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Phonon coupling in tunneling systems at zero temperature: An instanton approach

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We have found a new method for dealing with phonon modes in path integrals. Using it and an instanton calculation, we have developed a detailed theory of the tunneling event in the presence of phonons. This theory generalizes the traditional methods (truncating the energy spectrum of the defect, treating it as a discrete "spin" system) which are valid only in the weakly coupled low-mass regime. Most atomic tunneling will be described by an "effective mass" for the defect due to coupled lattice motion; we use ($KCl:Li^+$) as an example of this "slow-flip" regime. A physical picture describing electrons which are strongly coupled to phonon modes (i.e., self-trapped and polaronic electrons) is presented, but the instanton machinery does not simplify in this regime and direct calculation is necessary. We present a study of Anderson's negative-U centers to elucidate this type of tunneling. We also use a two-parameter model to distinguish the domains of validity for the truncation, self-trapped, and effective-mass regimes.

I. INTRODUCTION

Quantum tunneling in the presence of phonon modes is ubiquitous in solid-state physics. Quantum tunneling of atoms dominates the low-temperature behavior of glasses.[1,2] It describes the behavior of many well-studied defects in alkali halides,[3] and describes diffusion of light interstitials in metals.[4] Quantum tunneling of electrons is important in describing polaronic conduction in insulators,[5] electron transport in biophysics, [6] and possibly low-temperature behavior of amorphous semiconductors.[7] In all these cases, the tunneling entity couples to elastic deformations of the surrounding atoms. In all cases but glasses, this coupling has been shown to be crucial to a detailed understanding of the systems[3–6]; in glasses no detailed microscopic model exists.

When this is considered, it is surprising how little attention has been spent on this problem. In most theoretical treatments, a tunneling matrix element is assumed and is measured experimentally; attempts to calculate these have had mixed success. The most common approach uses what I call the truncation approximation: the Hamiltonian for the tunneling entity is simplified to a matrix, truncating the higher-energy states as "physically unimportant". The phonons are then coupled to the defect and act to suppress tunneling by the overlap integral of their initial and final ground states (variously termed the Frank-Condon or Debye-Waller factor). This approximation was developed to describe electronic tunneling with weak phonon coupling, and it gives poor answers out of this domain. Occasionally, other decriptions of tunneling are given without much theoretical justification. One of these is a quasiclassical description in which the surrounding atoms relax adiabatically as the defect moves over the barrier. We shall see that it is a good description for most atomic tunneling, if it is corrected by the use of an effective mass.

This paper contains a complete qualitative theory of the zero-temperature tunneling process with phonon coupling, and sets up machinery which should serve to quantitatively describe tunneling-center — phonon interactions at finite temperatures. It draws upon three theoretical sources. The concept of tunneling in glasses as motion along a path in a multidimensional-configuration space is described nicely by Anderson.[8] Methods of locating this "instanton" path have been used recently in studies of the strong interaction[9]; Coleman[10] presents a pedagogical version. Finally, the method of integrating away the phonon modes, leaving a tractable one-dimensional problem, is due to Feynman.[11,12]

Section II of this paper will discuss the truncation approximation and the nature of its failure. It serves also to introduce notation and ideas in a familiar context. Section III sets up the path-integral description of our system. It develops a new version of the phonon propogator, which replaces ugly

boundary terms and a time-retarded position-position interaction with an effective relaxed potential and a time-retarded velocity-velocity interaction. This formulation allows practical use of the path integral in this problem. Section IV discusses the nature of the instanton path in various physical regimes. It formally develops the truncation approximation and the adiabatic or slow-flip approximation. It discusses the self-trapped regime, where an attractive physical picture exists but no corresponding calculational tools are found. It then provides a two-parameter model which is numerically solved and used to distinguish the domains of validity of these three physical pictures. Section V develops the slow-flip approximation further by applying it to lithium substitutional defects in KCl (whose local potential and phonon coupling are at least roughly known). Direct calculation of the tunneling matrix element is not feasible with the available data; it depends exponentially on barrier heights and widths which are not known well. (This largely explains the lack of theoretical attention spent on this area—the truncation approximation can and has[13] failed by orders of magnitude without causing concern about its validity. Also, any refined theory is similarly unlikely to be convincingly supported by experiment.) We concentrate on describing the isotope effect in this system. Section VI describes self-trapped tunneling in more detail, by studying Anderson's negative-U model for electronic states in amorphous semiconductors. We study a paper of Phillips[14] in which he notes that lattice deformations will strongly suppress tunneling in these centers. He sets up a model in which the truncation approximation is in some sense valid, and concludes that tunneling is impossible for negative-U centers. We find that his model is pathological and tunneling in it is uncharacteristic of self-trapped tunneling. We conclude that Phillips has overestimated this suppression, and that negative-U centers may well contribute to the low-temperature specific heat. Section VII conclude with some general remarks.

II. TRUNCATION APPROXIMATION

In this paper, we analyze the nature of a single tunneling event in a many-dimensional-configuration space composed of a defect coordinate Q and a number of phonon coordinates q_k. The general system (which we shall use in Secs. V and VI) has the Hamiltonian,

$$\mathcal{H} = H(P,Q) + H_{\rm ph}(p_k,q_k) + H_{\rm int}(Q,q_k) \ ,$$

$$H(P,Q) = \frac{P^2}{2M} + V(Q) \ ,$$

$$H_{\rm ph}(p_k,q_k) = \sum_k \frac{p_k^2}{2M} + \tfrac{1}{2} m \omega_k^2 q_k^2 \ ,$$

$$H_{\rm int}(Q,q_k) = \sum_k \Lambda_k(Q) q_k \ .$$

Note first, the index k is a formal one, labeling the normal modes of the coordinates of the system minus the defect coordinate. At best, these modes will be plane waves only in the limit $k \to 0$. Secondly we shall see that $V(Q)$ need not be a double well for the system to behave as one. $V(Q)$ is the potential with other atoms "nailed down"; allowing them to relax will often form a "spontaneous" double well, i.e., self-trapping may be important (see Fig. 1). $V(Q)$ will, of course, be anharmonic.

The phonon-defect coupling above is quite general. If one makes the natural restriction that the phonon coordinates be harmonic for fixed Q, this coupling only assumes further that the phonon frequencies be independent of Q. A more traditional coupling in the literature ignores "breathing" during tunneling, and is linear in the defect coordinate:

$$H_{\rm int}(Q,q_k) = \sum_k \lambda_k q_k Q \ .$$

Here $\lambda_k \propto k$ as $k \to 0$ unless there is some special

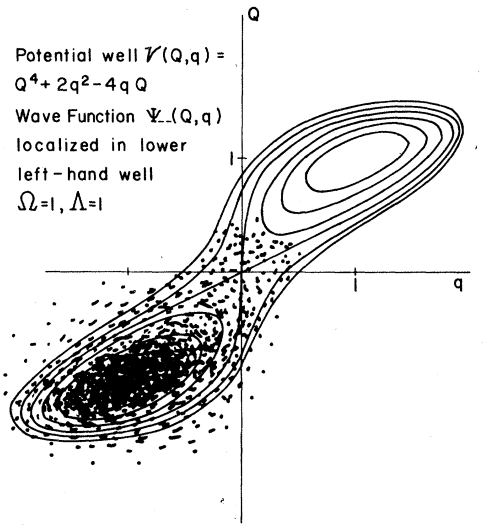

FIG. 1. Potential for a single quartic well coupled to a single phonon mode. Note that the double well is formed through self-trapping.

symmetry to the defect. For simplicity, in Secs. II–IV we shall use this interaction.

The truncation approximation involves restricting the Q part of the wave function to certain "low-energy" states $\psi_1 \cdots \psi_n$. The general pure state of the truncated system has the form $\sum_{i=1}^{n} \psi_i(Q)\phi_i(q_k)$ where the ϕ_i are arbitrary phonon states. The Hamiltonian becomes, if $A_{ij} = \langle \psi_i | A | \psi_j \rangle$,

$$\mathcal{H}_{ij} = H_{ij} + \sum_k \frac{p_k^2}{2m} + \tfrac{1}{2} m \omega_k^2 q_k^2 + \sum_k \lambda_k q_k Q_{ij} \quad .$$

This is a very substantial simplification of the problem. All the nonlinearity has been summarized into H_{ij} and Q_{ij}; we do not know the form of the potentials anyhow, so we are left with the tractable problem of experimentally measuring these parameters.

