

# Generalized path integral based quantum transition state theory

G. Mills<sup>a</sup>, G.K. Schenter<sup>b</sup>, D.E. Makarov<sup>b,c</sup>, H. Jónsson<sup>a</sup>

<sup>a</sup> Department of Chemistry, Box 351700, University of Washington, Seattle, WA 98195-1700, USA

<sup>b</sup> Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratories, Richland, WA 99352, USA

<sup>c</sup> University of California Santa Barbara, Santa Barbara, CA 93106, USA

Received 11 June 1997

## Abstract

A theory for calculating rates of transitions in quantum systems is presented and applied to desorption of H<sub>2</sub> from a Cu(110) surface. The quantum transition state is defined as a conical dividing surface in the space of closed Feynman paths and a 'reaction coordinate' in this extended space is used to parametrize a reversible work evaluation of the free energy barrier. In a low temperature, harmonic limit the theory reduces to instanton theory. Above the cross-over temperature for tunneling, the theory reduces to the centroid density approximation and in the classical limit, variational classical transition state theory is recovered. © 1997 Elsevier Science B.V.

Transition state theory (TST) is well established and widely used for calculating rates of slow transitions in classical systems [1,2]. It gives an approximation which frequently is quite accurate and it, furthermore, provides a viable computational procedure for obtaining the exact rate constant via dynamical corrections which require only short time trajectories starting at the transition state. For a system with  $N$  degrees of freedom, the transition state is a  $N - 1$  dimensional dividing surface separating reactants and products. The accuracy of the TST approximation depends strongly on the choice of the dividing surface. For classical systems, it can be shown that TST always gives an overestimate of the rate and this provides a variational principle for optimizing the location of the dividing surface [2]. Basically, TST transforms the dynamical problem into a statistical one by approximating the transition rate as being proportional to the probability of finding the system in a transition state. A good approximation to the rate constant can be obtained from TST if the

transition state is chosen to be a dividing surface representing a tight bottleneck for advancement of the system from reactants to products.

The challenge is to generalize TST to transitions in quantum systems. Several experimentally measured transition rates show temperature dependence where below a cross-over temperature the effective activation energy is significantly reduced [3]. This is characteristic of the onset of quantum behaviour where thermally assisted tunneling becomes the dominant mechanism. Several versions of quantum TST have been proposed [2]. The most widely used formulation is based on statistical (or imaginary time) Feynman path integrals where the partition function of a quantum system is given by [4]

$$Q = \int e^{-S_E[q(\tau)]/\hbar} \mathcal{D}[q(\tau)]. \quad (1)$$

(Throughout,  $q$  represents an  $N$ -dimensional vector.) Here  $S_E$  is the Euclidean action,  $S_E = \int_0^{\beta\hbar} H d\tau$  with  $H$  being the Hamiltonian. For discretized paths de-

scribed by  $P$  configurations of the system, the action can be approximated as

$$S_E(\mathbf{q}) = \Delta\tau \sum_{j=1}^P \left[ \frac{\mu}{2} \left| \frac{q_{j+1} - q_j}{\Delta\tau} \right|^2 + V(q_j) \right], \quad (2)$$

where  $\Delta\tau = \beta\hbar/P$  (boldface type is used here for  $NP$ -dimensional vectors). This leads to a mathematical analogy between the partition function of a quantum particle and the classical partition function of a string of  $P$  ‘images’ (or replicas) of the system connected by springs with a temperature dependent spring constant. The path integral formulation provides a practical method for evaluating the quantum statistical mechanics, but the key question is how to define the transition state. In previous theories, the transition state has been defined in terms of a  $(N-1)$ -dimensional dividing surface in the classical coordinate space [2]. In particular, in the centroid density method, proposed by Gillan [5] and later generalized by others [6–10], the transition state constraint is applied to the average, or centroid, of the Feynman paths  $\tilde{q}_0 = (1/\beta\hbar) \int q(\tau) d\tau$ . This was tested and found to work well for transitions involving symmetric barriers [5–7,11]. The centroid constraint, however, does not work well for asymmetric transitions at low temperature [12,13]. We present an example of that below. We also present a generalized path integral based quantum TST where the transition state is defined in a more general way, as a  $(NP-1)$ -dimensional cone in the space of all closed Feynman paths with  $P$  images. This theory represents a natural, anharmonic generalization of the so-called ‘instanton theory’ (see below). A methodology is described for evaluating the free energy barrier in this higher dimensional space, which we will refer to as ‘action-space’. The technique involves evaluating the reversible work required to shift the system confined to a dividing surface cone from the reactants towards products. We refer to the method as reversible action-space work quantum transition state theory (RAW-QTST).

