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Theory of neutron scattering from hydrogen in metals involving transitions to excited tunnel-split states

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A theory is developed for neutron-induced transitions to excited states of a proton trapped at a two-well potential near an interstitial impurity in a metal. The proton wave function is written as a linear combination of the states in each well (tight-binding approximation). Hence, in the main, the theory is limited to the low-lying excitations which lie below the central barrier. Otherwise, the theory is quite general and independent of the details of the potential. General expressions are derived for the differential cross section for transitions from the ground-state doublet to the excited states in terms of $\tilde{F}(\vec{q})$, the transition form factor. A corresponding quantity, $F(\vec{q})$, appears in expressions for $d\sigma/d\Omega$ associated with transitions within the ground-state doublet. As in earlier work, concerned only with the ground-state doublet, the effects of asymmetric displacements of the well bottoms due to strains are considered. As is the case for the ground-state doublet, the effect of the asymmetry in the two-well potential is to introduce a general mixing angle for the excited-state doublet describing the admixture of the left-hand and right-hand single-well states. Whereas the effect of nonequal mixing on the inelastic differential cross section for transitions within the ground-state doublet is to diminish it by a factor $\langle \sin^2 2\theta \rangle_{\rm av}$ (θ is the mixing angle), under suitable experimental conditions, I show that the corresponding cross section for neutron-induced transitions from the ground-state doublet to either component of the excited-state doublet is independent of both θ and ϕ (ϕ is the excited-state mixing angle). That is, the latter cross section is independent of ϵ, a measure of the asymmetry, provided $\epsilon/\hbar\omega \ll 1$ ($\hbar\omega$ is the excitation energy). Thus the ratio Λ of the higher-energy to the lower-energy inelastic cross section is, on the one hand, enhanced by a factor $1/\langle \sin^2 2\theta \rangle_{\rm av}$ and, on the other, diminished by the quantity $|\tilde{F}(\vec{q})|^2$. General expressions for Λ and for the ratios of various other cross sections are derived in terms of $\tilde{F}(\vec{q}')$ and $F(\vec{q})$. These are then estimated for the first excited state by making various simplifying approximations. Λ is finite in the limit $\vec{q} \to 0$, $\vec{q}' \to 0$, keeping their ratio fixed. If I assume that errors in making the small-$\vec{q}$ expansion tend to cancel in taking the ratio, then, utilizing the idealized oscillator model of Sussmann, I find the approximate relation $\Lambda = (\rho^2/8)(k_F/k_I)(\hbar\omega/V_0)/\langle \sin^2 2\theta \rangle_{\rm av}$. Here ρ is the actual experimental ratio of the high- to low-momentum transfers, k_F/k_I is the ratio of the final to initial neutron momenta, and V_0 is the barrier height. Results are applied to existent and ongoing experiments on hydrogen- and oxygen-doped niobium.

I. INTRODUCTION

The experimental observation and theoretical analysis of tunnel splittings of impurity complexes in solids via inelastic neutron scattering is a topic of current interest.[1-4] Also, the general subject of hydrogen in metals continues to receive impetus on both scientific and technological grounds.[5] Recently, a confluence of these interests has materialized in the experiments of Wipf, Magerl, Shapiro, Satija, and Thomlinson,[6] and of Magerl, Rush, and Rowe,[7] who observe elastic and (weak) inelastic peaks in the neutron scattering from samples of niobium doped with both hydrogen and oxygen. They attribute the 0.19-meV inelastic peak, which they observe at low temperatures [$O(0.1\ \text{K}) \to O(5\ \text{K})$], to transitions between the components of a tunnel-split oscillator ground state of the proton, trapped in a two-well potential at an impurity center, presumably associated with an oxygen atom. The two wells need not be symmetric. Wipf *et al.*[6] have, in fact, employed the assumption of a Lorentzian distribution in the

relative energy displacements of the constituent well minima (for which earlier analyses exist[8,9]) to explain the fact that the ratio of the inelastic to elastic cross sections is only $O(1\%)$.