Nonetheless, let us pursue briefly the (pargmatically pointless) question how ought we choose the ψ_i? We could choose the lowest eigenstates of $H = p^2/2m + V(Q)$. $V(Q)$, however, is the potential if the other atoms are nailed down; we expect at least the high-frequency phonon modes will relax in response to the motion of the defect. The potential energy of our systems is

$$V = V(Q) + \sum_k \tfrac{1}{2} m \omega_k^2 q_k^2 + \lambda_k q_k Q \quad ;$$

if we fix Q and allow the phonons to relax we get a modified potential

$$\tilde{V}(Q) = V(Q) - \textstyle\sum_k (\lambda_k^2 Q^2 / 2m\omega_k^2) \quad .$$

These two potentials V and $\tilde{V}$ will reappear later. For light defects, $V(Q)$ will be the "saddle-point" potential seen by the defect in the midst of the tunneling process; $\tilde{V}(Q)$ describes the motion within the two wells. We shall see to the extent the V and $\tilde{V}$ differ, no one-dimensional potential adequately models tunneling.

Since we are modeling a double well, we truncate to two states. We change basis to diagonalize Q; since our double well is symmetric we have

$$\mathcal{H} = \begin{bmatrix} 0 & -\Delta \\ -\Delta & 0 \end{bmatrix} + \sum_k \frac{p_k^2}{2m} + \tfrac{1}{2} m \omega_k^2 q_k^2 + \sum_k \lambda_k q_k \begin{bmatrix} -Q_0/2 & 0 \\ 0 & +Q_0/2 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & -\Delta \\ -\Delta & 0 \end{bmatrix} + \begin{bmatrix} \sum_k \frac{p_k^2}{2m} + \tfrac{1}{2} m \omega_k^2 \left[q_k - \frac{\lambda_k Q_0}{2m\omega_k^2} \right]^2 & 0 \\ 0 & \sum_k \frac{p_k^2}{2m} + \tfrac{1}{2} m \omega_k^2 \left[q_k + \frac{\lambda_k Q_0}{2m\omega_k^2} \right]^2 \end{bmatrix}$$

$$- \frac{\lambda_k^2 Q_0^2}{8m\omega_k^2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad .$$

The last term is the relaxation energy noted above, and here is unimportant. We assume Δ is small and compute the matrix element connecting the phonon ground state at $-Q_0/2$ with that at $+Q_0/2$:

$$\begin{bmatrix} \prod_k \phi_k^0 \left[q_k - \frac{\lambda_k Q_0}{2m\omega_k^2} \right] \\ 0 \end{bmatrix} \begin{bmatrix} 0 & -\Delta \\ -\Delta & 0 \end{bmatrix} \begin{bmatrix} 0 \\ \prod_k \phi_k^0 \left[q_k + \frac{\lambda_k Q_0}{2m\omega_k^2} \right] \end{bmatrix}$$

$$= -\Delta \prod_k \left\langle \phi_k^0 \left[q_k - \frac{\lambda_k Q_0}{2m\omega_k^2} \right] \middle| \phi_k^0 \left[q_k + \frac{\lambda_k Q_0}{2m\omega_k^2} \right] \right\rangle = -\Delta \exp\left[-\sum_k \frac{\lambda_k^2 Q_0^2}{4\hbar m \omega_k^3} \right] = -\Delta e^{-W} \quad .$$

The tunneling amplitude has been suppressed by the phonon overlap integral, sometimes termed a Frank-Condon or Debye-Waller factor. W is $m\omega_D Q_0^2/\hbar$ up to a numerical factor, where ω_D is the Debye frequency. It is roughly one-tenth the ratio of Q^2 to the mean-square zero-point fluctuation in the solid.

Why is this not a good description of tunneling? Consider a simplified system: $V(Q) = Q^4$ coupled

to a single oscillator (see Fig. 1); $\tilde{V}(Q)$ is given by the potential along the line connecting the two minima at $Q = q = \pm 1$. Let us assume that our system has been observed in the lower left-hand well ($Q = -1, q = -1$). The wave function $\Psi_{--}(Q,q)$ is that linear combination of the symmetric ground state and the antisymmetric first excited state which minimizes the amplitude in the upper right-hand well. The tunneling amplitude Δ gives the rate at which probability flows into the upper right-hand well, $\Delta = \langle \Psi_{++}(Q,q) \mid \mathcal{H} \mid \Psi_{--}(Q,q) \rangle$. Clearly this will depend strongly on $\Psi(Q,q)$ near the saddle point at $q = Q = 0$.

Our truncated space of Q states has only one function ψ_- which is localized mainly in $Q < 0$; we are modeling $\Psi_{--}(Q,q)$ with a product $\psi_-(Q)\phi(q)$ (see Fig. 2). Consider the behavior of this model wave function along $q = 0$. Since $\psi_-(Q)$ must be well localized around $Q = -1$ to model Ψ near the minimum, the product $\psi_-(Q)\phi(q)$ will be very small near $Q = 0$, while (absurdly) it has reasonably large amplitude at $Q = -1$, $q = 0$, where the potential energy is quite high. Similar behavior occurs along $Q = 0$. The truncation approximation fails precisely in the tunneling region at the saddle point; only when the barrier to tunneling does not change with the phonon coupling ($V \approx \tilde{V}$) will it give good answers.

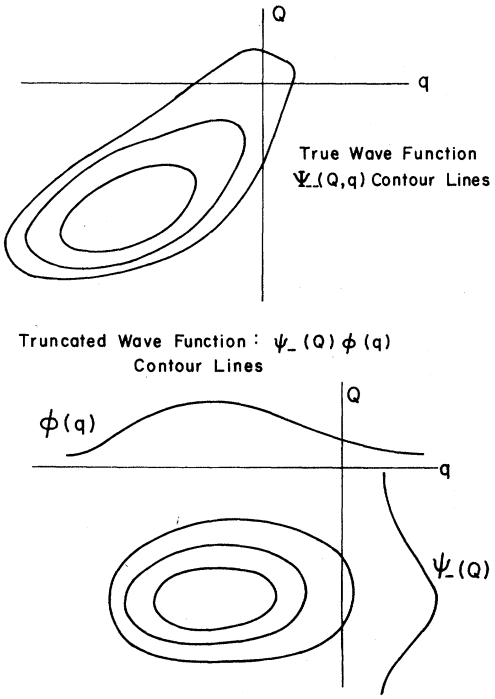

FIG. 2. The truncated wave function describes the state acceptably at the bottoms of the potential wells, but fails badly at the saddle point $Q = q = 0$.

Clearly, more Q-wave functions in which to expand the many-body wave function would help. The effective Hamiltonian would then use these "high-energy" states to move from well to well. I choose instead to avoid truncation—a choice which leads us into the forest of path integrals and instantons.

III. PATH INTEGRALS—INTEGRATING OUT THE PHONONS

Feynman's[11] path-integral methods are a formulation of quantum mechanics as a sum over classical trajectories, where a trajectory $Q(t)$ with action $S(Q)$ contributes $e^{iS(Q)/\hbar}$. These paths allow a direct visualization of tunneling as the motion of a defect accompanied by motions of the nearby atoms. One simply integrates over all routes between the two equilibrium points. Path integrals also mesh beautifully with phonons; all the integrals are Gaussians.

In this section we shall, for a fixed path $Q(t)$, integrate over all possible phonon paths $q_k(t)$. This will lead to an effective Lagrangian with our adiabatic potential $\tilde{V}$ and with a time-retarded interaction $\mathfrak{U}(t)$. We then rotate to imaginary time, which serves to make the contributions from various paths real and small (rather then complex and oscillatory). The path with the largest contribution is the instanton path.

