5. Discussion

It is evident from table 2 that for $n = 0, 1$ and 2 for a potential well depth of 89 K and 77.78 K and a scattering strength γ^{-1} of 1.09 Å and 0.97 Å, for LiF and NaF systems, respectively, the theoretical BS energies from the Morse potential give rise to sticking times ranging between 10^{-3} and 10^{-9} s. This is much higher than the phonon vibration time (10^{-13} s) as mentioned earlier and is of the order of reported desorption time t_d calculated from the Frenkel–Arrhenius formula $t_d = t_d^0 \exp(Q/k_B T)$, where Q is the activation energy. The above discussion supports the fact that, the larger the probability of sticking, the lower is the degree of desorption. Thus at higher gas temperatures the particle scattered from the continuum to these negative energy BS will be captured with a long lifetime, implying that the subsequent desorption is a slow process. This is certainly valid for situations in which the sticking probability is small and is illustrated in figures 1 and 2.

Figure 1 shows the sticking probability of the ^4He versus the temperature of incident particle energy for LiF and NaF substrates for different BS. The variation in BS lifetime with the substrate temperature is shown in figure 2.

We note from figure 1 that the sticking coefficient is a relatively smoothly varying function of the incident energy for the He–LiF and He–NaF systems. However, as the entry into the BS is a phonon-mediated process, the probability of capture by a BS increases with increasing temperature of the incident particles. At higher temperatures, higher-order effects become more important and more BS channels become probable. The major experimental problem is that at higher temperatures the residence time on the surface for the particles becomes too short to enable accurate measurements of the sticking to be made.

We have chosen the Morse potential for the gas–solid system in the present case as it is the most popular surface potential for fitting a limited number of parameters to the gas–surface scattering for which all wavefunctions and the BS energies can be determined analytically. The results obtained for other potentials such as the Lennard–Jones potential do not give a satisfactory fit to the BS energy and are therefore not considered in the present case [14].

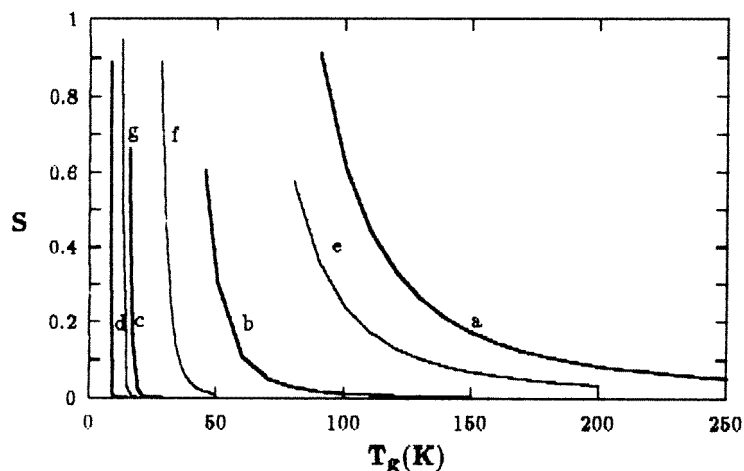


Figure 1. Variation in sticking coefficient with gas temperature for the He-LiF and He-NaF systems for different BS. Curves (a), (b), (c) and (d) are for He-LiF for $n = 0, 1, 2$ and 3 , respectively. Curves (e), (f) and (g) are for He-NaF for $n = 0, 1$ and 2 , respectively.

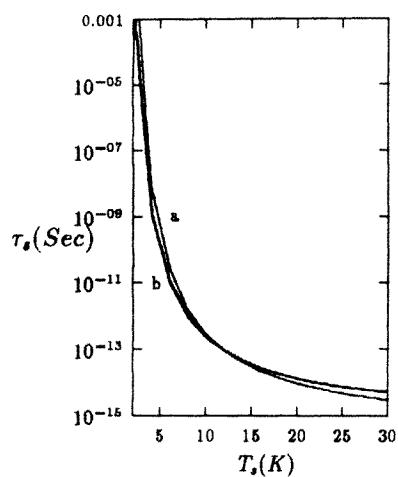


Figure 2. The variation in BS lifetime τ_s with substrate temperature. Curve (a) is for He-LiF and curve (b) for He-NaF systems, both for $n = 0$.

It may be noted from table 2 that the present theory which takes into account the higher-order term is less accurate for reproducing the substrate temperatures for higher BS ($n = 2$ and 3 for LiF and $n = 2$ for NaF). This again supports the facts that at very low temperatures the higher-order contributions constitute a smaller correction to the Born approximation and the substrate temperatures corresponding to higher BS may not be obtained very precisely. The fourth BS ($n = 3$) for the He-NaF system could not, however, be resolved with Morse potential parameters as the corresponding surface temperature is very small and the condition $n < \sigma_0 - \frac{1}{2}$ is not satisfied. This is also supported by the earlier finding using the same potential [8].

6. Conclusion

From the above discussion we conclude that our theory, which takes into account the higher-order contribution to the sticking coefficient of a phonon-mediated process, predicts a non-zero capture even at higher temperatures. Although the residence times on the surface for the He–LiF and He–NaF systems become much shorter at higher temperatures making accurate measurement of sticking coefficients difficult, the calculations presented here suggest that, at higher temperatures, capture into the physisorption BS is possible and can be monitored through careful measurements of the specular beam. The results so obtained depend on the nature of the potential, its well depth and the interaction strength. However, the multiphonon process which has not been considered in the present work will definitely improve the results.

Acknowledgments

The authors are grateful to the Department of Atomic Energy, India, for financial support and to Dr B K Talukdar and Dr M M Panja for valuable suggestions. The authors also thank Mr B C Gupta, Institute of Physics, Bhubaneswar, for his help with the computation work.

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