Quantum Rate Theory for Solids. III. N-Dimensional Tunneling Effects*

J. H. WEINER AND Y. PARTOM
Brown University, Providence, Rhode Island 02912
(Received 14 July 1969)

A theory for rate processes in solids is presented which includes the effects of quantum statistics, tunneling, and the N-dimensional character of the problem. It utilizes the concept of an ensemble of appropriate minimum-uncertainty wave packets to describe the conditions of thermal equilibrium in an N-dimensional potential well. An exact solution is found for the motion of Gaussian wave packets on a second-degree N-dimensional potential surface. This solution is valid also when the initial principal directions of the wave packet differ from those of the potential surface so that the problem is not separable. It is used to compute the tunneling probability for a Gaussian wave packet on a second-degree N-dimensional potential surface containing a saddle point. This probability depends only on the wave-packet characteristics in the saddle-point direction, and this facilitates its incorporation in the rate expression. Since the initial characteristics of the wave packets of the ensemble are determined by the potential-well character, and their subsequent tunneling probability is determined by the saddle-point character, the theory includes the effect of a difference in orientation between the two sets of principal directions. For an artificial two-dimensional problem formulated specifically to study this aspect of the process, an orientation difference is found to produce large effects only at low temperatures where tunneling is important.

1. INTRODUCTION

THE general problem treated in this paper may be described as follows: Consider a system with N degrees of freedom in a potential well corresponding to a stable equilibrium configuration S. Adjacent to this well is a second one containing a stable equilibrium configuration S', and between the two is a saddle point. The system is in thermal equilibrium at temperature T; what is desired is the rate of transition from S to S'. A typical example is the interchange of an atom and vacant site in a crystal lattice.

In a previous paper[1] (hereafter referred to as I), the effect of employing quantum statistics for the description of thermal equilibrium was studied. By the use of the concept of an ensemble of appropriate minimum uncertainty wave packets (coherent states[2]), it was found possible to keep the treatment close in spirit to the classical approach of Vineyard.[3] The formulation was N-dimensional; however the effects of tunneling were not included.

In a second paper[4] (hereafter referred to as II), the effects of tunneling together with the use of quantum statistics were studied in a one-dimensional treatment of the problem. It was found, at least in the present approach with quantum statistics described by an ensemble of coherent states, that the inclusion of tunneling effects along with quantum statistics was essential. Utilizing the latter without the former predicts much larger divergence from the classical results than is the case when both aspects of quantum behavior are included. For the study of the tunneling aspects of the problem, an exact formula for the motion of a wave packet on a parabolic barrier was developed, together with an approximate expression for the tunneling through a piece-wise quadratic barrier which represented a well plus barrier combination.

In the present paper the methods of I and II are combined to yield an N-dimensional treatment of the problem which includes both the effects of quantum statistics and tunneling.

In the spirit of classical rate theory, the present quantum theory does not deal with the subsequent behavior of the system immediately after the transition from S to S', that is with the question of whether or not or how soon the reverse transition occurs. This question would require knowledge of the character of the potential wells at both S and S' in addition to the shape of the barrier between them, whereas from the present viewpoint the rate of transition from S to S' does not depend on the specific character of the well at S'. The utility of a theory of this type is thus restricted to the regime where the time between such transitions is long compared with the time required for reestablishment of thermal equilibrium after a transition has occurred. The plan of the paper is as follows: In Sec. II the general problem of the motion of a wave packet on an N-dimensional second-degree potential-energy hypersurface is discussed. A system of second-order ordinary differential equations is derived for the time variation of the covariance matrices of the coordinates and momenta. This derivation generalizes to N dimensions the one-dimensional treatment given in Messiah.[5]

This discussion is specialized in Sec. III to Gaussian wave packets. It is shown there that such a wave packet

* Supported in part by the U. S. Air Force of Scientific Research under Grant No. AF-AFOSR-69-1738.

[1] J. H. Weiner, Phys. Rev. **169**, 570 (1968); hereafter referred to as I. References to and discussions of other treatments of this problem may be found in this paper and in that of Ref. 4.

[2] These states and ensembles of such states have been extensively employed in quantum electrodynamics; see R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

[3] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[4] J. H. Weiner and Y. Partom, Phys. Rev. **187**, 1134 (1969); hereafter referred to as II.

[5] A. Messiah, *Quantum Mechanics* (North-Holland Publishing Co., Amsterdam, 1964), Vol. I, p. 220.

remains Gaussian in its motion on a second-degree N-dimensional potential-energy hypersurface, even when the wave-packet principal directions are not aligned with that of the potential energy hypersurface.

A further specialization is made in Sec. IV to the case of a second-degree N-dimensional potential-energy hypersurface which contains a saddle point; that is, a point at which the first partials are all zero and the matrix of second partials has precisely one negative eigenvalue. In the motion of a Gaussian wave packet on such a surface its principal axes rotate while its spread in the saddle-point direction grows exponentially. An exact simple formula for the tunneling probability of such a wave packet is derived. Surprisingly, and fortunately in view of its intended use, the tunneling probability depends only on wave-packet characteristics in the saddle-point direction.

In Sec. V, a rate formula is derived, based on an ensemble of coherent states and utilizing the tunneling probability obtained in Sec. IV. It assumes the same form as the one-dimensional result of II. However, the N-dimensional character of the problem plays an important role in that the parameters depend upon the relative orientation of the principal directions of the potential-energy surface in the well and those at the saddle point. This dependence is explored quantitatively for an artificial two-dimensional problem. It is found that an orientation difference produces large effects only at low temperatures where tunneling is important. Finally, conclusions and summary are presented in Sec. VI.