Our Lagrangian is

$$\mathfrak{L}(Q,\vec{q}_k) = \tfrac{1}{2}M\dot{Q}^2 - V(Q) + \sum_k \tfrac{1}{2}m\dot{q}_k^2 - \tfrac{1}{2}m\omega_k^2 q_k^2 - \lambda_k Q q_k \ .$$

We want to integrate the phonons out of the path integral, to get an effective time-retarded interaction in Q. To do this we must choose the initial and final states for our phonon coordinates. The interesting paths have $Q(t) \to Q_0$ as $t \to -\infty$ and $Q(t) \to Q_1$ as $t \to +\infty$. Projecting the phonons into their unperturbed ($Q = 0$) ground state at the ends of our time interval introduces unnecessary phonon overlap terms. The ground state of oscillator k initially is a Gaussian about $q_{k_0} = \lambda_k Q_0/m\omega_k^2$, and finally one about $q_{k_1} = \lambda_k Q_1/m\omega_k^2$. I choose to project the phonons into these states:

$$
{}_T\langle Q_1, GS(\vec{q}_{k_1}) \mid Q_0, GS(\vec{q}_{k_0})\rangle_0
$$

$$
= \oint_{Q(0)=Q_0}^{Q(T)=Q_1} \mathfrak{D}Q \prod_k \left[\int dx_{k_1} \phi_0^*(x_{k_1} - q_{k_1}) \int dx_{k_0} \phi_0(x_{k_0} - q_{k_0}) \oint_{q_k(0)=x_{k_0}}^{q_k(T)=x_{k_1}} Dq_k \exp\left[\frac{i}{\hbar} \int_0^T L(Q, \vec{q}_k) dt \right] \right]
$$

Now, the phonon path integrals form a series of Gaussians, and like all forced harmonic oscillators, the integrations can be performed explicitly. Consider a fixed phonon mode. The contribution from coordinate q will be,

$$
C_q = \int dx_1 \left[\frac{m\omega}{\pi\hbar} \right]^{1/4} e^{-(m\omega/2\hbar)(x_1 - q_1)^2} \int dx_0 \left[\frac{m\omega}{\pi\hbar} \right]^{1/4} e^{-(m\omega/2\hbar)(x_0 - q_0)^2}
$$

$$
\times \oint_{q(0)=x_0}^{q(T)=x_1} \mathfrak{D}q \exp\left[\frac{i}{\hbar} \int_0^T \left(\tfrac{1}{2} m\dot{q}^2 - \tfrac{1}{2} m\omega^2 q^2 - \lambda Q q \right) dt \right] .
$$

This calculation is done in Feynman and Hibbs, p.234, Eq. 8—141 (Ref. 11), which has a misprint. If we set

$$
\rho(t) = \frac{\lambda}{(2m\hbar\omega^3)^{1/2}} Q(t) \quad \text{so} \quad \rho_i = \left[\frac{m\omega}{2\hbar} \right]^{1/2} q_i \ ,
$$

$$
\beta = \omega \int_0^T \rho(t) e^{-i\omega t} dt \ ,
$$

then

$$
C_q = e^{-i\omega T/2} \exp - \left[\tfrac{1}{2}(\rho_0^2 + \rho_1^2 - 2\rho_0\rho_1 e^{-i\omega T}) + i(\rho_0\beta + \rho_1\beta^* e^{-i\omega T}) - \omega^2 \int_0^T \int_0^t \rho(t)\rho(s) e^{-i\omega(t-s)} ds \ dt \right] .
$$

I have discovered that this can be simplified to an intuitively appealing form by expressing it in terms of $\dot{\rho}$ by integrating β and the double integral by parts:

$$
C_q = e^{-i\omega T/2} \exp\left[i\omega \int_0^T dt \ \rho^2(t) - \int_0^T dt \int_0^t ds \ \dot{\rho}(t)\dot{\rho}(s) e^{-i\omega(t-s)} \right]
$$

$$
= e^{-i\omega T/2} \exp\left[\frac{i}{\hbar} \int_0^T dt \frac{\lambda^2}{2m\omega^2} Q^2(t) - \frac{1}{\hbar} \int_0^T dt \int_0^t ds \ \dot{Q}(t)\dot{Q}(s) \frac{\lambda_k^2 e^{-i\omega(t-s)}}{2m\omega_k^3} \right] .
$$

The phase and the first term in the exponential renormalize V into the adiabatic potential

$$
\tilde{V}(Q) = V(Q) - \sum_k \frac{\lambda_k^2}{2m\omega_k^2} Q^2 + \sum_k \frac{\hbar\omega_k}{2} \ .
$$

The second term acts as an effective time-retarded self-interaction. It embodies the effect on $Q(t)$ of the "ringing" of the crystal induced by previous motion:

$$
\mathfrak{u}(t) = \sum_k \frac{\lambda_k^2}{2m\omega_k^3} e^{-i\omega_k t} \ .
$$

Now, consider our path integral, extended to all time. It is a path integral over Q alone:

$$
{}_{+\infty}\langle Q_1, GS(\vec{q}_{k_1}) \mid Q_0, GS(\vec{q}_{k_0})\rangle_{-\infty} = \oint \mathfrak{D}Q
$$

$$
\times \exp\left[\frac{i}{\hbar} \int_{-\infty}^{\infty} \left[\tfrac{1}{2} M\dot{Q}^2 - \tilde{V}(Q) + i \int_{-\infty}^t ds \ \dot{Q}(t)\dot{Q}(s) \mathfrak{u}(t-s) \right] dt \right] .
$$

The action integral in the exponent is a complex quantity. Each conceivable path $Q(t)$ contributes substantially to the path integral—most of the additions cancel one another in a complicated way. Real time has another disadvantage, the function $\mathfrak{u}$ looks more complicated than it has to be. It is complex. In crystals, the edges of Brillouin zones produce long-range oscillations in $\mathfrak{u}$ that die off slowly. In glasses, localized phonons will produce oscillations in $\mathfrak{u}$ that never die away. This reflects the mixing of the localized phonon modes with the

two-level system. Since these modes are high frequency and tunneling is very low frequency, the mixing should be very small. The same should be true of resonances within the extended spectrum; unless they are close to the (very low) tunneling frequency, they should behave no differently from more ordinary phonon spectra. Rotation to imaginary time will eliminate these unnecessary complications:

$$\oint \mathfrak{D}Q \exp\left[\frac{-1}{\hbar}\int_{-\infty}^{\infty}\left[\tfrac{1}{2}M\dot{Q}^2+\tilde{V}(Q)+\tfrac{1}{2}\int_{-\infty}^{\infty}d\sigma\,\dot{Q}(\sigma)\dot{Q}(\tau)U(\tau-\sigma)\right]d\tau\right] ,$$

$$U(\rho)=\sum_k \frac{\lambda_k^2}{2m\omega_k^3}e^{-\omega_k|\rho|}=U_0-U_1|\rho|+U_2\frac{|\rho|^2}{2}\cdots .$$

U is real, positive, and if $\lambda_k \propto k$ as $k \to 0$ it dies away like $1/\rho^2$ as $\rho \to \infty$, despite defects, localized modes, resonances, and Brillouin-zone boundaries. We have seen the first two coefficients of its Taylor series before:

$$W=\frac{U_0Q_0^2}{2\hbar}=\sum_k \frac{\lambda_k^2Q_0^2}{4m\omega_k^3} .$$

(e^{-W} is the phonon overlap integral)

$$\tilde{V}(Q)=V(Q)-U_1Q^2=V(Q)-\sum\frac{\lambda_k^2}{2m\omega_k^2}Q^2 .$$

The instanton path minimizes the Euclidean action

$$S_E=\int_{-\infty}^{\infty}\left[\tfrac{1}{2}M\dot{Q}^2+\tilde{V}(Q)+\tfrac{1}{2}\int_{-\infty}^{\infty}d\sigma\,\dot{Q}(\sigma)\dot{Q}(\tau)U(\tau-\sigma)\right]d\tau$$

subject to the boundary conditions $Q(\pm\infty)=\pm Q_0/2$, and given that the flip is at $\tau=0$. Among paths with exactly one flip located at the origin, this path and those near it dominate the contribution to the path integral. To get the full behavior of the two-level system, we would look at multiple flip paths and interactions between flips. Here we concentrate on the nature of a single tunneling event.

IV. THE INSTANTON PATH AND APPROXIMATIONS

In this section, we study approximations to the classical path Q_I (the instanton) which minimizes the Euclidean action S_E. To put this study in perspective, we first summarize the path-integral treatment of the one-dimensional double well.[10] We then briefly outline the formal techniques for computing the classical path for a general (linearly coupled, symmetric) tunneling system. We proceed to develop the two natural approximations in this theory, the slow- and fast-flip approximation. (The latter precisely corresponds to the truncation approximation discussed in Sec. II.) We also discuss an approximation which is physically relevant, but unnatural in this context: the self-trapped approximation. We conclude this section with a numerical study of the domains of validity of these three approximations, for a quartic well coupled to a single phonon mode.