The statistical weight of Feynman paths is given by the Euclidean action and topology of the action surface is of central importance [12]. Fig. 1 shows the action surface for a one-dimensional asymmetric Eckart barrier [13] and paths described by two Fourier components,  $x(\tau) = x_0 + x_1 \sin(2\pi\tau/\beta\hbar)$ . At high

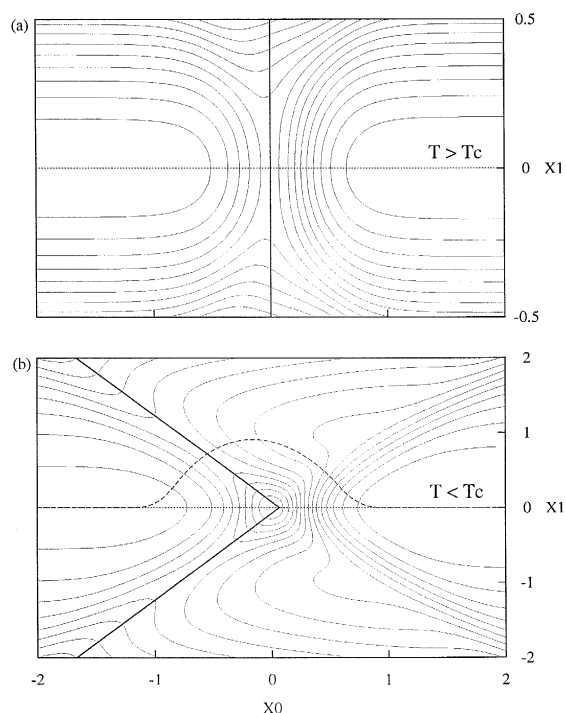


Fig. 1. Contour plots of the Euclidean action,  $S_E$ , for an asymmetric Eckart barrier (exoergic transition by 0.19 eV and barrier height 0.25 eV) in the space of closed paths represented by two Fourier components,  $x_0$  and  $x_1$ . The dotted line at  $x_1 = 0$  represents the collapsed, classical paths. (a)  $T = 300$  K, above the cross-over temperature. As the images spread apart, the action increases. The MAP therefore only includes collapsed paths and reduces to the MEP. (b)  $T = 50$  K, below the cross-over temperature. A local maximum in  $S_E(\mathbf{q})$  develops on the  $x_1 = 0$  line at the potential barrier. The projection of the MAP onto the two-dimensional space is shown with a dashed line. The MAP now includes delocalized paths, a signature of tunneling. The dividing surface with maximal action is indicated by thick, solid lines.

temperature, the action increases as the Feynman paths are opened ( $x_1 \neq 0$ ). But, below a certain cross-over temperature,  $T_c$  (275 K in this case), the topology changes as a local maximum of action appears at  $x_1 = 0$  in the barrier region. Then, the minimal action in the barrier region is obtained with open, delocalized paths and saddle points appear off the ‘classical’, collapsed path ( $x_1 = 0$ ) axis. A symmetry in the action surface corresponding to relabeling of images is evident in Fig. 1b where two symmetrically equivalent saddle points appear. In general,  $P$  saddle points form and, in the limit of

continuous representation of the Feynman paths ( $P \rightarrow \infty$ ), there is a continuum of saddle points.

An important concept in classical TST is the minimum energy path (MEP) connecting reactants and products. For a quantum system, we generalize this to the minimum action path (MAP) (see Fig. 1b). Above the cross-over temperature, the MAP reduces to the MEP. We denote the MAP with  $\Gamma_s$  where  $s$  is a scalar variable parametrizing progression along the MAP. We will choose  $s$  as ‘reaction coordinate’, a parameter that shifts the system from reactants to products. This choice is particularly good for numerical sampling since the probability density of Feynman paths is largest at the MAP. Also, we will choose a dividing surface that has normal vector tangent to the MAP,  $\hat{n}_s \equiv \Gamma'_s / \|\Gamma'_s\|$  (prime denotes d/ds). This ensures that displacement along the unstable mode at saddle points is not included in the dividing surface. A hyperplanar reaction coordinate constraint on the dividing surface can be written as  $\delta_{rp} \equiv \delta(\hat{n}_s \cdot (\mathbf{q} - \Gamma_s))$ .

