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NEUTRON SCATTERING LINESHAPES FOR HYDROGEN TRAPPED NEAR IMPURITIES IN METALS

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Abstract—The dynamics of a hydrogen atom confined to a pair of sites and interacting with a heat bath is considered using a stochastic Liouville equation (SLE). A modification of the standard degenerate-pair SLE is introduced to accommodate a non-degeneracy in the site energies, as is believed to occur in NbO_xH_y. Neutron scattering lineshapes are obtained explicitly, based on the modified SLE. A non-degeneracy in the site energies is shown to result in a coexistence of lineshape structures which may be associated with coherent and incoherent transport mechanisms. It is pointed out how this structure, which is characteristic of non-degenerate systems, may appear as a consequence of strong coupling of the hydrogen motion to phonons, even in impurity systems for which the electronic site states are nominally degenerate.

Keywords: Neutron scattering, metal hydrides, hydrogen tunneling, quantum diffusion, defect complexes, two-state systems, electron–phonon interaction, stochastic Liouville equation.

1. INTRODUCTION

In previous papers [1, 2] the authors have calculated lineshape functions for incoherent neutron scattering based on equations of motion for reduced density matrices of mobile hydrogen atoms in metal hydrides. The equations of motion have been forms of the stochastic Liouville equation, whose effective bath-interaction terms provide a model for the thermal degradation of the coherent evolution characteristic of the eigenstates of a closed system. Such models of microscopic dynamics and the determination of their consequences in neutron scattering have come to be of interest due to the observation of inelastic peaks in spectra obtained at low temperature from hydrogen dissolved in NbO_x. The interpretation being given to a growing body of experimental work [3–10] is as follows: with decreasing temperature, a fraction of the H population in a NbO_xH_y system becomes trapped in the vicinity of O impurities due to the strains resulting from the distortion of the Nb lattice by the O. The interstices near an O impurity may be classified and the possible distributions of an H atom among them examined in the face of the existing data. Magerl *et al.* [9] have concluded that the data may be consistently interpreted if the H atom occupies one of several pairs of tetrahedral interstices equidistant from the O impurity, in its second-neighbor shell. It may be argued that if tunneling occurs at all, tunneling between distinct pairs should be negligible, so that it is sufficient to consider the hydride as containing an ensemble of two-site systems. The observed inelastic peaks have been taken to be the consequence of tunneling within such pairs. The relative intensities of the quasielastic and inelastic peaks have suggested that the site energies within a pair are not identical.

Such a local system—a single particle confined to a few sites—presents a transport problem which differs from that found at higher temperatures; however, it allows the motion of interstitial hydrogen to be studied in a simplified situation. The impurity system and the tunneling-state interpretation of its dynamics carry a special importance for the study of non-trapped hydrogen because of the continued absence of any clear evidence from experiments on pure hydrides that interstitial hydrogen atoms exist in tunneling states at *any* temperature. It is apparent that the motion of hydrogen atoms in extended systems is either incoherent or nearly so. An adequate description of hydrogen transport in extended systems based on tunneling states must therefore possess the ability to unify or interpolate between the extremes of coherent and incoherent transport. Stochastic Liouville equations are particularly useful in this context in that they retain generic features of system–bath interactions that lead to the breakdown of coherence, yet allow the phenomenon of intermediate transport coherence to be simply parametrized [11–16]. The hydrogen atom trapped at an impurity provides a laboratory in which the consequences of such models may be determined with relative simplicity.

The primary interest of the first experiments was to determine whether or not trapped hydrogen atoms

occupied local tunneling states at low temperatures. The conclusion is largely affirmative in NbO_xH_y [8]. More recent studies over a range of temperatures [10] sought to determine how these tunneling states are destroyed with increasing temperature, i.e. how coherence is lost as a result of the interaction with the heat bath constituted by the rest of the solid.

A fully quantum mechanical treatment of hydrogen transport must address the difficult problem of the host–interstitial interaction, at least to the level of the interstitial–phonon interaction. Considerable complexity results from such interactions, even for a simple model of the unperturbed tunneling process. If the interaction is weak, the primary effect of phonons is to scatter a particle among the eigenstates of the unperturbed system. Although the strong coupling case continues to present difficulties for transport theory, some progress can be made through the theory of transport by polaron mechanisms [11, 12, 17, 18]. A systematic approach to the strongly coupled problem can be made in the basis of polaron states, in which the effect of residual phonon interactions is to scatter a polaron among the polaron states.