The easiest of all instanton calculations is the symmetric double well. The Euclidean action is

$$S(Q)=\int \tfrac{1}{2}M\dot{Q}^2+V(Q)dt ,$$

where $V(Q)$ has degenerate minima, say $V(\pm Q_0/2)=0$. The instanton path starts at $-Q_0/2$, ends at $+Q_0/2$, and minimizes S_E subject to these constraints. It obeys the Euclidean Lagrangian equations of motion

$$M\ddot{Q}_I=V'(Q_I) .$$

Since the system is invariant under time translations, there is a conserved "energy" along the classical path

$$E=\tfrac{1}{2}M\dot{Q}_I^2-V(Q_I)=0 ,$$

$$\dot{Q}_I=(2V(Q_I)/M)^{1/2} .$$

Thus the Euclidean action for the classical instanton path is

$$S_I=\int[2MV(Q)]^{1/2}dQ .$$

How does this fit into the path-integral calculations, say, of the tunneling amplitude? Consider

$$\left\langle \frac{Q_0}{2},\tau=+\infty \left| -\frac{Q_0}{2},\tau=-\infty \right.\right\rangle = \int\!\!\!\!\!\!\int_{\substack{Q(\infty)=Q_0/2\\ Q(-\infty)=-Q_0/2}} \mathfrak{D}Q\; e^{-S(Q)/\hbar}$$

$$= \int\!\!\!\!\!\!\int \mathfrak{D}Q \exp\left[\frac{-1}{\hbar}\left[S_I + \frac{\delta S_E}{\delta Q}\bigg|_{Q_I}(Q) + \frac{\delta^2 S_E}{\delta Q^2}\bigg|_{Q_I}(Q) + \cdots\right]\right]$$

$$= \left\{\int\!\!\!\!\!\!\int \mathfrak{D}Q \exp\left[\frac{-1}{\hbar}\left[\frac{\delta^2 S}{\delta Q^2}\bigg|_{Q_I}(Q) + \cdots\right]\right]\right\}$$

$$\times \exp\left[\frac{-1}{\hbar}\int [2MV(Q)]^{1/2} dQ\right] .$$

If we restrict this integral to paths which cross $Q = 0$ only within $d\tau$ of $\tau = 0$, it can be shown that this transition amplitude gives the tunneling matrix element $\Delta d\tau/\hbar$ for the double well. The first WKB approximation for this tunneling amplitude is

$$\Delta = A(\hbar S_I/\pi)^{1/2} e^{-S_I/\hbar} ,$$

$$S_I = \int [2MV(Q)]^{1/2} dQ .$$

Thus the instanton action in the path integral contributes the exponential term in the WKB expression. The linear variation of S_E vanishes because Q_I is a minimum; the quadratic variation can be shown[10] to give the prefactor in the WKB expression for Δ.

Now, consider our effective Euclidean action

$$S_E(Q) = \int \tfrac{1}{2} M\dot{Q}^2 + \tilde{V}(Q) + \tfrac{1}{2}\int_{-\infty}^{\infty} d\sigma\, \dot{Q}(\sigma)\dot{Q}(\tau)U(\tau-\sigma)d\tau .$$

If $\tilde{V}(\pm Q_0/2) = 0$, we again have equations of motion and a conserved energy:

$$M\ddot{Q} = \tilde{V}'(Q) - \int_{-\infty}^{\infty} d\sigma\, \dot{Q}(\sigma)U'(\tau-\sigma) ,$$

$$E = 0 = \tfrac{1}{2}M\dot{Q}^2 - \tilde{V}(Q) - \int_{-\infty}^{\tau} d\tau' \dot{Q}(\tau') \int_{\tau}^{\infty} d\sigma\, \dot{Q}(\sigma)U'(\tau'-\sigma) .$$

These may be solved for the instanton path. In pratice, we will find approximate paths by minimizing $S_E(Q)$ directly. These equations can be useful in finding general properties of the instanton path, and will be crucial in finding decay times (which we will not deal with in this paper).

Solving for the contributions of the paths nearby to the classical path involves evaluating

$$\int\!\!\!\!\!\!\int_{\substack{Q(\infty)=0\\ Q(-\infty)=0}} \mathfrak{D}Q \exp\left[\frac{-1}{\hbar}\left[\frac{\delta^2 S_E}{\delta Q^2}\bigg|_{Q_I}(Q)\right]\right] .$$

The integrations are Gaussians, but we are left with the problem of taking the determinant of a nonlocal differential operator. It is likely that this can be done in the slow- and fast-flip approximations, but little physics is likely to result. The quadratic fluctuations are qualitatively no different from those of the single well, and accuracy is not as crucial as it is for the instanton action, which is exponentiated. We will discuss this prefactor again in Sec. V.

We now turn to the slow-flip approximation. Consider the inequality

$$\tfrac{1}{2}\int d\tau \int d\sigma [\dot{Q}(\sigma) - \dot{Q}(\tau)]^2 U(\tau-\sigma) = \left[\int d\tau\, \dot{Q}^2(\tau)\right]\left[\int d\rho\, U(\rho)\right] - \int d\tau \int d\sigma\, \dot{Q}(\sigma)\dot{Q}(\tau)U(\tau-\sigma) \geq 0 .$$

This becomes an approximate equality if Q stays nearly constant while U is large, i.e., if the path has no sharp bumps. Specifically, if the flip time for

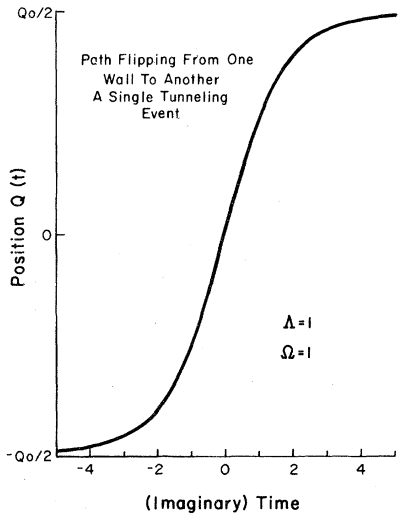

FIG. 3. A sample instanton path; the exact form depends upon the phonon coupling (as this paper discusses).

the instanton path (see Fig. 3) is long compared to the time scale on which U decays, we can use an effective-mass approximation to put a good upper bound on the instanton action.

$$S_E(Q) \leq \int [\tfrac{1}{2}M^*\dot{Q}^2 + \tilde{V}(Q)]d\tau \ ,$$

$$M^* = M + U_{-1} = M + \sum_k \frac{\lambda_k^2}{m\omega_k^4} \ .$$

This approximation will be good for the calculation of the instanton action for heavy defects or shallow barriers. It should describe fluctuations well for heavy defects, however, light defects whose instanton paths happen to be smooth will still fluctuate about this path quickly, and probably a prefactor based on the bare defect mass is more accurate. This approximation will be discussed more fully in Sec. V.

Now, consider the fast-flip approximation. Since $U(\tau)$ is a sum of expontials and $\dot{Q}$ is monotone we know

$$U_0 > U(\rho) > U_0 - U_1|\rho| \ ,$$

$$\frac{U_0Q_0^2}{2} > \tfrac{1}{2}\int d\tau \int d\sigma \, \dot{Q}(\tau)\dot{Q}(\sigma)U(\tau-\sigma)$$

$$> \frac{U_0Q_0^2}{2} - U_1\int d\tau \left[\frac{Q_0^2}{4} - Q^2(\tau)\right] \ .$$

The first term gives precisely the phonon wave-function overlap integral. The last term renormalizes $\tilde{V}$ back to V. Thus, if $\tilde{V}'(\pm Q_0/2) = 0$ and $V'(\pm Q_1/2) = 0$ $(Q_1 < Q_0)$, then

$$\int_{-Q_0/2}^{Q_0/2}[2\tilde{M}V(Q)dQ]^{1/2} + \frac{U_0Q_0^2}{2}$$

$$> S_E(Q_I) > \int_{-Q_1/2}^{Q_1/2}[2MV(Q)]^{1/2}dQ + \frac{U_0Q_0^2}{2}$$

The actual instanton action is not well described either by V or by $\tilde{V}$ unless they are nearly the same. The truncation approximation works only when the phonon contribution to the potential is small, i.e., for weak coupling. Not only does it fail to give the right answer, but the physical picture of transitions between two wave functions is wrong for strongly coupled (self-trapped) electronic tunneling.

In the slow-flip approximation, the motion of the defect across the barrier was slow on phonon timescales, and the atoms surrounding it followed adiabatically. There is a converse approximation, where the defect wave function relaxes adiabatically as the phonons move; for electronic tunneling this is familiar as the Born-Oppenheimer approximation. If $V(Q)$ (the saddle-point potential) has no barrier, the defect is self-trapped in a "spontaneous" well. In this case, tunneling proceeds via a polaronic motion and the defect moves along as the phonons push it over the barrier.

As helpful as this physical picture of self-trapping is, it is not a useful computation aid. We may use it to remove the defect coordinate from the problem, but we are left with 10^{23} phonon modes now with a nonlinear coupling. Computationally, the full instanton methods are necessary. We shall study this picture again in Sec. VI.