Since the Feynman paths,  $q(\tau)$ , are closed,  $q(\tau) = q(\beta\hbar + \tau)$ , and the Euclidean action is invariant under imaginary time translation,  $S_E[q(\tau)] = S_E[q(\tau + t)]$ . The origin of the imaginary time is arbitrary. The set of all Feynman paths equivalent by this symmetry form a ‘circle’ in action-space. We, therefore, construct a dividing surface from a sequence of hyperplanes defined by the imaginary time translation of  $\hat{n}_s$  and  $\Gamma_s$ . This family of hyperplanes envelops a cone with an axis consisting of all collapsed paths. The time translational symmetry of the system is retained in the conical dividing surface and this ‘zero mode’ can be integrated out separately. This facilitates numerical sampling of the Feynman paths. The contribution of the zero mode to the partition function is  $Q_0^{\text{loc}}(\mathbf{q}) \equiv \beta\hbar(\hat{v}_s \cdot \dot{\mathbf{q}})$  where  $\hat{v}_s \equiv \dot{\Gamma}_s / \|\dot{\Gamma}_s\|$  and  $\dot{\mathbf{q}} = d\mathbf{q}/d\tau$ . The cone dividing surface partition function,  $Q_s$ , can then be evaluated from

$$Q_s = \int e^{-S_E(q)/\hbar} Q_0^{\text{loc}}(\mathbf{q}) \delta_{rp} \delta_0 \mathcal{D}q[\tau], \quad (3)$$

where  $\delta_0 \equiv \delta(\hat{v}_s \cdot (\mathbf{q} - \Gamma_s))$ . The constraint,  $Q_0^{\text{loc}}\delta_{rp}\delta_0$ , specifies a  $(NP - 2)$ -dimensional wedge of the dividing surface cone.

The transition state in our theory is chosen to be the cone corresponding to the tightest statistical bot-

tleneck, i.e. the cone with maximum free energy<sup>1</sup>. The calculation is carried out in terms of the reversible work of shifting the dividing surface from the reactant region towards products, using the reaction coordinate,  $s$ , to parametrize the progression. We choose the transition state to be the cone,  $s^\ddagger$ , which gives a maximum in the free energy function  $\mathcal{F}_s$ . To simplify the notation, we define an effective potential for the Feynman paths as

$$V_{\text{eff}}(\mathbf{q}) \equiv -k_B T \ln(e^{-S_E(q)/\hbar} Q_0^{\text{loc}}(\mathbf{q})) \quad (4)$$

and effective force  $\mathbf{F}_{\text{eff}}(\mathbf{q}) = -\nabla_{\mathbf{q}} V_{\text{eff}}$ . The change in the free energy,  $\mathcal{F}_s$ , as the dividing surface is shifted is

$$\left\langle \mathbf{F}_{\text{eff}} \cdot \left\{ \hat{n}_s - (\hat{n}_s \hat{n}'_s + \hat{v}_s \hat{v}'_s) \cdot (\mathbf{q} - \Gamma_s) \right\} - \frac{\hat{v}'_s \cdot \dot{\mathbf{q}}}{\beta \hat{v}_s \cdot \dot{\mathbf{q}}} \right\rangle. \quad (5)$$

The first term is due to translation of the dividing surface along the reaction coordinate. The remaining terms account for rotation in the  $\mathbf{n}_s$  and  $\mathbf{v}_s$  directions. In the numerical sampling, we start with the path  $\mathbf{q} = \Gamma_s$  and then run classical dynamics simulations subject to the constraint  $\delta_{rp}\delta_0$  and the statistical weight function  $e^{-S_E/\hbar} Q_0^{\text{loc}}$ . The weight function automatically imposes the constraint  $Q_0^{\text{loc}} > 0$  by making the ‘phantom’ force,  $\nabla_{\mathbf{q}}(-\hbar \ln Q_0^{\text{loc}}(\mathbf{q}))$ , which points towards paths with larger  $Q_0^{\text{loc}}$ , infinite wherever  $Q_0^{\text{loc}} = 0$ . The free energy barrier is  $\Delta\mathcal{F} = \int_{\mathbb{R}}^{\ddagger} \mathcal{F}'_s ds = -(1/\beta) \ln Q_{s^\ddagger} / Q_{s_R}$  and the rate constant is given by

$$Q_{\parallel}^R k^{\text{QTST}} = \nu e^{-\beta\Delta\mathcal{F}}, \quad (6)$$

where  $\nu$  is a weakly temperature dependent prefactor, given below, and  $Q_{\parallel}^R \equiv Q_R / Q_{s_R}$ .