While the earlier work of Wipf *et al.* [8] gave consideration to polaron effects, and hence the hydrogen–phonon interaction, the more recent work of Magerl *et al.* [10] suggests that the observed temperature dependences are attributable to electron scattering. In order to account for the damping effects due to the hydrogen–phonon interaction and/or electron scattering, there are two essential questions: (1) What are the states connected by the scattering (damping) mechanism, and (2) What are the temperature dependences of the relevant scattering rates? In this paper, we are concerned with the former question. In section 2 we consider the states connected by thermal scattering to be the eigenstates of the isolated two-state system; in section 3 we consider the relevant states to be the corresponding polaron states. In each case, we determine the manner in which broken site-symmetry alters the manifestation of system–bath interactions in neutron scattering. Since we leave the temperature dependences of the microscopic scattering rates undetermined, both electron and phonon scattering mechanisms are subsumed.

In this paper we model the evolution of trapped hydrogen with a stochastic Liouville equation (SLE) [19] and, with the help of methods developed in Ref. [1], evaluate the incoherent neutron scattering function for a non-degenerate pair of sites. Being a high-temperature equation, the SLE fails to reproduce some of the properties expected in finite-temperature results. A detailed study of this difficulty was made in Ref. [1] and a prescription was provided for its resolution. The prescription consists of a symmetrization procedure which restores the exact detailed balance properties to scattering lineshapes calculated from the SLE. Since the prescription is appropriate also to the two-state system considered in the present paper, we restrict our attention to the symmetric part of the scattering lineshape; it being understood that complete temperature dependences are to be obtained through the procedure of Ref. [1].

The scattering function $S(\mathbf{q}, \omega)$ may be obtained from the Laplace transform of the intermediate scattering function $I(\mathbf{k}, t)$ through the relation

$$S(\mathbf{q}, \omega) = \frac{1}{\pi} \mathrm{Re}[\tilde{I}(\mathbf{q}, i\omega)], \tag{1.1}$$

in which the Laplace transform is indicated by a tilde. On rewriting $I(\mathbf{q}, t)$ as a trace with a quasi-density matrix $\rho'(t)$

$$I(\mathbf{q}, t) = Tr[e^{i\mathbf{q}\cdot\mathbf{x}}(e^{-iHt}\rho_0 e^{-i\mathbf{q}\cdot\mathbf{x}} e^{iHt})] \tag{1.2a}$$

$$\equiv Tr[e^{i\mathbf{q}\cdot\mathbf{x}}\rho'(t)], \tag{1.2b}$$

the quasi-density matrix is found [1] to follow the same equation of motion as the true density matrix, but to propagate from the non-standard initial value $\rho'(0) = \rho(0)e^{-i\mathbf{q}\cdot\mathbf{x}}$.

The simplest SLE for transport among energetically degenerate sites has the form

$$\dot{\rho}_{mn} = -i[H, \rho]_{mn} - \alpha(1 - \delta_{mn})\rho_{mn}, \tag{1.3}$$

with $\hbar = 1$. In this basis of site states, the Hamiltonian for the degenerate two-state problem is represented by

$$H = \begin{bmatrix} 0 & V \\ V & 0 \end{bmatrix}. \tag{1.4}$$

If one defines the new variables $R^{\pm}(t) = \rho'_{11}(t) \pm \rho'_{22}(t)$, one can express the Laplace transform $\tilde{I}(\mathbf{q}, i\omega)$ of the intermediate scattering function using only part of the full density matrix solution:

$$\tilde{I}(\mathbf{q}, i\omega) = \tilde{R}^{+}(i\omega)\cos\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) - i\tilde{R}^{-}(i\omega)\sin\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right). \tag{1.5}$$

For the evaluation of the scattering function one requires the initial values

$$R^{+}(0) = \cos\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right), \tag{1.6a}$$

$$R^{-}(0) = i\sin\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) \tag{1.6b}$$

which, when used in eqn (1.5), give

$$S(\mathbf{q}, \omega) = \delta(\omega)\cos^2\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) + \frac{1}{\pi}\frac{4V^2\alpha}{(4V^2 - \omega^2)^2 + \omega^2\alpha^2}\sin^2\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right). \tag{1.7}$$

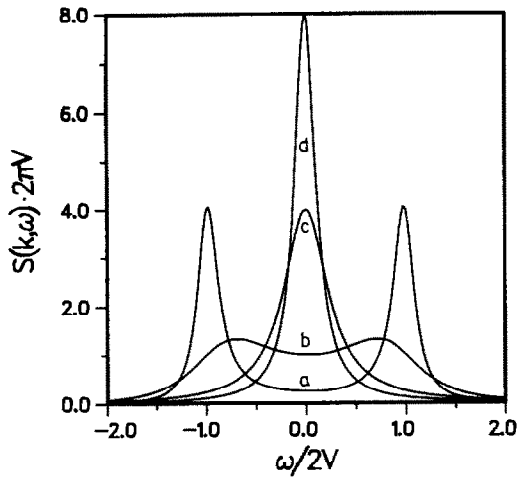

Fig. 1. Quasielastic scattering function for a particle confined to a degenerate pair of sites. The variation in lineshape reflects the variation in the degree of transport coherence. Parameter values: (a) $\alpha/2V = 0.25$, (b) $\alpha/2V = 1.0$, (c) $\alpha/2V = 4.0$ and (d) $\alpha/2V = 8.0$.