For the remainder of this section, we will analyze the simplified problem of a single phonon mode coupled to a quartic symmetric double well (see Fig. 1). Certain aspects of the problem (such as phonon scattering and decay rates) are lost entirely with the low-frequency modes, however, they are not the subject of this paper. What we can get is a good qualitative notion of the nature of a single tunneling event by using a phonon mode with coupling and frequency modeling the true spectrum. Similar simplifications are used in Holstein's molecular crystal model.[5]

We now wish to study in detail the instanton path for the following Euclidean Lagrangian:

$$S_E = \tfrac{1}{2}M\dot{Q}^2 + V_0\left[1 - \left[\frac{2Q}{Q_0}\right]^2\right]^2$$

$$+ \frac{\lambda^2}{4m\omega^3}\int_{-\infty}^{\infty} d\sigma \, \dot{Q}(\sigma)\dot{Q}(\tau)e^{-\omega|\sigma-\tau|} \ .$$

The instanton path will retain its form under scalings of distance, time, and overall magnitude of the Lagrangian (i.e., of $\hbar$). Using these scalings, we may reduce to two parameters, Ω and Λ:

$$S = (MV_0)^{1/2}Q_0\int d\tau \left[\tfrac{1}{2}\dot{Q}^2 + \tfrac{1}{4}(1-Q^2)^2 + \frac{\Lambda}{4\Omega}\int_{-\infty}^{\infty} d\sigma\dot{Q}(\sigma)\dot{Q}(\tau)e^{-\Omega|\sigma-\tau|}\right] \ ,$$

$$\Omega = \frac{\omega}{\omega_{\mathrm{DW}}}, \quad \Lambda = \frac{\lambda^2}{m\omega^2 M\omega_{\mathrm{DW}}^2}\omega_{\mathrm{DW}} = 4\left[\frac{V_0}{MQ_0^2}\right]^{1/2}, \quad V(Q) = V_0 - \tfrac{1}{2}M\omega_{\mathrm{DW}}^2Q^2 + O(Q^4),$$

Λ is a dimensionless coupling strength and Ω is a dimensionless phonon frequency. For this simplified sys-

tem, we have minimized the action for fixed Ω, Λ by a variational technique. Figure 4 shows, on the Ω,Λ plane, the domains of validity of the slow-flip and truncation approximations, and the domain where the self-trapped picture holds. Figure 5 shows the action along a line connecting the slow-flip and truncation domains. Figure 8 shows the action along a self-trapped to slow-flip transition line. In the next two sections, we shall try to give concrete applications of our formalism.

V. ANALYSIS OF A SLOW TUNNELING EVENT-(KC1:Li^+)

Atomic tunneling centers appear to dominate the low-temperature behavior of glasses.[1,2] We believe these centers tunnel slowly, since the tunneling mass is at least as large as the phonon masses. There is no detailed microscopic model of these tunneling centers. We shall study lithium substitutional defects in KC1 instead; they were studied in great detail[3] at one time.

In (KC1:$^7Li^+$) one finds experimentally absorption at about 0.82 cm^{-1}, and again at 42 cm^{-1}. Doping with lithium-6 one finds the lower absorption region increases in frequency by $40 \pm 5\%$. It is generally agreed that Li^+ substitutes for K^+, that because of its smaller atomic radius it can lower its energy by sitting off center in a $\langle 111 \rangle$ direction, and that the lower absorption band reflects the tunnel splitting between the Li^+ wave functions of various symmetry properties.

I claim, despite that small lithium mass, the tunneling of this defect is slow. The relaxation of the neighboring Cl^- will proceed roughly at the Debye frequency 3×10^{13} sec^{-1}.[15] We assume the potential well is fairly regular, so the curvature at the top of the barrier can be roughly equated to the curvature at the bottoms of the wells. If we further assume the 42-cm^{-1} resonance is near the first excited state of one of the wells, the double-well frequency is roughly 1.26×10^{12} sec^{-1}, giving $\Omega \sim 24$, well within the slow-flip regime.

To evaluate the effective mass we shall use the results of a computer model.[16] This model relied upon effective interatomic potentials, and varied a hardness parameter in the Li^+-Cl^- potential in order to fit the experimental data. They do allow the lattice to relax adiabatically about various lithium positions, but do not correct for the effective mass of the chlorine motions. We will not use their energies (which fit the data using a truncation approximation), but we shall use their ionic motions (which should be qualitatively correct).

Note that two of the Cl^- ions (marked A, see Fig. 6) move a very substantial distance. Each moves a total of 0.139 lattice spacings, about a third of the lithium motion of 0.426 lattice spacings. Since they are so much more massive, the kinetic energy of their average velocity would match that of the lithium, drastically reducing the isotope effect. This was pointed out by Narayanamurti and Pohl,[3]

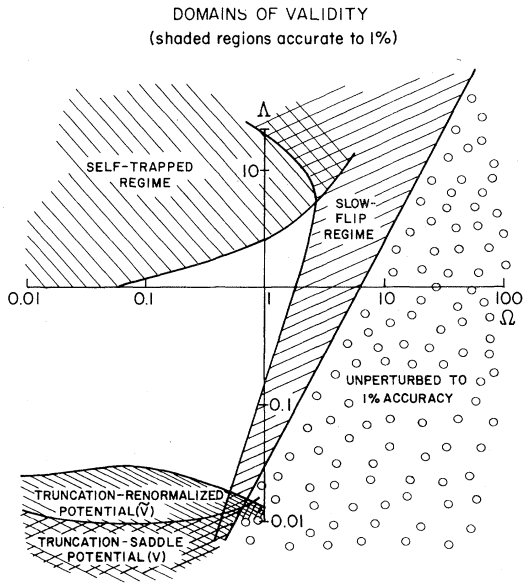

FIG. 4. Domains of validity for the various approximations. Λ is a coupling strength and Ω is a phonon frequency. The action for this figure and Figs. 5 and 8 was computed by a variational calculation using piecewise exponentials for $Q(\tau)$.

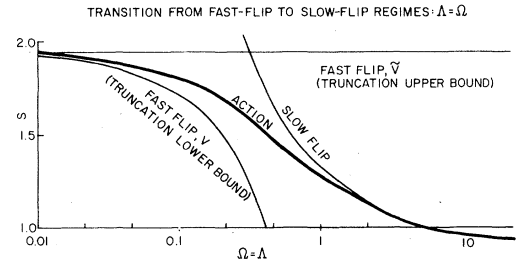

FIG. 5. Action and three approximations along a line where the phonon wave-function overlap integral (Λ/Ω) is roughly equal to the unperturbed action $(2\sqrt{2/3})$. Note that neither truncation approximation is accurate until both are nearly equal; if the phonon significantly affects the local potential seen by the tunneling entity, truncation fails.

who left it as an unresolved problem. We shall resolve it.

Wilson *et al.* calculate the ionic positions at the middle and two ends of of the tunneling process. One is struck by the nonlinearity of the motion [Fig. 6(b)]; the assumption of an average velocity is clearly unjustified. The Euclidean Lagrangian allowing nonlinear coupling is

$$\mathcal{L}_E = \tfrac{1}{2}M\dot{Q}^2 + V(Q) + \sum_k [\tfrac{1}{2}m\dot{q}_k^2 + \tfrac{1}{2}m\omega_k^2 q_k^2 - \Lambda_k(Q)q_k] \ .$$

Integrating over the phonon coordinates and rotating to imaginary time, we obtain

$$\mathcal{L}_E = \tfrac{1}{2}M\dot{Q}^2 + V(Q) - \sum_k \left[\frac{\Lambda_k^2(Q)}{2m\omega_k^2} + \frac{\hbar\omega_k}{2}\right] + \tfrac{1}{2}\int_{-\infty}^{\infty} d\sigma \sum_k \Lambda_k'(Q(\tau))\Lambda_k'(Q(\sigma))\dot{Q}(\tau)\dot{Q}(\sigma)\frac{e^{-\omega_k|\sigma-\tau|}}{2m\omega_k^3} \ .$$