In order to derive a rate, we expand the dividing surface free energy around  $s^\ddagger$  up to second order in  $s$ . This represents an unstable state, but a total free energy,  $\exp(-\beta\mathcal{F}) = \int \exp(-\beta\mathcal{F}(s)) ds$ , can be evaluated by rotating the integration contour to the

<sup>1</sup> This gives a systematic way of defining the transition state and ensures that instanton theory is recovered at low temperature and variational classical transition state theory at high temperature. However, this choice is not as well justified as in the classical case where a variational principle has been established.

imaginary  $s$  axis. The decay rate of this state is directly related to imaginary part of the free energy [14]. This ‘ImF’ formalism has been shown to work well both for classical and low temperature quantum systems [3,14,16,17] and can be related to the flux-flux correlation function formulation of the rate [8,18]. The resulting prefactor for RAW-QTST is

$$\nu = \frac{1}{\beta \hbar} \sqrt{2\pi/\beta |\mathcal{F}''(s^\ddagger)|} \phi, \quad (7)$$

where  $\phi$  is the Affleck switching factor,  $\phi = 1$  for  $T < T_c$  and  $\phi = T_c/T$  for  $T > T_c$  [17]. With this prefactor, RAW-QTST becomes variational classical transition state theory [2] in high temperature, classical limit [18].

At sufficiently low temperature, the statistical sampling of Feynman paths is dominated by regions of small  $S_E$ . A harmonic approximation to  $S_E(\mathbf{q})$  obtained by expanding around the MAP can then be used. The saddle point of the action surface, i.e. the maximum of the action along the MAP, becomes the bottleneck. This is analogous to the situation in classical systems where the saddle point of the potential energy surface becomes the bottleneck at low temperature. In fact, TST is most often applied within the harmonic approximation where a normal mode expansion around the saddle point and the reactant minimum is used to evaluate the partition functions [19]. A quantum theory based on an analogous harmonic expansion of the action has been developed. The dominant, exponential variation of the rate with temperature is given by the action at the saddle point while the prefactor is given by the eigenvalues of the normal modes, except the zero mode which has to be treated separately. The saddle point Feynman path is often referred to as the ‘instanton’ and the rate theory as ‘instanton theory’ (see Ref. [3], and references therein). Being a stationary point of the action, the instanton is typically described in terms of a classical trajectory on the inverted potential. Instanton theory, which is known to give accurate rate estimates at low temperature, is naturally obtained from RAW-QTST by taking the harmonic limit. The high temperature limit of RAW-QTST is variational classical transition state theory, which is known to work well for classical systems. At all temperatures, RAW-QTST treats tunneling on an equal footing