The non-elastic part of eqn (1.7), i.e. the second term on the right side, is presented in Fig. 1. For small α, this is a doubly peaked function with distinct inelastic peaks centered at $\omega = \pm 2V$, corresponding to neutron-induced transitions between well-defined tunneling states. With increasing α, these peaks broaden and shift toward zero frequency. When α reaches the value $2\sqrt{2}V$, the inelastic peaks merge into a single quasielastic peak which approaches the asymptotic Lorentzian form

$$S^{qe}(\mathbf{q}, \omega) \approx \frac{1}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}, \tag{1.8}$$

where $\Gamma = 4V^2/\alpha$. The condition for this form to be valid is that $\alpha \gg 2\sqrt{2}V \gg \sqrt{2}\omega$. This inequality implies that the portion of the lineshape which is well represented by a single Lorentzian must lie well within the band of frequencies $\Delta\omega$ defined by the pure tunneling transitions at $\pm 2V$. Conversely, experimental observation of a Lorentzian lineshape in such a system would indicate that the tunneling matrix element responsible for transport is greater than the halfwidth of the observed Lorentzian line. This is consistent with the existing experiments on trapped hydrogen [8, 10, 20] where early experiments yielded Lorentzian lineshapes (HWHM ≈ 0.05 meV at 150 K) [20] which fell well within the tunneling peaks resolved in later experiments at lower temperatures ($\Delta\omega \approx 0.4$ meV at 0.09 K) [8]. It is thus possible that motional narrowing of the tunneling doublet may be able to account for lineshape structure over the entire temperature range.

2. NON-DEGENERATE STATES

It is thought on the basis of the coherent tunneling interpretation of scattering data that a two-state model of impurity-trapped hydrogen must incorporate a relative shift in the site energies due to strain fields of surrounding impurities [8–10]. In order to incorporate such a non-degeneracy in the site energies, the SLE (1.3) and the transport analysis following from it must be modified. The simple procedure of maintaining eqn (1.3) but replacing eqn (1.4) by

$$H = \begin{bmatrix} E_1 & V \\ V & E_2 \end{bmatrix}, \tag{2.1}$$

where E_1 and E_2 denote the site energies, fails because it does not account for changes in the form of the bath interaction terms in the site representation caused by the lack of degeneracy. We wish to describe the dynamical consequences of microscopic scattering processes which induce transitions between the pair eigenstates. In the degenerate case, the site energy difference $\Delta = E_1 - E_2 = 0$, and the eigenstates are simply the "Bloch states" of the pair $|\pm> = (1/\sqrt{2})(|1> \pm |2>)$. However, in the non-degenerate case, $\Delta \neq 0$, and the form and evolution of the eigenstates differ from that of the Bloch states.

The idea behind the modification of the SLE we carry out here is similar in spirit to, but different in content from, a modification carried out by Rahman *et al.* [13] in their study of fluoresence depolarization of optical excitations in molecular solids. As in Ref. [13], we take the SLE to have a specific form in the basis of H-eigenstates, regardless of the degree of degeneracy. The physical content of this assertion is that we take the bath interactions to be sensitive primarily to subsystem eigenvalues and insensitive to subsystem spatial symmetry. We then transform the SLE into the site representation. The details of our modification are in the Appendix, eqn (A.3) being the modified SLE in the eigenstate representation. The result is that in the basis of sites, system–bath interactions bear explicit dependences on the degree of degeneracy:

$$\begin{aligned} \dot{\rho}_{11} = &+ iV(\rho_{12} - \rho_{21}) - \frac{\Delta}{2E}(\gamma - \gamma') \\ &- \frac{\Delta}{2E^2}(\gamma + \gamma')\{\Delta(\rho_{11} - \rho_{22}) \\ &+ 2V(\rho_{12} + \rho_{21})\}, \end{aligned} \tag{2.2a}$$

$$\begin{aligned} \dot{\rho}_{22} = &- iV(\rho_{12} - \rho_{21}) - \frac{\Delta}{2E}(\gamma - \gamma') \\ &+ \frac{\Delta}{2E^2}(\gamma + \gamma')\{\Delta(\rho_{11} - \rho_{22}) \\ &+ 2V(\rho_{12} + \rho_{21})\}, \end{aligned} \tag{2.2b}$$

$$\begin{aligned} \dot{\rho}_{12} = &- i\Delta\rho_{12} + iV(\rho_{11} - \rho_{22}) \\ &- \frac{1}{2}(\gamma + \gamma')(\rho_{12} - \rho_{21}) \\ &- \frac{V}{E^2}(\gamma + \gamma')\{\Delta(\rho_{11} - \rho_{22}) \\ &+ 2V(\rho_{12} + \rho_{21})\}, \end{aligned} \tag{2.2c}$$