In the slow-flip approximation, we get a position-dependent effective mass and the relaxed potential

$$\mathcal{L}_E^{\text{slow}} = \left[M + \sum_k \frac{[\Lambda_k'(Q)]^2}{m\omega_k^4}\right]\dot{Q}^2 + V(Q) - \sum_k \frac{\Lambda_k^2(Q)}{2m\omega_k^2} + \sum_k \frac{\hbar\omega_k}{2}$$

$$= \tfrac{1}{2}M^*(Q)\dot{Q}^2 + \tilde{V}(Q) \ .$$

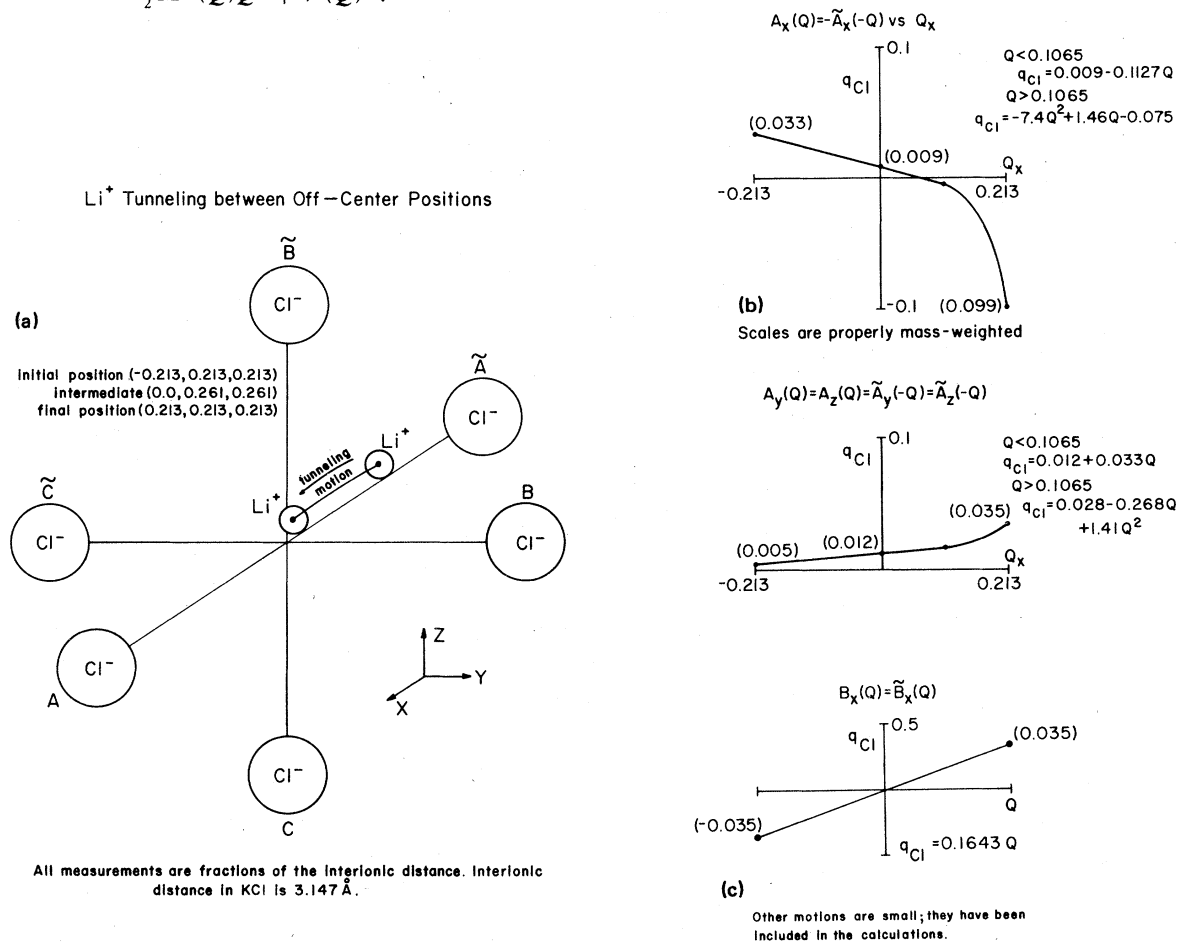

FIG. 6. (a) The lithium ion substitutes for a potassium in the KCl lattice. Its smaller atomic radius and the lattice relaxation allow it to have a lower energy in an off-center position. (b) and (c) The motions of the ions as the lithium tunnels. The points at the ends and middle are from Wilson *et al.* (Ref. 16); the interpolation is ours.

Here, as in the uncoupled problem, there is a conserved energy along the instanton path, allowing its action to be expressed neatly:

$$E = 0 = \tfrac{1}{2}M^*(Q)\dot{Q}^2 - \tilde{V}(Q), \quad \dot{Q} = \left[\frac{2\tilde{V}(Q)}{M^*(Q)}\right]^{1/2}$$

$$S_I = \int_{-\infty}^{\infty} M^*(Q)\dot{Q}^2 d\tau = \int_{-Q_0}^{Q_0} [2M^*(Q)\tilde{V}(Q)]^{1/2} dQ \ .$$

Thus, even in the nonlinear case, the tunnel splitting is easily computed. Note that $\frac{1}{2}M^*(Q)\dot{Q}^2$ is the kinetic energy of the total system as the lithium moves. The effective mass can thus be computed without first transforming to phonon coordinates:

$$M^*(Q) = M_{\mathrm{Li}} + \sum_{\mathrm{Cl}} M_{\mathrm{Cl}} \frac{\dot{q}_{\mathrm{Cl}}^2}{\dot{Q}_{\mathrm{Li}}^2} \ .$$

Now, we must interpolate motion between the three points given by Wilson *et al*. We expect the motion of the A chlorines will be largest while the Li^+ is nearby; we interpolate (rather arbitrarily) its motion as shown [Fig. 6(b)] and other motions by fitting parabolas. In units of the interatomic spacing,

$$M^*(Q) = M_{\mathrm{Li}} + M_{\mathrm{Cl}} \begin{cases} 0.9012Q^2 = 0.826, & (|Q| < 0.1065) \\ 228.2568Q^2 - 44.9034|Q| + 2.286, & (0.213 > |Q| > 0.1065) \end{cases} .$$

Qualitatively, we expect the nonlinear chlorine motions to increase the isotope effect. Their contribution to the effective mass is concentrated near the bottoms of the wells where $\tilde{V}(Q)$ is small. The mass during the main part of the flip is nearly that of the bare lithium ion; the chlorine ions of importance move before and after the flip. The increase due to this nonlinear motion turns out to be not very large. Assuming a quartic well, there is a $1 - (M_6/M_7)^{1/2} = 7.42\%$ shift in the Euclidean action for the uncoupled well, the shift assuming linear coupling is 3.08%, that for our choice of the nonlinear motion is 3.75% (Fig. 7).

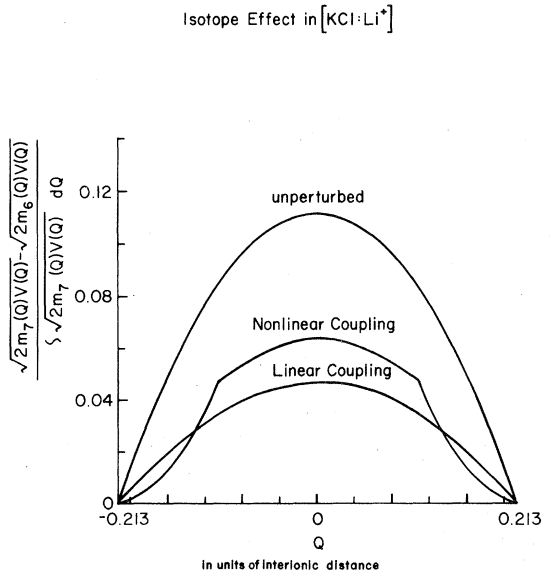

FIG. 7. The isotope effect for three assumptions about the chlorine motion. The difference in actions for ^{7}Li and ^{6}Li is given by the areas under the curves.