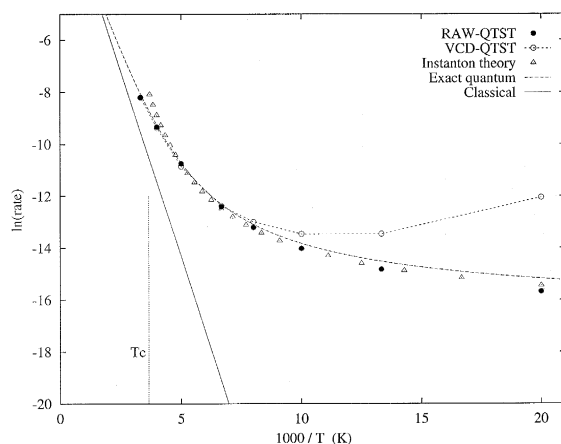
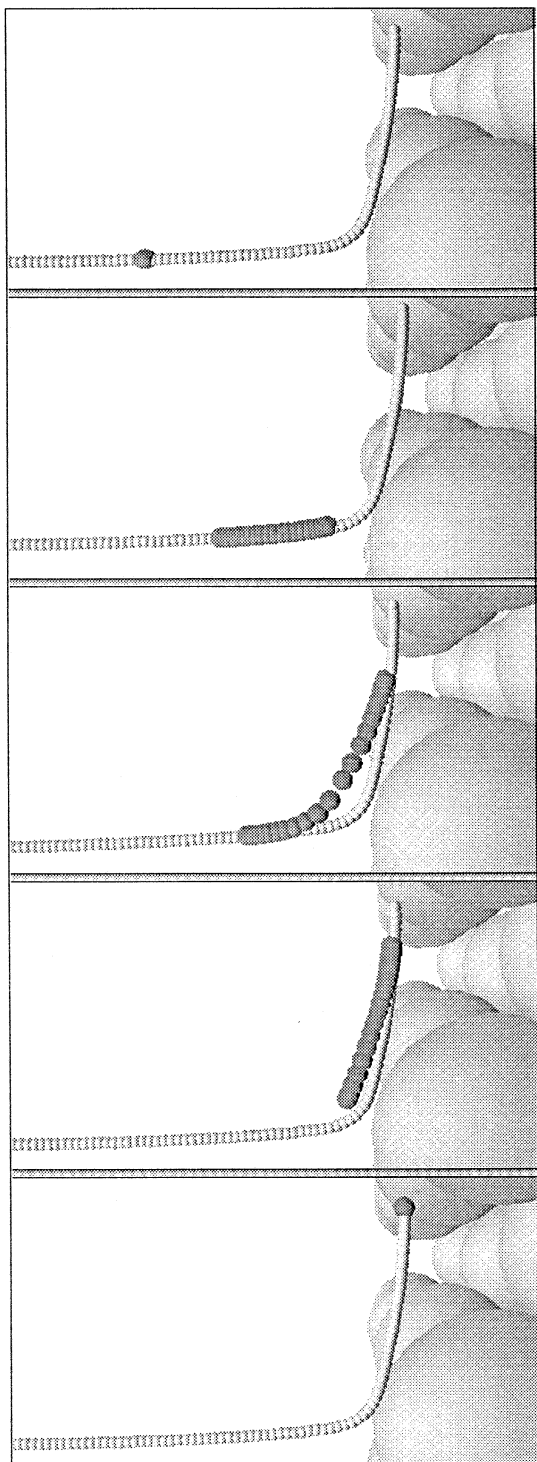


Fig. 2. The calculated transition rate for the asymmetric Eckart barrier. At low temperature, below 100 K, the results of the variational centroid density approximation (VCD-QTST) show an unphysical increase in the rate as temperature is reduced. At high temperatures, near the cross-over temperature  $T_c = 273$  K, the instanton results overestimate the rate. The RAW-QTST calculations, which include full anharmonicity, agree well with the exact results and coincide with the centroid density results at high temperature and are close to the harmonic, instanton limit at low temperature.

with over-the-barrier transitions and includes full anharmonic effects in both the transition and reactant states. Above  $T_c$ , where tunneling is unimportant, our theory reduces to variational centroid density theory [9], but below  $T_c$  the centroid variable does not play any special role in either our theory or in our simulation methodology.

We now discuss an application of the theory to a one-dimensional Eckart test problem. The rate calculated by the RAW-QTST is found to give good agreement with the exact rate over the whole temperature range as shown in Fig. 2. At just below the cross-over temperature, the centroid density theory gives similar results. But, at lower temperature the results of the centroid density calculation become unphysical, the calculated rate constant increases as temperature is further reduced (even though the dividing surface is adjusted at each temperature to minimize the rate). The problem is that the dividing surface defined in terms of the centroid coordinate becomes too weak a constraint and the system can avoid the bottleneck region by sliding down towards reactants or products along the unstable mode at the saddle point (the centroid density dividing surface, as



any dividing surface defined only in terms of the  $N$  classical coordinates, corresponds to a vertical line in Fig. 1) [12]. On the other hand, instanton theory gives very good results at low temperature, but overestimates the rate at high temperature, as can be expected [3].