$$\dot{\rho}_{21} = +i\Delta\rho_{21} - iV(\rho_{11} - \rho_{22}) + \frac{1}{2}(\gamma + \gamma')(\rho_{12} - \rho_{21}) - \frac{V}{E^2}(\gamma + \gamma')\{\Delta(\rho_{11} - \rho_{22}) + 2V(\rho_{12} + \rho_{21})\}, \quad (2.2d)$$

in which the energy difference between the eigenstates of the non-degenerate pair is $E = \sqrt{\Delta^2 + 4V^2}$. The scattering rate α has been replaced in the non-degenerate case by a pair of scattering rates γ and γ' which may be taken to be related through detailed balance such that $\gamma'/\gamma = e^{-\beta E}$. (In the limit $\Delta \to 0$ we find that $\alpha \leftrightarrow (\gamma + \gamma')$.) Thus, the appearance of a single rate α in the usual SLE is an accident of degeneracy. One consequence of the modification is the appearance of new terms in the SLE identifiable as "hopping" terms, i.e. terms representing incoherent transfer between site states. These terms arise from the incoherent scattering between eigenstates because deviations from degeneracy cause the eigenstates to be rotated away from the Bloch states, with the consequence that previously forbidden transitions between site states become allowed.

Equations (2.2) are the starting point for our calculations of neutron scattering lineshapes. They may be solved immediately to yield the Laplace transform solutions

$$\tilde{R}^+(\epsilon) = \frac{1}{\epsilon}R^+(0), \quad (2.3a)$$

$$\tilde{R}^-(\epsilon) = -\frac{1}{\epsilon}\frac{\Delta(\gamma - \gamma')}{E(\epsilon + \gamma + \gamma')} + \frac{2iVD(0) - 2\Delta VE^{-2}(\gamma + \gamma')S(0) + 4V^2E^{-2}(\epsilon + \gamma + \gamma')R^-(0)}{\epsilon(\epsilon + \gamma + \gamma') + E^2} + \frac{\Delta^2}{E^2}\frac{R(0)}{\epsilon + \gamma + \gamma'}. \quad (2.3b)$$

The initial values for the quasi-density matrix in this case are given by

$$R^+(0) = \cos\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) - i\frac{\Delta}{E}\tanh\left(\frac{\beta E}{2}\right)\sin\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right), \quad (2.4a)$$

$$R^-(0) = i\sin\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) - \frac{\Delta}{E}\tanh\left(\frac{\beta E}{2}\right)\cos\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right), \quad (2.4b)$$

$$S(0) = \rho'_{12}(0) + \rho'_{21}(0) = \frac{2V}{E}\tanh\left(\frac{\beta E}{2}\right)\cos\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right), \quad (2.4c)$$

$$D(0) = \rho'_{12}(0) - \rho'_{21}(0) = i\frac{2V}{E}\tanh\left(\frac{\beta E}{2}\right)\sin\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right); \quad (2.4d)$$

however, in this two-state problem, application of the symmetrization procedure [1] has the effect of eliminating the temperature-dependent contributions to the initial data. The consequence is that the relevant initial data for the non-degenerate case are the same as those of the degenerate case, eqn (1.6).

The modified equation results in the scattering function

$$S(\mathbf{q}, \omega) = \delta(\omega)\cos^2\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) + \frac{1}{\pi}\frac{\Delta^2(\gamma + \gamma')}{E^2(\omega^2 + (\gamma + \gamma')^2)}\sin^2\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right) + \frac{1}{\pi}\frac{4V^2(\gamma + \gamma')}{(\omega^2 - E^2)^2 + \omega^2(\gamma + \gamma')^2} \times \sin^2\left(\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right). \quad (2.5)$$

Typical examples of this lineshape are shown in Figs 2 and 3. The coherence parameter is given here by $(\gamma + \gamma')/2V$. The present results differ from those of the degenerate case (Fig. 1) in that the tunneling