2. MOTION IN QUADRATIC POTENTIAL FIELD

In this section we generalize some results given in Messiah[5] for the quantum-mechanical one-dimensional motion in a quadratic potential to the case of N dimensions. We are dealing, therefore, with a system with coordinates q_i and momenta p_i, $i=1,\ldots,N$, whose Hamiltonian is

$$H=(1/2m)p_ip_i+\tfrac{1}{2}V_{ij}q_iq_j, \tag{2.1}$$

where summation from 1 to N over repeated indices is understood. Consider a time-dependent state of the system with wave function $\Psi(\mathbf{q},t)$. We denote the associated time-dependent quantum means of observables for the system by either carets or superposed bars, e.g., $\langle q_i\rangle(t)=\bar{q}_i(t)$. For the quadratic potential, it then follows from Ehrenfest's theorem that the mean motion behaves classically, that is,

$$\bar{p}_i=m d\bar{q}_i/dt, \tag{2.2a}$$

$$d\bar{p}_i/dt=-V_{ij}\bar{q}_j, \tag{2.2b}$$

or

$$m d^2\bar{q}_i/dt^2=-V_{ij}\bar{q}_j. \tag{2.2c}$$

Furthermore, let

$$\chi_{ij}=\langle q_iq_j\rangle-\langle q_i\rangle\langle q_j\rangle, \tag{2.3a}$$

$$\Omega_{ij}=\langle p_ip_j\rangle-\langle p_i\rangle\langle p_j\rangle \tag{2.3b}$$

be the covariance matrices for the coordinates and momenta, respectively. Then $\chi_{ij}(t)$, $\Omega_{ij}(t)$ satisfy a system of coupled second-order ordinary differential equations which may be derived in a manner analogous to that employed by Messiah[5] for the one-dimensional case. The derivation is based on the general equation

$$i\hbar(d/dt)\langle A\rangle=\langle[A,H]\rangle+i\hbar\langle\partial A/\partial t\rangle, \tag{2.4}$$

valid for any observable A. We begin by setting

$$A=q_iq_j-\langle q_i\rangle\langle q_j\rangle$$

so that $\langle A\rangle=\chi_{ij}$. It is then found that

$$d\chi_{ij}/dt=\langle q_ip_j+p_iq_j\rangle-(\langle q_i\rangle\langle p_j\rangle+\langle p_i\rangle\langle q_j\rangle).$$

This equation is now again differentiated with respect to time. In this process, Eq. (2.4) is again employed with $A=q_ip_j+p_iq_j$ together with the equations of motion for $\langle q_i\rangle$, $\langle p_i\rangle$, Eqs. (2.2). The final result is

$$d^2\chi_{ij}/dt^2=(2/m^2)\Omega_{ij}-1/m(V_{ip}\chi_{pj}+V_{jp}\chi_{pi}). \tag{2.5}$$

The equations for the second derivatives of the momenta-covariance matrix elements Ω_{ij} are obtained in an analogous fashion. The final result is

$$d^2\Omega_{ij}/dt^2=2V_{ip}V_{jq}\chi_{pq}-(1/m)(V_{ip}\Omega_{pj}+V_{jp}\Omega_{pi}). \tag{2.6}$$

With prescribed initial values of $\bar{q}_i$, $d\bar{q}_i/dt$, χ_{ij}, $\dot{\chi}_{ij}$, Ω_{ij}, $\dot{\Omega}_{ij}$, the system of Eqs. (2.2c), (2.5), and (2.6) allows the computation of the subsequent time evolution of these quantities. In Sec. 3 we show that if the wave packet is initially Gaussian on a quadratic potential it remains Gaussian. Therefore the values of $\bar{q}_i(t)$ and $\chi_{ij}(t)$ are sufficient (in the coordinate representation) to completely characterize the wave-packet probability distribution.

3. GAUSSIAN WAVE-PACKET MOTION

We continue to consider wave-packet motion of an N-degree-of-freedom system subject to a quadratic potential, specifically with Hamiltonian given by Eq. (2.1). However, in this section we specialize the problem to that of an initially N-dimensional Gaussian wave packet, and we show that such a wave packet remains Gaussian. The result is thus an extension to N dimensions of the one-dimensional treatment previously presented in II. If the principal axes of the initial coordinate covariance matrix of the wave packet coincides with those of the quadratic potential, then the problem is separable and the one-dimensional treatment is immediately applicable. The analysis of this section is valid, however, for general relative orientation of the two sets of principal axes.

Let the wave function $\Psi(\mathbf{q},t)$ be written in the form

$$\Psi(\mathbf{q},t)=A(\mathbf{q},t)e^{(i/\hbar)S(\mathbf{q},t)}. \tag{3.1}$$

Then the time-dependent Schrödinger equation for the Hamiltonian of Eq. (2.1) leads to the following equations for $A(\mathbf{q},t)$ and $S(\mathbf{q},t)$:

$$m(\partial/\partial t)(A^2)=-(A^2S_{,i})_{,i}, \tag{3.2}$$

$$\partial S/\partial t=(\hbar^2/2m)(A_{,ii}/A)-(1/2m)S_{,i}S_{,i}-V_{ij}q_iq_j. \tag{3.3}$$

In writing these equations we have employed the comma notation for partial differentiation with respect to the coordinates q_i, that is,

$$\partial S/\partial q_i=S_{,i},$$

and again employed the summation conventions on repeated indices.