We finally turn to an application of RAW-QTST to a very large system, the associative desorption of  $H_2$  from a Cu(110) surface, a transition involving two quantum particles. In addition to the H atoms, we include eight of the Cu atoms quantum mechanically with  $P = 25$  (those nearest to the H atoms) and 208 Cu atoms classically in a six layer slab with movable atoms in the top three layers. The empirical, many-body interaction potential has been described previously [10]. The desorption is exoergic by 0.17 eV with a potential barrier of 0.52 eV. The MAP was obtained by forming an ‘elastic band’ formed by a sequence of closed Feynman paths connected by elastic springs and then minimizing the total action plus spring energy using a ‘nudging’ algorithm subject to fixed end-point constraints [10,18]. Fig. 3 shows snapshots from the MAP for desorption, in particular the instanton, the Feynman path of maximum action. Our MAP finding procedure is, in fact, an efficient way of finding instantons in large systems. The cross-over temperature is found to be at  $T_c = 280$  K. While the calculated free energy barrier is 0.46 eV at 300 K, it drops to 0.34 eV at 100 K and to 0.18 eV at 50 K due to tunneling. The calculation illustrates that RAW-QTST is applicable to large systems with several quantum as well as classical degrees of freedom.

### Acknowledgements

We gratefully acknowledge helpful discussions with Bruce Garrett and Horia Metiu. This work was

Fig. 3. Snapshots from the MAP for  $H_2$  desorption from Cu(110) at 100 K. Only one of the H atoms is shown, since the MAP is symmetric. The MEP is shown with light gray string of small spheres. Away from the barrier region, for the adsorbed atom and the gas phase molecule, the Feynman paths (dark gray) are collapsed. In the barrier region they fall open, which is a signature of tunneling. The middle panel shows the Feynman path of maximum action along the MAP, the instanton. The tunneling path clearly cuts off the sharp corner on the MEP.

supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under grant No. DE-FG06-91ER14224 (GM and HJ) and under Contract No. DE-AC06-76RLO 1830 with Battelle Memorial Institute which operates the Pacific Northwest National Laboratory (GS and DM). GM is a Hertz foundation graduate fellow.

## References

- [1] P. Pechukas, in: Dynamics of Molecular Collisions, part B, Ed. W.H. Miller (Plenum Press, N.Y. 1976).
- [2] D.G. Truhlar, B.C. Garrett, S.J. Klippenstein, *J. Phys. Chem.* 100 (1996) 12771.
- [3] V.A. Benderskii, D.E. Makarov, C.A. Wight, *Chemical Dynamics at Low Temperature* (Wiley, New York, 1994).
- [4] R.P. Feynman, A.R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw Hill, New York, 1965).
- [5] M.J. Gillan, *J. Phys. C: Solid State Phys.* 20 (1987) 3621; *Phys. Rev. Lett.* 58 (1987) 563; *Philosophical Magazine A* 58 (1988) 257.
- [6] G.A. Voth, D. Chandler, W.H. Miller, *J. Chem. Phys.* 91 (1989) 7749.
- [7] J. Lobaugh, G.A. Voth, *J. Chem. Phys.* 100 (1994) 3039.
- [8] A.A. Stuchebrukhov, *J. Chem. Phys.* 95 (1991) 4258.
- [9] M. Messina, G.K. Schenter, B.C. Garrett, *J. Chem. Phys.* 98 (1993) 8525; 99 (1993) 8644.
- [10] G. Mills, H. Jónsson, G.K. Schenter, *Surf. Science* 324 (1995) 305.
- [11] R.P. McRae, G.K. Schenter, B.C. Garrett, G.R. Haynes, G.A. Voth, G.C. Schatz, *J. Chem. Phys.* 97 (1992) 7392.
- [12] D.E. Makarov, M. Topaler, *Phys. Rev. E* 52 (1995) 178.
- [13] M. Messina, G.K. Schenter, B.C. Garrett, *J. Chem. Phys.* 103 (1995) 3430.
- [14] J.S. Langer, *Ann. Phys. (NY)* 41 (1967) 108.
- [15] W.H. Miller, *J. Chem. Phys.* 62 (1975) 1899.
- [16] S. Coleman, in: *The Whys of Subnuclear Physics*, Ed. A. Zichichi (Plenum, New York, 1979).
- [17] I. Affleck, *Phys. Rev. Lett.* 46 (1981) 388.
- [18] G. Mills, G.K. Schenter, D.E. Makarov, H. Jónsson, to be published.
- [19] C. Wert, C. Zener, *Phys. Rev.* 76 (1949) 1169.