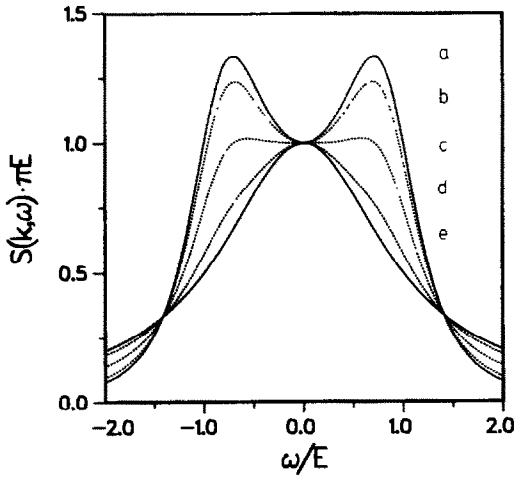

Fig. 2. Quasielastic scattering function for two non-degenerate sites, evaluated using eqns (2.2). The coherence parameter $(\gamma + \gamma')/2V$ has been set equal to unity, reflecting modestly coherent transport. Each curve represents a different Δ and V constrained so that E is the same for all curves. Defining $\sin\theta = \Delta/E$ and $\cos\theta = 2V/E$, we have: (a) $\theta = 0$, (b) $\theta = \pi/8$, (c) $\theta = \pi/4$, (d) $\theta = 3\pi/8$ and (e) $\theta = \pi/2$. The dotted curves ($\theta = \pi/8, \pi/4, 3\pi/8$) represent systems in which both Δ and V are non-zero. The solid curves ($\theta = 0, \pi/2$) represent the extremes of pure tunneling between degenerate sites, and pure hopping between non-degenerate sites, respectively. The latter case results in a Lorentzian lineshape.

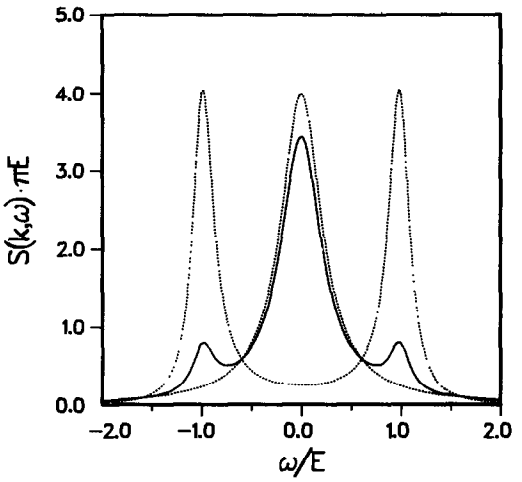

Fig. 3. Quasielastic scattering function for two non-degenerate sites, evaluated using eqns (2.2). The coherence parameter $(\gamma+\gamma')/2V$ has been set equal to 0.25, reflecting transport more coherent than that in Fig. 2. The dotted curves ($\theta = 0, \pi/2$; $\tan\theta = \Delta/2V$) represent the extremes of pure tunneling between degenerate sites, and pure hopping between non-degenerate sites, respectively. The solid curve ($\theta = 3\pi/8$) represents a tunneling system in which $\Delta/E = 0.92$, i.e. more than 90% of the eigenvalue separation E is due to static inhomogeneity.

peaks are shifted to the positions of the new eigenvalues, and a central peak having the form of a Lorentzian has emerged. The strength of the tunneling peaks has been reduced from unity to $4V^2/\Delta^2+4V^2$. One may say that the Lorentzian component is always present, with a strength given by Δ^2/Δ^2+4V^2, since in the limit of degenerate site states the strength of this component vanishes. The central Lorentzian is directly due to the 'hopping" terms which appear in the non-degenerate basis as a manifestation of the bath interactions. That such a peak must appear in the absence of degeneracy may be seen by noting that in the $V\to 0$ limit, scattering between eigenstates continues to occur; however, in this limit the eigenstates and site states become identical. The incoherent scattering between eigenstates is thus transformed into an incoherent transport channel. The failure of such a peak to emerge from the usual SLE is a shortcoming which is remedied by the present modification.

3. DEGENERATE, INEQUIVALENT SITES—COUPLING TO PHONONS

In this section we point out how our analysis of the non-degenerate pair of sites given above may have relevance to a physical system in which no static nondegeneracy exists. Our present concern is that broken site symmetry caused by disorder in the impurity strain field may affect the hydrogen–phonon coupling, and in this way introduce nondegeneracy through polaron effects. The breaking of spatial symmetry may affect quantities other than the site energies. Magerl *et al.* [10], for example, have considered in addition a distribution of tunneling matrix elements. The polaron effects we consider below extend also to the tunneling matrix elements; however, this does not materially alter the discussion and so is not addressed explicitly.

When the width of a particle's energy band is narrow with respect to the bandwidth of phonons, the particle cannot be scattered through interactions with a single phonon [20]. The dominant scattering mechanism due to phonons is then expected to be a two-phonon process, unless temperatures are so low that impurity-assisted one-phonon processes emerge as the dominant mechanism. An alternate mechanism has been proposed for the case of mobile particles on non-Bravais lattices. Teichler and Seegar [21] have shown that differences among phonon coupling constants at sites of different symmetry will generally result in a T^{-1} dependence in the transition rate at low temperature. Their demonstration was based on the linear coupling Hamiltonian

$$H=\sum_{m,i}E_{mi}a\dagger_{mi}a_{mi}+\sum_{m,n,i,j}V_{minj}a\dagger_{mi}a_{nj}+\sum_{q}\hbar\omega_q b\dagger_q b_q+\sum_{m,i,q}\chi_i^q\hbar\omega_q e^{-i\mathbf{q}\cdot\mathbf{R}_m}\times(b\dagger_{-q}+b_q)a\dagger_{mi}a_{mi}. \tag{3.1}$$