A solution to these equations may be obtained in the form

$$A=(2\pi)^{-N/4}|\chi|^{-1/4}\exp-\tfrac{1}{4}(\chi^{-1}{}_{ij}\xi_i\xi_j), \tag{3.4a}$$

$$S=\tfrac{1}{2}a_{ij}\xi_i\xi_j+b_i\xi_i+c, \tag{3.4b}$$

where $\xi_i=q_i-\bar{q}_i(t)$, $|\chi|$ is the determinant of the matrix $\mathfrak{X}$ with components $\chi_{ij}(t)$, $\chi^{-1}{}_{ij}$ are the components of $\mathfrak{X}^{-1}$, and a_{ij}, b_i, and c are functions of time. It is seen that the postulated solution is in the form of a moving N-dimensional Gaussian wave packet with mean $\bar{q}_i(t)$ and coordinate covariance matrix $\chi_{ij}(t)$. It may also be verified that for this wave function

$$\Omega_{ij}=\tfrac{1}{4}\hbar^2\chi^{-1}{}_{ij}+a_{im}a_{jn}\chi_{mn}. \tag{3.5}$$

Substitution of Eqs. (3.4) into Eq. (3.2) leads to the equation

$$m(\tfrac{1}{2}\dot{\chi}^{-1}{}_{ij}\chi_{ij}+\chi^{-1}{}_{ij}\xi_i d\bar{q}_j/dt-\tfrac{1}{2}\dot{\chi}^{-1}{}_{ij}\xi_i\xi_j)=\chi^{-1}{}_{ij}a_{ik}\xi_j\xi_k+\chi^{-1}{}_{ij}b_i\xi_j-a_{ii}.$$

By comparison of like powers of ξ_i we see that Eq. (3.2) will be satisfied if

$$b_i=md\bar{q}_i/dt=\bar{p}_i, \tag{3.6}$$

$$m\dot{\chi}^{-1}{}_{ij}=-(\chi^{-1}{}_{mi}a_{mj}+\chi^{-1}{}_{mj}a_{mi}). \tag{3.7}$$

Similarly, by substitution of Eq. (3.4) into Eq. (3.3), it is seen that the latter equation will be satisfied if

$$\dot{b}_i=md^2\bar{q}_i/dt^2=-V_{ij}\bar{q}_j, \tag{3.8}$$

$$m\dot{a}_{ij}+a_{ki}a_{kj}=-mV_{ij}+\tfrac{1}{4}\hbar^2\chi^{-1}{}_{ki}\chi^{-1}{}_{kj}, \tag{3.9}$$

$$\dot{c}=\left(\tfrac{1}{2}m\frac{d\bar{q}_i}{dt}\frac{d\bar{q}_i}{dt}-\tfrac{1}{2}V_{ij}\bar{q}_i\bar{q}_j\right)-(\hbar^2/4m)\chi^{-1}{}_{ii}. \tag{3.10}$$

The matrix a_{ij} may be eliminated from Eqs. (3.7) and (3.9) by differentiation of the former with respect to time. If Eq. (3.5) is then employed, the result is the previously derived equation for $d^2\chi_{ij}/dt^2$, Eq. (2.5).

4. SADDLE-POINT TUNNELING

We now consider the case in which the quadratic potential surface possesses a saddle point at $\mathbf{q}=0$. For this discussion it is convenient to employ a coordinate system[6] q_α in which the potential-energy matrix $V_{\alpha\beta}$ is diagonal, that is (with the summation convention not employed in this section for repeated indices),

$$V_{\alpha\alpha}=k_\alpha, \quad V_{\alpha\beta}=0, \quad \alpha\neq\beta. \tag{4.1}$$

It is furthermore assumed that

$$k_1<0,\ k_\alpha>0, \quad \alpha=2,\ \ldots,\ N. \tag{4.2}$$

In this coordinate system, Eqs. (2.2c), (2.5), and (2.6) assume the form

$$md^2\bar{q}_\alpha/dt^2+k_\alpha\bar{q}_\alpha=0, \tag{4.3}$$

$$d^2\chi_{\alpha\beta}/dt^2=(2/m^2)\Omega_{\alpha\beta}-(1/m)(k_\alpha+k_\beta)\chi_{\alpha\beta}, \tag{4.4}$$

$$d^2\Omega_{\alpha\beta}/dt^2=2k_\alpha k_\beta\chi_{\alpha\beta}-(1/m)(k_\alpha+k_\beta)\Omega_{\alpha\beta}. \tag{4.5}$$

As initial conditions for these equations we take the following:

$$\begin{aligned}&\bar{q}_\alpha(0)=-q_\alpha{}^b, \quad d\bar{q}_\alpha/dt|_{t=0}=v_\alpha{}^0, \quad \text{with} \quad v_1{}^0>0\\ &\chi_{\alpha\beta}(0)=\chi_{\alpha\beta}{}^0, \qquad \dot{\chi}_{\alpha\beta}(0)=0,\\ &\Omega_{\alpha\beta}(0)=\Omega_{\alpha\beta}{}^0, \qquad \dot{\Omega}_{\alpha\beta}(0)=0.\end{aligned} \tag{4.6}$$