Analogous neutron-induced transitions, both among components of the tunnel-split ground state[3] and also the higher-energy excitations from the ground to the libronically *excited* tunnel-split states[1,3,4] associated with the motion of CN^- molecules in KBr and KCl, have been observed earlier. It is believed that in these systems the observation of the neutron-induced transitions is made possible by the *coherent* forward resonant scattering of the phonons in the host lattice from the CN^- impurities, which results in mixed modes, part phonon and part libronic excitation, and/or reorientation of the CN^- dumbbells.[1-4] This interaction induces splitting of the phonon spectrum and renders the CN^- excitation spectrum accessible to the neutron probe via coherent inelastic scattering from the mixed modes. For the case of hydrogen in metals, experimental difficulties are expected to block this coherent view of the excited states. Nevertheless, the very large total cross section for low-energy *n-p* scattering allows observation of the *direct* excitation by the neutron of the bound proton to the excited oscillator levels and has presumably already been observed (as have the lower-energy excitations across the tunnel-split components of the two-well oscillator ground state).[6,7] Hence, a thorough theoretical analysis of the process of neutron excitation to these higher-lying states seems worthwhile. I give such an analysis here, both for the case of symmetric wells and that of wells with statistically distributed asymmetries in the component well depths.

To discuss the two-well structure in which the proton is assumed trapped at low temperatures, it is helpful to keep in mind a concrete model potential. Here, each potential minimum can be visualized as that of a three-dimensional harmonic-oscillator well which is cut off by its intersection with its neighboring well in the two-center complex. Corresponding force constants are assumed equal from well to well; hence, in the absence of possible (strain-induced) relative displacements of the minima, the unperturbed levels coincide. To be definite, I assume that the force constant of each for motion parallel to the vector $\vec{r}$ connecting the two minima in space is somewhat weaker than the force constants associated with motion perpendicular to $\vec{r}$. In the tight-binding approximation, the proton wave functions are taken to be linear combinations of the eigenstates of the single-well potential (without cutoff) centered at each site. The above assumption concerning the anisotropy in the force constants, in addition to being physically reasonable, serves to remove the angular momentum degeneracy of the first excited unperturbed oscillator state which would result if all three force constants for each well were selected equal.[10] In this picture, the first excited state involves only excitation of the oscillator quantum number $n_{||}$ associated with motion parallel to $\vec{r}$ and the problem is reduced to an effective one-dimensional two-well problem for which the analysis of the ground-state splitting (for both the symmetric and displaced-minima cases) has been given by Sussmann.[8]

While it is helpful to keep in mind an explicit model, such as the above, it must be emphasized that much of the present analysis is based upon more general considerations and essentially depends only upon the (tight-binding) assumption that the eigenstates are linear combinations of local well states, from which it follows that the approximate eigenstates assume the form,

$$\begin{bmatrix} |g\rangle \\ |u\rangle \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} |L\rangle \\ |R\rangle \end{bmatrix} . \tag{1}$$

Here $|L\rangle$ and $|R\rangle$ are the left and right eigenstates, e.g.,

$$\langle \vec{x}\,|L\rangle = \psi_L(\vec{x}) = f(\vec{x}-\vec{L}) , \tag{2}$$

where, for a symmetrically chosen origin $\vec{L} = -\vec{r}/2$ and $\vec{R} = +\vec{r}/2$. θ is the mixing angle which, for $\theta = \pi/4$ (symmetric-well case), leads to states which are even or odd under reflection in a plane perpendicular to and bisecting $\vec{r}$. In general, if the excited and ground states of the single-well problem are separated by energies that are large compared with the tunnel-induced splitting of each, the factorization into two-dimensional manifolds is justified. However, the mixing angle for the excited states will, in general, differ from that of the ground-state complex, except for the symmetric-well case where reflection symmetry dictates that $\phi = \theta = \pi/4$. (ϕ is the excited-state mixing angle connecting $|L,E_{ex}\rangle$ and $|R,E_{ex}\rangle$, the excited single-well states.) As noted above, the general tight-binding results are independent of the details of the oscillator model. Only the assumption that the first excited local-well state is nondegenerate[10] is abstracted from the model. Moreover, time-reversal invariance is invoked. On occasion, I shall estimate model parameters by reverting to the explicit harmonic-oscillator model, being careful to point out when

this is the case. Renormalization of the proton (effective) mass and of the well parameters due to interaction with the phonon field may be assumed to be included in the phenomological description.