In eqn (3.1) a_{mi} destroys a particle at the interstice i of unit cell m, b_q destroys a phonon of mode $\mathbf{q}$, and $\mathbf{R}_m$ is the position vector assigned to the unit cell m. It is easy to see that eqn (3.1) leads to an effective non-degeneracy in the "polaron" site states even when the "bare" site states are degenerate. If one defines polaron operators $A_{mi}=e^{-S}a_{mi}e^{S}$, etc., where

$$S=\sum_{q,m,i}\chi_i^q\hbar\omega_q e^{-i\mathbf{q}\cdot\mathbf{R}_m}(b\dagger_{-q}-b_q)a\dagger_{mi}a_{mi}, \tag{3.2}$$

the Hamiltonian for a single particle takes the form

$$H=\sum_{m,i}(E_{mi}-\sum_q|\chi_i^q|^2\hbar\omega_q)A\dagger_{mi}A_{mi}+\sum_q\hbar\omega q\,B\dagger_q B_q+\sum_{m,n,i,j}V_{minj}A\dagger_{mi}A_{nj}\exp\Big\{\sum_q(\chi_i^q e^{-i\mathbf{q}\cdot\mathbf{R}_m}-\chi_j^q e^{-i\mathbf{q}\cdot\mathbf{R}_n})(B\dagger_q-B_{-q})\Big\}. \tag{3.3}$$

It is common practice [11, 12] to separate the transfer interaction into its thermal average and a remainder term containing the transformed phonon operators B_q. The averaged terms constitute a band Hamiltonian and the remainder term induces transitions among the corresponding band states. The averaged band Hamiltonian may be written

$$\langle H\rangle=\sum_{m,i}\tilde{E}_{mi}A\dagger_{mi}A_{mi}+\sum_{m,n,i,j}V_{minj}\exp\Big\{-\frac{1}{2}\sum_q X_{minj}^q\times\coth\Big(\frac{\hbar\omega_q}{2k_BT}\Big)\Big\}A\dagger_{mi}A_{nj}, \tag{3.4a}$$

$$X^q_{minj} = |\chi^q_i|^2 + |\chi^q_j|^2 - 2\mathrm{Re}\{\chi^q_i \chi^{-q}_j \cos[\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)]\}$$
$$+ 2\mathrm{Im}\{\chi^q_i \chi^{-q}_j \sin[\mathbf{q}\cdot(\mathbf{R}_m - \mathbf{R}_n)]\}. \quad (3.4b)$$

Although the above results are well known, several observations are of interest in the present context. In the case of non-Bravais lattices, the coupling function X^q_{minj} may be of lower symmetry than the tunneling matrix elements V_{minj}. In such a case the effective tunneling interactions of the dressed particle created by $A\dagger_{mi}$ are of lower symmetry than those of the bare particle created by $a\dagger_{mi}$. Such a reduction in symmetry can produce a gap in the $\langle H\rangle$ band structure which will generally allow the one-phonon process since energy and momentum conserving transitions may take place across the gap with the emission or absorption of a single phonon.

The foregoing discussion holds for the two-state system of present interest if all sums over unit cell labels are restricted to the single label of the cell containing the relevant pair of interstices. The effective site energies have the form

$$\tilde{E}_i = E_i - \sum_q |\chi^q_i|^2 \hbar\omega_q,$$

and the effective tunneling matrix element is

$$\tilde{V}_{12}(T) = V_{12} \exp\left\{-\frac{1}{2}\sum_q X^q_{12} \coth\left(\frac{\hbar\omega_q}{2k_B T}\right)\right\},$$

in which unit cell indices have been suppressed. Following the above, we may immediately write the $\langle H\rangle$ eigenvalues for the two-site system as

$$\lambda_{\mu(\nu)}(T) = \frac{1}{2}(\tilde{E}_1 + \tilde{E}_2 + (-)\sqrt{(\tilde{E}_1 - \tilde{E}_2)^2 + 4|\tilde{V}_{12}(T)|^2}). \quad (3.5)$$

The existence of a "gap" is dependent on whether or not the site energy difference

$$\tilde{\Delta} \equiv \tilde{E}_1 - \tilde{E}_2 = E_1 - E_2 + \sum_q (|\chi^q_1|^2 - |\chi^q_2|^2)\hbar\omega_q \quad (3.6)$$

is non-zero. The polaron shift $\tilde{\Delta}$ differs from the static shift Δ only if there is a difference in the polaron binding energies at the two sites. This would not be possible but for disorder, since sites 1 and 2 belong to the point group of the isolated impurity [9]. However, the same disorder which allows the would-be "symmetry-equivalent" sites 1 and 2 to have different static energies E_1 and E_2 allows the polaron binding energies to differ at these sites. Equation (13.6) shows that the coupling of a particle to the phonon field may produce an effective site energy difference $\tilde{\Delta}$, even if $\Delta = 0$. If the consequences of the remaining terms of the Hamiltonian ($H - \langle H\rangle$) may be approximated through a scattering mechanism as discussed in section 2, then our analysis shows that such a "gap" would introduce hopping terms into the density matrix equation of motion and be manifested as a central peak in the neutron scattering lineshape.