The solution to Eqs. (4.3), (4.4), and (4.5) with these initial conditions are (for $\alpha,\beta\neq1$)

$$\bar{x}_\alpha=-x_\alpha{}^b\cos\omega_\alpha t+(v_\alpha/\omega_\alpha)\sin\omega_\alpha t,$$

$$\chi_{\alpha\beta}=\chi_{\alpha\beta}{}^0\cos\omega_\alpha t\cos\omega_\beta t+\frac{\Omega_{\alpha\beta}{}^0}{m^2\omega_\alpha\omega_\beta}\sin\omega_\alpha t\sin\omega_\beta t, \tag{4.7}$$

$$\Omega_{\alpha\beta}=-m^2\omega_\alpha\omega_\beta\chi_{\alpha\beta}{}^0\sin\omega_\alpha t\sin\omega_\beta t+\Omega_{\alpha\beta}{}^0\cos\omega_\alpha t\cos\omega_\beta t,$$

where $\omega_\alpha=(k_\alpha/m)^{1/2}$, $\alpha\neq1$. Since $k_1<0$, the corresponding solutions involve hyperbolic in place of the trigonometric functions. In particular, we note here for future reference the solutions for $\bar{q}_1$ and χ_{11}:

$$\bar{q}_1=-q_1{}^b\cosh\omega_1 t+(v_1{}^0/\omega_1)\sinh\omega_1 t, \tag{4.8}$$

$$\chi_{11}=\tfrac{1}{2}\chi_{11}{}^0\left[\left(1-\frac{\Omega_{11}{}^0/\chi_{11}{}^0}{mk_1}\right)\cosh2\omega_1 t+\left(1+\frac{\Omega_{11}{}^0/\chi_{11}{}^0}{mk_1}\right)\right], \tag{4.9}$$

where $\omega_1{}^2=-k_1/m$. An example of wave packet motion on a two-dimensional saddle point is shown in Fig. 1. It is seen that as the mean moves classically, the principal axes of the wave packet change direction and the wave packet spreads rapidly in the direction of

[6] We are here using the kernel index notation of J. Schouten [*Tensor Analysis for Physicists* (Clarendon Press, Oxford, 1954)], in which only the subscript alphabet changes, so that q_i and q_α refer to different coordinate systems. This notation is further utilized and discussed in Sec. 5 of this paper.

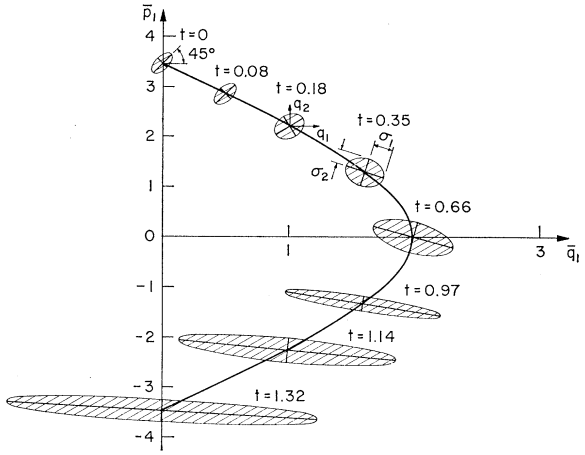

FIG. 1. Gaussian wave-packet motion on two-dimensional saddle-point surface $V=E_b+\frac{1}{2}V_{11}{}^U(q_1-q_1{}^b)^2+\frac{1}{2}V_{22}{}^Uq_2{}^2$; $-V_{11}{}^U=V_{22}{}^U=2$, $q_1{}^b=4$, $E_b=16$. (Units in which $m=\frac{1}{2}$, $\hbar=1$ are employed.) Initial wave-packet conditions: $\bar{q}_1=\bar{q}_2=0, d\bar{q}_1/dt=4\sqrt{3}$, $d\bar{q}_2/dt=0$, $(E_k=12)$; the initial wave-packet principal directions are at an angle of 45° with the q_1, q_2 axes, with principal values of $\varkappa$ given by $\varkappa_1=\frac{1}{2}$, $\varkappa_2=\frac{1}{8}$. The axes of the ellipses shown are equal in length to $\sigma_1(t)$ and $\sigma_2(t)$, where $\sigma=(2\varkappa)^{1/2}$; they are drawn to a scale $\frac{1}{10}$ that used for the $\bar{q}_1$ axis. The trajectory is shown in the phase plane $(\bar{q}_1,\bar{p}_1)$; the wave-packet shape is shown as projected on the (q_1,q_2) plane.

negative curvature because of the hyperbolic time dependence of $\varkappa_{11}$.

The probability $P(t)$ of finding the particle within the region $q_1>0$, i.e., beyond the crest of the saddle point is given by

$$P(t)=\int_0^\infty dq_1\int_{-\infty}^\infty dq_2\cdots dq_N\rho(q_1,\ldots,q_N,t), \quad (4.10)$$

where

$$\rho=A^2=(2\pi)^{-N/2}|\varkappa|^{-1/2}\exp-(\tfrac{1}{2}\sum_{\alpha,\beta=1}^{N}\varkappa^{-1}{}_{\alpha\beta}\xi_\alpha\xi_\beta), \quad (4.11)$$

with $\xi_\alpha=q_\alpha-\bar{q}_\alpha$, and the other notation is also defined in an analogous fashion to Eq. (3.4). The integral in Eq. (4.10) may be replaced by one over all of configuration space by use of the unit step function

$$U(y)=1, \quad y>0$$
$$=0, \quad y<0$$

so that

$$P(t)=\int_{-\infty}^\infty dq_1\cdots dq_N\rho(q_1,\ldots,q_N,t)U(q_1). \quad (4.12)$$