To actually estimate the isotope effect, we must investigate the mass dependence of the Gaussian fluctuation "prefactor": prefactor $= A(\hbar S_I/\pi)^{1/2}$ (one dimension) $= 2\sqrt{3}\omega_{\mathrm{DW}}(\hbar S_I/\pi)^{1/2}$ (quartic well[17]) which equals

$$\oint_{Q(-\infty)=Q(\infty)=0} \mathfrak{D}Q \times \exp\left[\frac{-1}{\hbar}\left[\frac{\delta^2 S}{\delta Q^2}\bigg|_{Q_I}(Q)\right]\right] \quad \text{(general)} \ .$$

For the uncoupled quartic well,

$$\mathfrak{L}_E = \tfrac{1}{2}M\dot{Q}^2 + V_0\left[1 - \left[\frac{2Q}{Q_0}\right]^2\right]^2 ,$$

$$\omega_{\mathrm{DW}} = \left[\frac{4}{Q_0}\right]\left[\frac{V_0}{M}\right]^{1/2} ,$$

$$S_I = \tfrac{2}{3}(2mV_0Q_0^2)^{1/2} \ .$$

Leaving Q_0 fixed at 1.34 Å, and varying V_0 to match $\Delta_7 = 0.82\ \mathrm{cm}^{-1}$, we obtain, for the uncoupled well,

$$\frac{\Delta_7 m_7 Q_0^2 \sqrt{\pi}}{\hbar^2 6\sqrt{6}} = (S_I^7/\hbar)^{3/2} e^{-S_I^7/\hbar} = 3.69 \times 10^{-2} ,$$

$$S_I^7 = \hbar(5.98) ,$$

$$S_I^6 = S_I^7[(m_6/m_7)^{1/2}] = 5.536 ,$$

$$\frac{\Delta_6}{\Delta_7} = \left[\frac{m_7}{m_6}\right]^{1/4} e^{(S_7 - S_6)} = 1.62 \ .$$

This uncoupled calculation roughly agrees with other similar calculations.[18]

How many we estimate the quadratic fluctuations

in the coupled case? We have integrated the phonon modes out, and the remaining problem integrates over only one variable Q, so at least the fluctuations will be dimensionally the same as that of the uncoupled case. Furthermore, most of the contributions to the quadratic fluctuations are likely to come from paths "wiggling" quickly, since the lithium is light. In fact, only those Fourier components of the fluctuation which are slow compared to the phonon time will contain chlorine masses; most of the components represent the lithium ion wiggling in its cage. Thus, it is reasonable to use the uncoupled prefactor for the coupled case, using the bare lithium mass. (Actually, the isotope effect is quite insensitive to this prefactor, and our numbers would be virtually unchanged by another choice.) By this choice the actions for ^{7}Li tunneling are the same for all three cases, and we find

$$\frac{\Delta_6}{\Delta_7} = \left[\frac{m_7}{m_6}\right]^{1/2} \exp\left[S_7\left[\frac{S_7 - S_6}{S_7}\right]\right]$$

$$= (1.04)e^{5.98(0.0308)} = 1.25 \text{ (linear)}$$

$$= (1.04)e^{5.98(0.0375)} = 1.30 \text{ (nonlinear)} .$$

Thus a careful treatment of lithium tunneling in KCl gives a 30% isotope effect, even when large chlorine motions are included. This compares reasonably well with the experimental $40 \pm 5\%$ energy shift.

VI. SELF-TRAPPED TUNNELING

(Phillips's analysis of Anderson's Negative-U Model)

The slow-flip approximation adequately describes single tunneling events for phonon relaxation times $\gtrsim$ the timelength of the tunneling event ($\Omega \gtrsim 1$). The fast-flip or truncation approximation describes slow phonons coupled weakly ($\Omega < 1$, Λ small). The strong-coupling, slow-phonon region ($\Omega < 1$, $\Lambda \sim 1$) is more complex. In this region, the barrier in the adiabatic potential $\tilde{V}(Q)$ is largely or entirely due to the phonon coupling; the fast or saddle-point potential $V(Q)$ has little or no barrier. We call this the self-trapped regime (see Fig. 1).

In this section, we shall attempt to find the qualitative factors which determine the behavior of self-trapped tunneling. We shall first consider possibly the simplest case of self-trapped tunnneling—our interpretation of Phillips's[14] model of Anderson's[7] negative-U center. Phillips uses a truncation approximation in his model, estimates the phonon wave-function overlap integral, and finds that it suppresses tunneling to a point where it becomes experimentally unobservable. We will first find that his use of the truncation approximation in his model is valid. We then contrast this with our quartic double well (for which the truncation approximation is not adequate for $\Lambda = 1$, see Fig. 8). We find the saddle-point potential, despite its lack of a barrier, remains an important factor in determining the flip time. Phillips's model is singular in that its saddle-point potential is zero. We conclude with an attempt at verbally generalizing this effect, and with a discussion of the likelihood of frequent tunneling events in this system.

Anderson's negative-U model describes the electronic ground state of amorphous semiconductors in terms of bound pairs of electrons. The binding force is given by the phonon relaxation—the second electron sees the potential hole sunk by the first, and together they make an even deeper hole, using a rubber-sheet analogy. Many physical properties of glassy semiconductors are explained using this model. Phillips uses some of these predictions to put a lower bound on the phonon wave-function overlap integral and claims that these centers must take a macroscopic time to tunnel. This is unfortunate, as one would like to use these centers to explain a linear term in the specific heat near $T = 0$; however, the use of a phonon wave-function overlap integral in the self-trapped regime is highly suspect. We interpret Phillips's model very freely to allow use of path integrals and we believe we have not

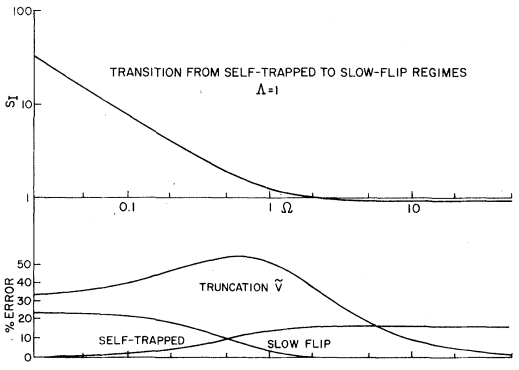

FIG. 8. Along $\Lambda = 1$, the entire potential well for the defect is due to its phonon coupling. The truncation approximation is not an acceptable approximation for the action.

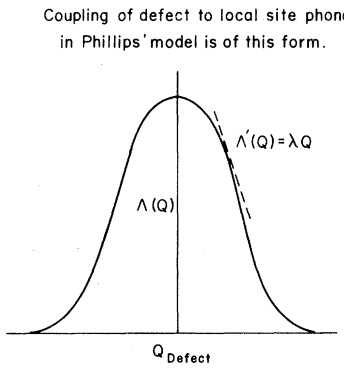

FIG. 9. A nonlinear coupling; the coupling of the pair of electrons to the phonon mode depends on their proximity to the mode's "location".

done violence to his central ideas.

Phillips's model of a single center involves one phonon mode q interacting linearly with the pair of electrons as long as they are in the vicinity of the center. If we call the coordinate of the electron pair Q we may write the Lagrangian

$$\mathcal{L}_E = \tfrac{1}{2}M\dot{Q}^2 + \tfrac{1}{2}m\dot{q}^2 + \tfrac{1}{2}m\omega^2 q^2 + \Lambda(Q)q \quad ,$$

where $\Lambda(Q)$ is large only when Q is near the defect position (see Fig. 9). Tunneling between centers in this model involves separately escaping from one and falling into the other. Thus we are interested in calculating the minimum action for paths constrained to escape from the well.

We may integrate out the phonon mode as before,

$$\mathcal{L}_E = \tfrac{1}{2}M\dot{Q}^2 - \frac{\Lambda^2(Q)}{2m\omega^2} + \tfrac{1}{2}\int_{-\infty}^{\infty} d\sigma\, \Lambda'(Q(\tau))\Lambda'(Q(\sigma)) \times \dot{Q}(\tau)\dot{Q}(\sigma)\frac{e^{-\omega|\sigma-\tau|}}{2m\omega^3} \quad .$$

We expand the exponential, and drop terms $O(|\sigma-\tau|^3)$ (we will see that the flip time is fast, so this is justified). Again, the constant term contributes the phonon wave-function overlap integral $\mathcal{I}_{\mathrm{PO}}$ and the linear term cancels the potential due to phonon relaxation. We minimize the resulting action by varying $Q(t)$:

$$S_I \simeq I_{\mathrm{PO}} + \min_{Q(t)}\left[\int d\tau \left[\tfrac{1}{2}M\dot{Q}^2 + \frac{1}{8m\omega}\int d\sigma \Lambda'(Q(\tau))\Lambda'(Q(\sigma))\dot{Q}(\tau)\dot{Q}(\sigma)(\sigma-\tau)^2\right]\right] \quad .$$

By varying the time scale, we find the minimum action path satisfies the equation

$$\int \tfrac{1}{2}M\dot{Q}^2 d\tau = 2\left[\frac{1}{8m\omega}\int d\tau \int d\sigma \Lambda'(Q(\tau))\Lambda'(Q(\sigma))\dot{Q}(\tau)\dot{Q}(\sigma)(\sigma-\tau)^2\right] \quad .$$

Let us choose λ a characteristic coupling constant— some mean value of $\Lambda'(Q)$ (Fig. 9). Then,

$$\left[\frac{2Mm\omega}{\lambda^2}\right] = \frac{\int\int \dot{Q}(\sigma)\dot{Q}(\tau)(\sigma-\tau)^2[\Lambda'(Q(\tau))\Lambda'(Q(\sigma))/\lambda^2]d\sigma d\tau}{\int \dot{Q}^2 d\tau} \quad .$$

The right-hand side has units of (time)^3; it can be thought of as a cube of a characteristic flip time. The left-hand side is $(2\Omega^2/\Lambda)/\omega^3$; since $\Lambda = 1$, this indicates that the flip time $(2\Omega^2/\Lambda)^{1/3}/\omega$ becomes much shorter than the phonon relaxation time $(1/\omega)$ as $\Omega \to 0$. Since electrons are very light, their natural frequencies are high and Ω will be small. The truncation approximation should be good for small Ω; the action will be at least the phonon overlap integral term.