Since the gap energy is independent of temperature in this approach, the hopping mechanism and its concomitant scattering peak would be expected to contribute at all temperatures unless $\tilde{\Delta} \ll \tilde{V}_{12}(0)$. The strength of such a peak would be temperature dependent through $\tilde{V}_{12}(T)$, and should increase with increasing temperature approaching unity at infinite temperature. The shape would be independently determined by the damping parameters. The positions of the tunneling peaks should also depend on temperature through $\tilde{V}_{12}(T)$; however, such shifts may be mixed with dynamical shifts originating in the motional narrowing phenomenon and thus may prove difficult to interpret.

It is thus possible to arrive at the same scattering law from quite different microscopic considerations. If the site energy difference Δ is given the strictly inhomogenous interpretation, the arguments of section 2 apply and the resultant lineshape must be averaged over the appropriate distribution of Δ's. If, on the other hand, Δ is given the interpretation of this section, i.e. $\tilde{\Delta}$, definite modifications and temperature dependences are implied as well.

4. SUMMARY

With the help of a formalism constructed recently [1, 2] for the purpose, we have calculated lineshapes for the scattering of thermal neutrons by a particle which is confined to a pair of *non-degenerate* sites and is interacting with a heat bath. The physical systems addressed consist of hydrogen atoms moving among interstices in the vicinity of impurity atoms in metals [3–10]. The lineshapes we have calculated show expected features such as motional narrowing (or broadening) for strong (or weak) system–bath interactions.

In order to calculate the lineshapes, we have introduced a modification into the standard stochastic Liouville equation. This modification is required in order to accommodate the non-degeneracy in the site energies which tunneling-state analyses of recent experimental results suggest exists in the metal hydrides studied. Our analysis results in a coexistence of lineshape structures normally asssociated with coherent and incoherent transport mechanisms. In the present case, however, the mechanism is one and the same for both types of motion. The difference in the site energies is responsible for allowing the bath to induce transitions between the two site states directly, i.e. without mediation by the tunneling process. Since the bath-induced transitions occur incoherently, a purely incoherent channel of motion is introduced. The component of the lineshape attributable to coherent processes is identical in form to that resulting for degenerate site states. The component attributable to incoherent processes is a Lorentzian whose width is given directly by the rates of bath-induced

transitions between the pair eigenstates. The relative strength of the two contributions is controlled by the relative values of the tunneling matrix element and the difference in site energies.

The traditional approach to problems involving strong phonon coupling employs a canonical transformation [11, 12] to states reflecting a relaxation of a deformable lattice about a particle coupled to it. We considered the form of the Hamiltonian which results from such a transformation in the present case, and showed how inelastic and quasielastic structure may appear simultaneously, even for degenerate site states. It was shown that an effective site energy difference may appear if the particle couples to the phonon field differently when occupying different sites as is generally the case in disordered systems. The parameters entering the lineshape calculation bear explicit temperature dependences due to polaron effects. Within the model considered, the strength of the quasielastic component increases from a minimum at zero temperature to unity at high temperature, and the strength of the inelastic component decreases correspondingly from a maximum at zero temperature to zero at high temperature. In no case is the relative strength of the two components affected by the rates of bath-induced transitions; these affect the shapes of the separate components only.

The specific calculations we have shown and the figures we have displayed correspond to the symmetric part of the lineshape only. The complete lineshape for a particular temperature may be obtained by applying the prescription given in Ref. [1], using the transition rates γ, γ' appropriate to the given temperature.

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APPENDIX

Density matrix elements in a basis of localized states (ρ_{12}, etc.) may be obtained from the Hamiltonian eigenstates ($\rho_{\mu\nu}$, etc.) by orthogonal transformation, expressed through the transformation equations:

$$\rho_{11}=\frac{1}{2}(\rho_{\mu\mu}+\rho_{\nu\nu})+\frac{\Delta}{2E}(\rho_{\mu\mu}-\rho_{\nu\nu})-\frac{V}{E}(\rho_{\mu\nu}+\rho_{\nu\mu}), \quad \text{(A.1a)}$$

$$\rho_{22}=\frac{1}{2}(\rho_{\mu\mu}+\rho_{\nu\nu})-\frac{\Delta}{2E}(\rho_{\mu\mu}-\rho_{\nu\nu})+\frac{V}{E}(\rho_{\mu\nu}+\rho_{\nu\mu}), \quad \text{(A.1b)}$$