The integral may now be evaluated by introducing the ξ_α as variables of integration and use of a formula of Schlömilch as generalized by Rice.[7] The result is

$$P(t)=\tfrac{1}{2}\operatorname{erfc}[-\bar{q}_1(t)/(2\varkappa_{11})^{1/2}], \quad (4.13)$$

which is precisely the same as the one-dimensional solution previously presented [Eq. (2.15) of II]. As in that case we define the tunneling probability K by the limiting process

$$K=\lim_{t\to\infty}P(t)$$
$$=\tfrac{1}{2}\operatorname{erfc}\left[\frac{(q_1{}^b-v_1{}^0/\omega_1)}{(2\varkappa_{11}{}^0-2\Omega_{11}{}^0/(mk_1))^{1/2}}\right]$$
$$=\tfrac{1}{2}\operatorname{erfc}\left[\frac{q_1{}^b}{(2\varkappa_{11}{}^0)^{1/2}}\frac{(1-(E_k/E_b)^{1/2})}{(1-\Omega_{11}{}^0/\varkappa_{11}{}^0(mk_1))^{1/2}}\right], \quad (4.14)$$

where $E_b=-\frac{1}{2}k_1(q_1{}^b)^2$ is the potential-energy difference between the starting position of the wave packet mean and the saddle point and $E_k=\frac{1}{2}m(v_1{}^0)^2$ is the initial classical kinetic energy to be ascribed to the wave-packet motion in the q_1 direction. It is interesting to note that although the process is multidimensional, the tunneling probability depends only on the wave-packet and barrier characteristics in the saddle-point direction q_1, even when the initial principal directions of the wave packet are not aligned with the saddle-point principal directions. This greatly simplifies its use in the rate expression, and we turn next to this question.

5. RATE THEORY

We consider a system with N degrees of freedom whose potential-energy function $V(q_1,\ldots,q_N)$ admits of two stable equilibrium configurations S and S' with an intermediate saddle-point configuration U (Fig. 2). Reduced-mass coordinates[8] are used so that $m=1$ in Eq. (2.1) for the Hamiltonian of the system. Under the assumption that an ensemble of such systems is in thermal equilibrium in the neighborhood of S we wish to determine the ensemble average rate with which transitions from S to S' occur.

In general the principal directions of the potential-energy matrix (that is of the second partials of the potential-energy function) will not coincide at S and U. Two different orthogonal coordinate systems are therefore utilized; q_i, $i=1,\ldots,N$ in the principal directions at S and q_α, $\alpha=1,\ldots,N$ in the principal directions at U with q_α, $\alpha=1$ in the saddle-point direction (Fig. 2). Here, and throughout this section, kernel-index notation[6] for vectors and tensors is utilized. That is only the subscript alphabet changes upon change of coordinate system. Thus A_{ij} and $A_{\alpha\beta}$ refer to components of the same tensor referred to the q_i and q_α coordinate systems, respectively. While this notation is compact, it does introduce possibilities for confusion when it is necessary to refer to particular tensor components. In the present discussion, however, it is only necessary to specifically designate components in the saddle-point direction, that is in the direction q_α, $\alpha=1$. Hereafter, therefore, it is understood that q_1 refers to q_α, $\alpha=1$, A_{11} refers to $A_{\alpha\beta}$, $\alpha=\beta=1$, etc. In this section, unless

[7] S. O. Rice, Bell System Tech. J. **24**, 58 (1945).

[8] See, e.g., the discussion in I, Eqs. (2.1)–(2.3).

otherwise noted, the summation convention is employed for repeated Greek or Latin indices.

In order to describe the thermal-equilibrium characteristics of the ensemble in the potential well at S, the minimum-uncertainty ensemble[2] described in I is employed. That is, the quantum states of all members of the ensemble are observed at a given instant of time in a manner to introduce minimum uncertainty for conjugates and momenta. These states will then be given in the coordinate representation by Gaussian wave functions of the general form described by Eq. (3.4) with $a_{ij}\equiv c\equiv 0$, $b_i=\bar{p}_i$, χ_{ij} and Ω_{ij} diagonal with

$$\chi_{ii}\Omega_{ii}=\tfrac{1}{4}\hbar^2, \quad \text{(N. S.)} \tag{5.1}$$

where "(N.S.)" indicates that the summation convention is suspended. Furthermore, we set

$$\chi_{ii}=\hbar/(2\omega_i), \quad \text{(N.S.)} \tag{5.2}$$

where[9]

$$\omega_i=(V_{ii}{}^S)^{1/2}, \quad \text{(N.S.)} \tag{5.3}$$

and

$$V_{ii}{}^S=\left.\frac{\partial^2 V}{\partial q_i{}^2}\right|_S; \quad V_{ij}{}^S=0, \quad i\neq j \quad \text{(N.S.)}. \tag{5.4}$$