In Sec. II, the formalism is developed for the symmetric-well case, both for the elastic and inelastic scattering among the tunnel-split ground states, where, to the extent that deviations of $F(\vec{q})$ from isotropy can be ignored, the results are known,[6] and then for the inelastic scattering at low temperatures due to neutron-induced transitions to the excited states. Here, the quantity $\tilde{F}(\vec{q})$ enters. A general expression is obtained for the ratio of the inelastic cross section associated with transitions to the excited states divided by the sum of the cross sections associated with transitions between the components of the ground-state doublet. The ratio is then evaluated by making a series of simplifying assumptions. In Sec. III, the effects of a distribution of asymmetric wells on these processes are considered. The experimental situation for niobium is discussed in Sec. IV.

II. SYMMETRIC WELLS

Let T_{FI} be the appropriate mass-weighted reduced T matrix between the initial and final states of the neutron plus impurity center. T_{FI} is normalized such that the differential cross section can be written in the form

$$\frac{d\sigma}{d\Omega}=\frac{k_F}{k_I}|T_{FI}|^2 . \tag{3}$$

k_I and k_F are the magnitudes of the incident and scattered neutron momenta, respectively, in units with $\hbar=1$. In terms of the standard Fermi pseudopotential,

$$V(\vec{x},\vec{x}')=(2\pi a/m)\delta^3(\vec{x}-\vec{x}') , \tag{4}$$

and in Born approximation,

$$T_{FI}=\frac{m}{2\pi}\int d^3x\int d^3x'\psi_F^*(\vec{x})e^{-i\vec{q}\cdot\vec{x}'}V(\vec{x},\vec{x}')\psi_I(\vec{x}) , \tag{5}$$

whence

$$T_{FI}=a\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}\psi_F^*(\vec{x})\psi_I(\vec{x}) . \tag{6}$$

In the above, $\vec{q}=\vec{k}_F-\vec{k}_I$, $\psi_I(\vec{x})$ and $\psi_F(\vec{x})$ are the initial- and final-state wave functions of the proton bound to the two-well impurity center, m is the neutron mass, and a is the bound n-p scattering length (summed over final- and averaged over initial-spin states) multiplied by the lattice Debye-Waller factor, $\exp[-W(\vec{q})]$.[11] As noted earlier, for symmetric wells the ground-state mixing angle θ in Eq. (1) equals $\pi/4$ as does the analogous excited-state angle, ϕ.

A. Ground-state doublet

For the ground-state doublet, with the phase conventions adopted in Eq. (1),

$$\psi_{I,F}=\pm(\tfrac{1}{2})^{1/2}[f(\vec{x}-\vec{L})\pm f(\vec{x}-\vec{R})] . \tag{7}$$

At $T=0$ K the inelastic cross section satisfies

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{in}}^{0}=|a|^2\frac{k_F}{k_I}\left\langle|F(\vec{q})|^2\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle . \tag{8}$$

Here,

$$F(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}|f(\vec{x})|^2 , \tag{9}$$

and the angular brackets in Eq. (8) denote an average over the angular distribution of the directions in which the impurities are oriented, i.e., over $\vec{r}/d$ where $d=|\vec{r}|$. At finite but sufficiently low temperatures that only the doublet ground states are occupied, Eq. (8) is to be modified by including the usual thermal occupation factors Z^{-1} and $Z^{-1}\exp(-\beta\delta E)$ for transitions involving neutron energy loss and gain, respectively. $Z=1+\exp(-\beta\delta E)$, $\beta=1/k_BT$, and δE is the ground-state energy splitting. Neglecting the overlap $\Delta(\vec{q})$, where

$$\Delta(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}f^*(\vec{x}-\vec{L})f(\vec{x}-\vec{R}) , \tag{10}$$

the elastic cross section is given by the expression

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{el}}=|a|^2\left\langle|F(\vec{q})|^2\cos^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle . \tag{11}$$