$$\rho_{12}=\frac{1}{2}(\rho_{\mu\nu}-\rho_{\nu\mu})+\frac{\Delta}{2E}(\rho_{\mu\nu}+\rho_{\nu\mu})+\frac{V}{E}(\rho_{\mu\mu}-\rho_{\nu\nu}), \quad \text{(A.1c)}$$

$$\rho_{21}=\frac{1}{2}(\rho_{\nu\mu}-\rho_{\mu\nu})+\frac{\Delta}{2E}(\rho_{\mu\nu}+\rho_{\nu\mu})+\frac{V}{E}(\rho_{\mu\mu}-\rho_{\nu\nu}), \quad \text{(A.1d)}$$

and their inverses

$$\rho_{\mu\mu}=\frac{1}{2}(\rho_{11}+\rho_{22})+\frac{\Delta}{2E}(\rho_{11}-\rho_{22})+\frac{V}{E}(\rho_{12}+\rho_{21}), \quad \text{(A.2a)}$$

$$\rho_{\nu\nu}=\frac{1}{2}(\rho_{11}+\rho_{22})-\frac{\Delta}{2E}(\rho_{11}-\rho_{22})-\frac{V}{E}(\rho_{12}+\rho_{21}), \quad \text{(A.2b)}$$

$$\rho_{\mu\nu}=\frac{1}{2}(\rho_{12}-\rho_{21})+\frac{\Delta}{2E}(\rho_{12}+\rho_{21})-\frac{V}{E}(\rho_{11}-\rho_{22}), \quad \text{(A.2c)}$$

$$\rho_{\nu\mu}=\frac{1}{2}(\rho_{21}-\rho_{12})+\frac{\Delta}{2E}(\rho_{12}+\rho_{21})-\frac{V}{E}(\rho_{11}-\rho_{22}). \quad \text{(A.2d)}$$

Here $H_{12}=H_{21}=V$, $\Delta=E_1-E_2$, and $E=\sqrt{\Delta^2+4V^2}$. As in the treatment of Rahman *et al.* [13]—see their eqn (3.7)—we use the following form of the SLE in the representation of eigenstates μ, ν:

$$\dot{\rho}_{\mu\mu}=-\gamma\rho_{\mu\mu}+\gamma'\rho_{\nu\nu}, \quad \text{(A.3a)}$$

$$\dot{\rho}_{\nu\nu}=+\gamma\rho_{\mu\mu}-\gamma'\rho_{\nu\nu}, \quad \text{(A.3b)}$$

$$\dot{\rho}_{\mu\nu}=-iE\rho_{\mu\nu}-\frac{1}{2}(\gamma+\gamma')(\rho_{\mu\nu}-\rho_{\nu\mu}), \quad \text{(A.3c)}$$

$$\dot{\rho}_{\nu\mu}=+iE\rho_{\nu\mu}+\frac{1}{2}(\gamma+\gamma')(\rho_{\mu\nu}-\rho_{\nu\mu}). \quad \text{(A.3d)}$$

The off-diagonal elements oscillate at frequencies $\pm E$ and the diagonal elements equilibrate through scattering at rates γ and γ' related to each other through detailed balance. Differentiating the eqns (A.1) for ρ_{mn} and substituting eqns (A.3), we find

$$\dot{\rho}_{11} = -\frac{\Delta}{2E}(\gamma - \gamma')(\rho_{\mu\mu} - \rho_{\nu\nu}) + iV(\rho_{\mu\nu} - \rho_{\nu\mu}), \quad \text{(A.4a)}$$

$$\dot{\rho}_{22} = +\frac{\Delta}{2E}(\gamma - \gamma')(\rho_{\mu\mu} - \rho_{\nu\nu}) - iV(\rho_{\mu\nu} - \rho_{\nu\mu}), \quad \text{(A.4b)}$$

$$\dot{\rho}_{12} = -\frac{iE}{2}(\rho_{\mu\nu} + \rho_{\nu\mu}) - \frac{1}{2}[i\Delta + \gamma + \gamma'](\rho_{\mu\nu} - \rho_{\nu\mu}) - \frac{V}{E}(\gamma - \gamma')(\rho_{\mu\mu} - \rho_{\nu\nu}), \quad \text{(A.4c)}$$

$$\dot{\rho}_{21} = +\frac{iE}{2}(\rho_{\mu\nu} + \rho_{\nu\mu}) - \frac{1}{2}[i\Delta - \gamma - \gamma'](\rho_{\mu\nu} - \rho_{\nu\mu}) - \frac{V}{E}(\gamma - \gamma')(\rho_{\mu\mu} - \rho_{\nu\nu}). \quad \text{(A.4d)}$$

Finally, applying the transformations (A.2) yields the desired form of the SLE in the site representation, *viz.* (2.2).