With this value of χ_{ii} (N.S.) the state would remain one of minimum uncertainty if the system were subject to a harmonic potential with the same character as at S. The ensemble characteristics corresponding to thermal equilibrium can be described in terms of a distribution function $\rho(\bar{\mathbf{q}},\bar{\mathbf{p}})$ defined on a phase space whose coordinates are $(\bar{\mathbf{q}},\bar{\mathbf{p}})$, the quantum means of the coordinates and momenta of the ensemble elements which are in the minimum-uncertainty states just defined. As derived in I,

$$\rho(\bar{\mathbf{q}},\bar{\mathbf{p}})=\mathcal{C}\exp\{-\sum_{i=1}^{N} c_i(2\hbar\omega_i)^{-1}(p_i{}^{-2}+\omega_i{}^2 q_i{}^{-2})\}, \tag{5.5}$$

where

$$c_i=\exp(\hbar\omega_i/kT)-1, \quad \mathcal{C}=(2\pi\hbar)^{-N}\prod_{i=1}^{N} c_i. \tag{5.6}$$

We may rewrite the expression for $\rho(\bar{\mathbf{q}},\bar{\mathbf{p}})$ in tensor notation as follows:

$$\rho(\bar{\mathbf{q}},\bar{\mathbf{p}})=\mathcal{C}\exp\{-(2\hbar)^{-1}c_{ij}(\omega^{-1}{}_{jk}\bar{p}_i\bar{p}_k+\omega_{jk}\bar{q}_i\bar{q}_k)\}, \tag{5.7}$$

where c_{ij} and ω_{ij} are diagonal in the q_i system with $c_{ii}=c_i$, $\omega_{ii}=\omega_i$, (N.S.), as defined in Eqs. (5.6) and (5.3), respectively, $\omega^{-1}{}_{ij}$ are the components of the tensor inverse to ω_{ij}, and

$$\mathcal{C}=(2\pi\hbar)^{-N}\det(c_{ij}).$$

This notation permits the transcription of $\rho(\bar{\mathbf{q}},\bar{\mathbf{p}})$ to the q_α coordinate system simply by replacing all Latin subscripts in Eq. (5.7) by Greek subscripts. Of course c_{ij} and $c_{\alpha\beta}$, etc., are related by the usual rules for transformation of cartesian tensors.

[9] Recall that reduced-mass coordinates are employed in this section.

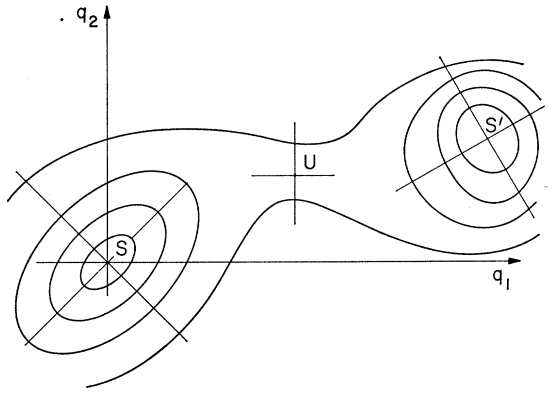

FIG. 2. Schematic representation of potential wells containing stable equilibrium configurations S and S' and separated by a saddle point at U.

As discussed in I the ensemble average f of the rate at which transitions from S to S' occur may be written as

$$f=\int_0^\infty \bar{p}_1 d\bar{p}_1 \int_{\Omega_0} K(\bar{\mathbf{q}},\bar{\mathbf{p}})\rho(\bar{q},\bar{p})\prod_{\alpha=2}^{N} d\bar{q}_\alpha d\bar{p}_\alpha, \tag{5.8}$$

where Ω_0 is the subspace $\bar{q}_1=0$, $-\infty<\bar{q}_\alpha<\infty$, $-\infty<\bar{p}_\alpha<\infty$, $\alpha=2,\ldots,N$. Equation (5.8) may be interpreted as integrating over the rates at which a system arrives with $\bar{p}_1>0$ at the hyperplane $q_1=0$ with values $(\bar{\mathbf{q}},\bar{\mathbf{p}})$ (and therefore, under our assumption, with known wave-packet characteristics) multiplied by $K(\bar{\mathbf{q}},\bar{\mathbf{p}})$ the transmission coefficient or the tunneling probability that it will go on to the next valley.

In II the tunneling probability for one-dimensional motion was computed for a piece-wise quadratic barrier by replacing this problem by one for the parabolic barrier. This replacement involved two steps: (1) The assigned classical initial wave-packet kinetic energy $E_k{}^*$ for the piece-wise quadratic barrier was replaced by a slightly augmented value E_k. This was motivated by the fact that the total classical energy E_{cl}, conserved for the parabolic barrier, is not conserved for the piece-wise quadratic case. (2) It was then assumed that the tunneling probability would be the same for the two problems if (a) the barrier heights, E_b, (b) starting distance of wave packet mean from barrier, (c) initial wave-packet characteristics, including E_k, were the same for both problems. Further discussion of this heuristic procedure may be found in II, together with numerical solutions of the time-dependent Schrödinger equation which verify that it leads to quite accurate values of the tunneling probability for the piece-wise quadratic barrier. It was also noted in II that although step (1) above improved the

accuracy of the tunneling probability values, its omission produced relatively small error in the final rate expression for large values of $E_b/\hbar\omega$, say $E_b/\hbar\omega \geq 2$ (where E_b is the barrier height and ω is the frequency corresponding to the potential well). Guided by this result we here omit[10] the energy correction of step (1) (a correction which would appear to be quite complicated in the N-dimensional case) and we compute the tunneling probability from Eq. (4.14) with all the quantities appearing as arguments there being interpreted [in accordance with step (2) of the procedure just described] as relating to the well-barrier combination under consideration in this section. It is now convenient to relate E_b, the energy difference between the S and U configuration to $q_1{}^b$ the well-barrier distance. We proceed in a manner analogous to the one-dimensional case. If, as in II (Eq. 3.3), we regard V as piece-wise quadratic in the q_1 direction and impose continuity of V and $\partial V/\partial q_1$, then