Thus the phonon wave-function overlap integral does fully suppress tunneling in Phillips's model. We now must investigate why this result does not hold for the quartic double well.

We return to our quartic model Lagrangian with $\Lambda = 1$ (self-trapped), and expand the exponential (the time-retarded interaction):

$$\mathcal{L}_E = \tfrac{1}{2}\dot{Q}^2 + \tfrac{1}{4}(1-Q^2)^2 + \frac{1}{4\Omega}\int \dot{Q}(\sigma)\dot{Q}(\tau)e^{-\Omega|\sigma-\tau|} \quad .$$

The instanton action is found by minimizing the action with respect to Q:

$$S_I = \frac{1}{\Omega} + \min_{Q}\left[\int \tfrac{1}{2}\dot{Q}^2 + \tfrac{1}{4}(1-Q^2)^2 + \frac{1}{2}\left[Q^2 - \frac{Q_0^2}{4}\right] + \frac{1}{4\Omega}\int \dot{Q}(\sigma)\dot{Q}(\tau)(e^{-\Omega|\sigma-\tau|} - 1 + \Omega|\sigma-\tau|)\right].$$

$$= \frac{1}{\Omega} + \min_{Q}\left[\int \tfrac{1}{2}\dot{Q}^2 + \frac{Q^4}{4} - \tfrac{1}{4} + \frac{1}{4\Omega}\int \dot{Q}(\sigma)\dot{Q}(\tau)G(\Omega|\sigma-\tau|)\right],$$

where G is quadratic for small $\Omega|\sigma-\tau|$, and linear for large $\Omega|\sigma-\tau|$. The saddle-point potential here is *negative* near $Q=0$; it will tend to slow the flip down. The time-retarded interaction in this formulation is what pulls the electron across; it reflects the atomic motion through the saddle point. If we look only at the quadratic region of G and ignore the electronic kinetic energy, varying the time scale again leads to the equation:

$$\int\left[\frac{1}{4} - \frac{Q^4}{4}\right]d\tau = \frac{1}{2\Omega}\int\int \dot{Q}(\sigma)\dot{Q}(\tau)\frac{\Omega^2|\sigma-\tau|^2}{2}d\sigma\,d\tau\,,$$

$$\frac{1}{\Omega} = \frac{\int\int \dot{Q}(\sigma)\dot{Q}(\tau)\frac{\Omega^2|\sigma-\tau|^2}{2}d\sigma\,d\tau}{2\int\left[\frac{1}{4} - \frac{Q^4}{4}\right]d\tau}\,,$$

leading to a characteristic time for the flip comparable to the phonon relaxation time $1/\Omega$. Physically, since the saddle-point potential is repulsive at the endpoints of the electron's motion, the electron must wait for the atoms to move for it to continue (see Fig. 10). By assuming the saddle-point potential to be zero, Phillips avoided this complication, but also reduced himself to an anomalous special case.

Let us try to gain a general physical picture of self-trapped tunneling in the $\Omega \to 0$ (low-frequency-phonon) limit. The atomic (phonon) motion are very slow compared to the electronic (tunneling) relaxation time; thus the electronic wave function will relax adiabatically as the atoms move. In the truncation limit, the saddle-point potential still has a barrier, and the electron will tunnel over this barrier very quickly. In the self-trapped limit, this barrier disappears at the saddle point; the barrier penetration is accomplished by phonon motion and phonon timescales apply to the fliptime. The motion of the minimum in the instantaneous electronic potential as the ions move describes qualitatively the electronic motion. In Phillips's model, this minimum does not move.

Is it reasonable to expect such effects to allow tunneling for negative-U centers? Phillips calculates the phonon suppression of the rate to be 10^{-17} (this is the square of the phonon wave-function overlap). His basic rate is of 10^{16}/sec, giving a time of around 10 sec between tunneling events. To contribute to the specific heat, the time between tunneling should be shorter than the time scale of the experiment, thus, a reduction of 10 or 20% in the exponent would suffice. Our model quartic well has an action $\sim$ 30% lower than its phonon wave-

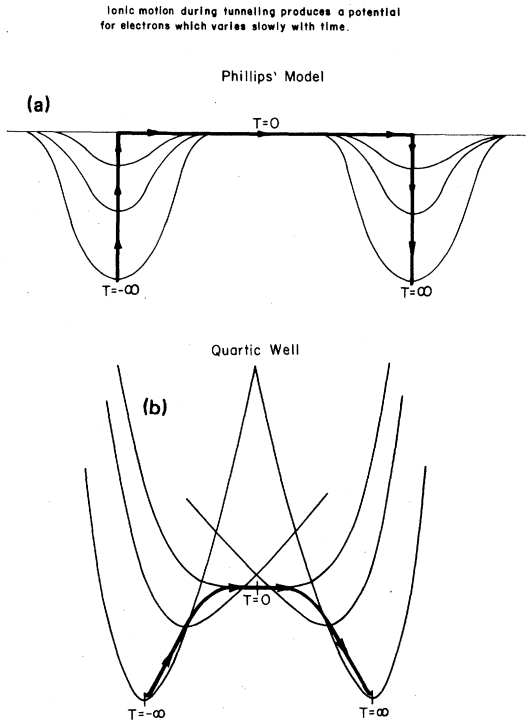

FIG. 10. Phillips's model is pathological; the motion of the electron pair is fast in his model because the phonon modes do not relax along its path.

function overlap (see Fig. 8.). It seems reasonable to suppose that the electron pair remains localized during tunneling, and that it will deform the lattice as it passes. This will act both to lower the barrier to tunneling and to stretch out the fliptime. We conclude that Phillips's calculation is not compelling.

VII. SPECULATIONS

We will refrain from itemizing the future applications and developments we forsee for the theory presented here. We will conclude with some speculations about broader implications we can draw from the two physical systems.

It is interesting to note that the motion of the lithium ion during tunneling is slow compared to the naturel frequencies of the KC1 lattice. Lithium is light, and one expects its frequencies to be higher, rather than an order of magnitude lower. However, if it is to tunnel at all, the barrier cannot be too large; if its width Q_0 is on the order of a lattice spacing, the height V must be low, and the natural frequency will be thus bounded. $\omega_{\mathrm{DW}} \approx (V/M)^{1/2} Q^{-1}, S = Q_0 \sqrt{MV}$ = (barrier size) is bounded by human time scales, so $\omega_{\mathrm{DW}} \lesssim S_{\max}/MQ_0^2$. One can draw a very strong implication from this: virtually all atomic tunneling must be slow. (Exceptions might occur for light atoms which tunnel infrequently.) Thus the effective-mass approximation to the phonon coupling for slow flips should be very useful.

Another thing to note is the form of the potential which allowed the lithium ion to tunnel. The lithium ionic radius is small compared to the potassium which it replaces; it has a box in which it can rattle around. This hints that the key factor may be space, leading into "free volume" theories. More modestly, one certainly must have a weak quadratic binding to allow sufficient motion for the defect to "see" anharmonicities. It can then use these anharmonicities to form a second equilibrium site (impossible in the harmonic theory). Thus we expect formation of tunneling defects only when there is a "weak spring" for motion in some direction. Surely this must connect with the low coordination numbers for bonding in covalent glasses.

In our study of Anderson's negative-U model we found that in self-trapped tunneling, the phonon relaxation in the intermediate state led to an increased transition rate. The hopping process takes on attributes of polaronic motion here; the motion is partly electronic and partly atomic, and proceeds at phonon velocities. This picture is very different from that of an electron wandering through a complicated but fixed potential.

In conclusion, we have shown that quantum tunneling in the solid state is more complicated and contains more physics than has previously been suspected. We believe path integrals are the appropriate vehicle for thinking about tunneling, both from a theoretical point of view and for purposes of visualizing concrete physical situations. Finally, we again emphasize the physical appeal, simplicity, and accuracy of the approximations we have found, especially the slow-flip, effective-mass approximation which should describe almost all cases of atomic tunneling.

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