$$E_b = \frac{-V_{11}{}^U (q_1{}^b)^2}{2(1-V_{11}{}^U/V_{11}{}^S)} \tag{5.9}$$

or

$$q_1{}^b = \left[\frac{2(1-V_{11}{}^U/V_{11}{}^S)E_b}{-V_{11}{}^U}\right]^{1/2},$$

where

$$V_{11}{}^U = \left.\frac{\partial^2 V}{\partial q_1{}^2}\right|_U, \tag{5.10}$$

and, in accordance with the notational convention of this section, $V_{11}{}^S$ is the $\alpha=\beta=1$ component of $V_{\alpha\beta}{}^S$, which are the tensor components in the q_α system corresponding to $V_{ij}{}^S$ [Eq. (5.4)]. Substitution for $q_1{}^b$ from Eq. (5.9) into Eq. (4.14) then yields

$$K(\bar{\mathbf{q}},\bar{\mathbf{p}}) = K(\bar{p}_1) = \tfrac{1}{2}\operatorname{erfc}[(2E_b/\hbar\omega^*)^{1/2} - (2E_k/\hbar\omega^*)^{1/2}], \tag{5.11}$$

where $2E_k = \bar{p}_1{}^2$ and

$$\hbar\omega^* = \frac{2(\Omega_{11}/m - \chi_{11}V_{11}{}^U)}{(1-V_{11}{}^U/V_{11}{}^S)}, \tag{5.12}$$

and the notational significance of χ_{11}, Ω_{11}, is analogous to that of $V_{11}{}^S$. With the introduction of the notation of Eq. (5.12), the formula for K, Eq. (5.11), takes on a completely analogous form to that for the one-dimensional case [Eq. (3.15) of II], and it may in fact be verified that if the present problem is specialized to one dimension, $\omega^*=\omega$, the single-frequency corresponding to the potential well. We may now express the rate f in Eq. (5.8) as an unrestricted integral over all of phase space, namely,

$$f = \tfrac{1}{2}\mathrm{e}\int_{-\infty}^{\infty} \delta(\bar{q}_1)\bar{p}_1 U(\bar{p}_1)\operatorname{erfc}\left[\left(\frac{2E_b}{\hbar\omega^*}\right)^{1/2} - \frac{\bar{p}_1}{(\hbar\omega^*)^{1/2}}\right] \times \exp[-A_{\alpha\beta}\bar{q}_\alpha\bar{q}_\beta - B_{\alpha\beta}\bar{p}_\alpha\bar{p}_\beta] \prod_{\delta=1}^{N} d\bar{q}_\delta d\bar{p}_\delta, \tag{5.13}$$

where, in addition to the symbols already defined,[11]

$$A_{\alpha\beta} = (2\hbar)^{-1}c_{\alpha\delta}\omega_{\delta\beta}, \tag{5.14}$$

$$B_{\alpha\beta} = (2\hbar)^{-1}c_{\alpha\delta}\omega^{-1}{}_{\delta\beta}, \tag{5.15}$$

and $\delta(x)$ is the Dirac δ function. This integral may be transformed to the following one-dimensional integral by the Schlömilch-Rice method[7]:

$$f = \frac{1}{4\pi}\left(\frac{B^{-1}{}_{11}}{A^{-1}{}_{11}}\right)^{1/2} \times \int_0^\infty x e^{-x^2/2}\operatorname{erfc}\left[\left(\frac{2E_b}{\hbar\omega^*}\right)^{1/2} - x\left(\frac{B^{-1}{}_{11}}{2\hbar\omega^*}\right)^{1/2}\right]dx, \tag{5.16}$$

an integral which is of the same form as that encountered in the one-dimensional analysis of II. The result may be put in the same form, namely,

$$f = \frac{\omega}{2\pi}\left[\tfrac{1}{2}\operatorname{erfc}U + \frac{1}{2(1+c/2)^{1/2}} e^{-U^2 c/(2+c)} \times \operatorname{erfc}\left(\frac{-U}{(1+c/2)^{1/2}}\right)\right], \tag{5.17}$$

providing the following identifications are made for the present N-dimensional situation:

$$\omega = (B^{-1}{}_{11}/A^{-1}{}_{11})^{1/2}, \quad c = 2\hbar\omega^*/B^{-1}{}_{11}, \quad U = (2E_b/\hbar\omega^*)^{1/2}. \tag{5.18}$$

Although the final result has thus been expressed in equivalent one-dimensional form, it is clear that the multidimensional aspect of the problem enters implicitly through the tensor transformations. To explore the quantitative effects of this aspect of the process, we have considered an artificial two-dimensional problem for which the evaluation of Eq. (5.14) is shown in Fig. 3. In Fig. 3(a) the effect of the relative orientation of the principal directions in the well and on the saddle-point surface is shown. For $\theta=0$, the result is the same as the one-dimensional case [Eq. (5.4) of II], with all quantities which relate to the q_2 direction playing no role. At higher-temperature

[10] The corresponding approximation in the one-dimensional case leads to Eq. (5.4) of II, and when present results are compared with the one-dimensional theory, it is this equation which is meant.

[11] Note that the components $A_{\alpha\beta}$ were denoted by $C_{\alpha\beta}'$ in I [Eq. (4.4) of that paper]. The change in notation was made to avoid confusion with the tensor components $c_{\alpha\beta}$.

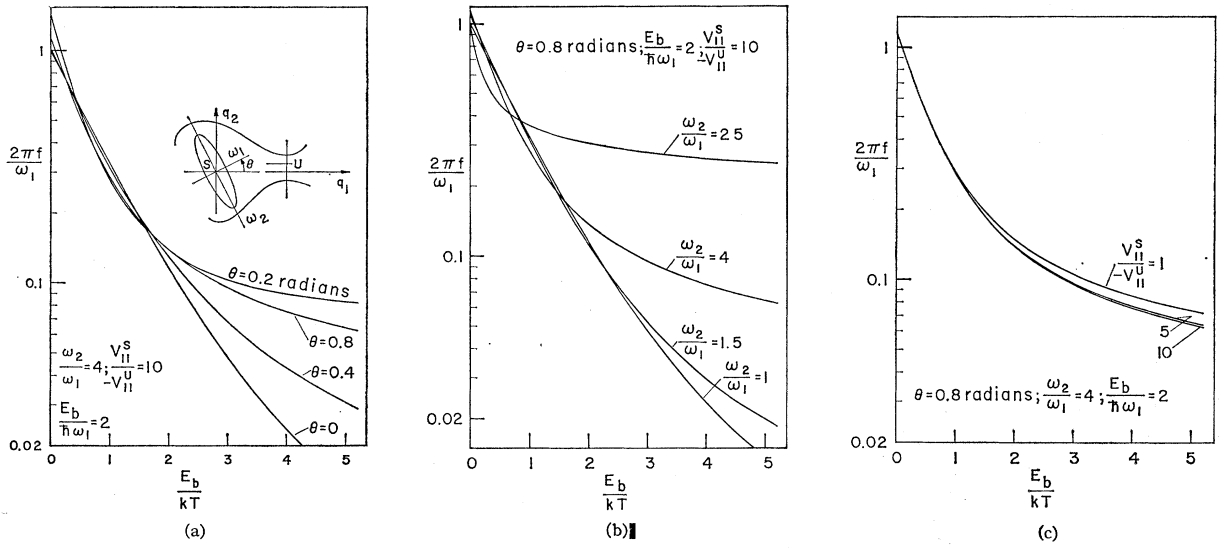

FIG. 3. Parameter study of the rate equation, Eq. (5.17), for hypothetical two-dimensional problem. (a) Effect of relative orientation between principal directions in potential well and on saddle point. (b) Effect of frequency ratio in potential well. (c) Effect of well-to-barrier curvature ratio.

levels, where the rate curve is nearly straight as in the classical calculation, the effect of nonzero θ is slight; however, it becomes pronounced at the lower-temperature levels where tunneling plays a significant role. Of course there can be no orientation effect when the potential well has cylindrical symmetry, that is, when $\omega_1=\omega_2$. The effect of variable ω_2/ω_1 is shown in Fig. 3(b). Again, the principal divergence occurs in the temperature range where tunneling is important. The ratio of curvatures, $V_{11}^S/(-V_{11}^U)$, does not enter explicitly (see Ref. 24 of II) in the one-dimensional theory as given by Eq. (5.4) of II. It does appear explicitly in the N-dimensional theory [Eq. (5.12)]. It is seen in Fig. 3(c), however, that at least for the parameters here considered its effect is small.

6. CONCLUSIONS

A theory for rate processes in solids has been developed which includes (a) the use of quantum statistics to describe the thermal-equilibrium characteristics in the potential well, (b) tunneling through the saddle-point surface between wells, and (c) the N-dimensional character of the problem.

Basic to the development is the use of an appropriate minimum-uncertainty wave-packet ensemble in the well. This then allows a description of the process in the spirit of classical-rate theory in which members of the ensemble make an attempt upon the barrier with a frequency corresponding to the well characteristics, and with an energy distribution determined by the temperature level. The success of such an attempt is given by a tunneling or transmission probability which is determined by the barrier characteristics. It was found possible in this paper to derive a simple compact expression for the tunneling probability for Gaussian wave packets on a second-degree N-dimensional saddle-point surface. This transmission probability depends only upon the characteristics of the wave packet in the saddle-point direction even when the initial principal directions of the wave packet are not aligned with the saddle-point principal directions. The simplicity of this result contrasts with the difficulty of treating multidimensional tunneling when energy states rather than Gaussian wave packets are employed.[12]

Since the initial characteristics of the wave packets of the ensemble are determined by the potential well character and their subsequent tunneling probability is determined by the saddle-point character, the theory includes the effect of a difference in orientation between the two sets of principal directions. This is explored quantitatively for a hypothetical two-dimensional problem. It is found that while this relative orientation has little effect at high-temperature levels, it has a large effect at lower temperatures where tunneling is important. This result should have some bearing on the isotope effect in diffusion, and it is hoped to explore this in subsequent work.

ACKNOWLEDGMENT

One of us (Y. P.) would like to acknowledge the hospitality of Brown University where he was ARPA Interdisciplinary Fellow for the academic year 1968–69.

[12] See, for example, the discussion of H. S. Johnston and D. Rapp, J. Am. Chem. Soc. **83**, 1 (1961).