Under experimental conditions where the ground-state splitting is sufficiently small that the deviation from unity of the ratio k_F/k_I can be neglected,

$$\sum\left.\frac{d\sigma}{d\Omega}\right|_{\text{in}}+\left.\frac{d\sigma}{d\Omega}\right|_{\text{el}}=|a|^2\langle|F(\vec{q})|^2\rangle , \tag{12}$$

and the ratio R of the sum of the inelastic (energy loss and gain) cross sections divided by the total is given by the expression

$$R=\left\langle|F(\vec{q})|^2\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle\Big/\langle|F(\vec{q})|^2\rangle . \tag{13}$$

To the extent that the average of the product can be replaced by the product of the averages, the ratio R reduces to the known expression[6]

$$R=\left\langle \sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle , \tag{14}$$

which is independent of $F(\vec{q})$. That $F(\vec{q})$ can depend upon the orientation $\vec{r}/d$ follows from the (reasonable) assumption that $f(\vec{x})$ is not, in general, spherically symmetric. For example, in the harmonic-oscillator model discussed earlier, the anisotropy in the force constants associated with motion along $\vec{r}$ (as opposed to motion perpendicular to $\vec{r}$) produces this deviation from spherical symmetry in $f(\vec{x})$, but the result is more general. If the anisotropy is negligible, Eq. (14) follows even when $F(\vec{q})$ differs significantly from unity. From Eq. (9) it is also clear that as $\vec{q}\to 0$, $F(\vec{q})\to 1$, independently of the degree of anisotropy in $f(\vec{x})$ and the result (14) is again recovered. To estimate finite-$\vec{q}$ corrections, note that when the unperturbed single-well ground state $f(\vec{x})$ is an eigenstate of the parity operator, $F(\vec{q})$ is an even function of $\vec{q}$. In the small-$\vec{q}$ regime,

$$F(\vec{q})=1-B^{\mu\nu}q_\mu q_\nu+O(\vec{q}^4) , \tag{15}$$

where $B^{\mu\nu}$ is the second-moment tensor:

$$B^{\mu\nu}=\int d^3x\, x^\mu x^\nu |f(\vec{x})|^2 . \tag{16}$$

Thus, deviations from unity occur only in second order in $\vec{q}$, and, when $f(\vec{x})$ can be approximated by $\delta^3(\vec{x})$, can be ignored altogether. Under typical experimental conditions, $1<q<3$ Å^{-1}. Hence, deviations from unity may not be negligible in $F(\vec{q})$, given that the proton wave functions have sufficient extent to produce tunneling. [The assumption of parity symmetry employed in the above, is a reasonable one if, in the effective one-dimensional two-well problem, the unperturbed ground-state energy E_0 lies considerably below the energy V_0 at which the two potential wells intersect. (In the oscillator model $E_0=\omega/2$, the zero-point energy associated with motion along $\vec{r}$.)]

B. Excited-state transitions

First consider $T=0$ K. Then $|I\rangle=|g,\vec{k}_I\rangle$ and $|F\rangle$ is either $|g,E_{ex},\vec{k}_F\rangle$ or $|u,E_{ex},\vec{k}_F\rangle$. Again neglecting overlap terms of the type

$$\tilde{\Delta}(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}} f^{ex*}(\vec{x}-\vec{L})f(\vec{x}-\vec{R}) , \tag{17}$$

the expression for the (even $\leftarrow$ even) cross section becomes

$$\left[\frac{d\sigma}{d\Omega}\right]^0_{gg}=\frac{k_F}{k_I}|a|^2\left\langle |\tilde{F}(\vec{q})|^2\cos^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle . \tag{18}$$

The (odd $\leftarrow$ even) cross section reads

$$\left[\frac{d\sigma}{d\Omega}\right]^0_{ug}=\frac{k_F}{k_I}|a|^2\left\langle |\tilde{F}(\vec{q})|^2\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle , \tag{19}$$

where, in each case, k_F and k_I are related by energy conservation. At finite but sufficiently low temperatures that only the ground-state doublet is occupied, the usual factor Z^{-1} enters in Eqs. (18) and (19). Transitions initiating from the odd component of the ground-state doublet are associated with cross sections given by the expressions

$$\left.\frac{d\sigma}{d\Omega}\right|_{uu}=\left[\frac{d\sigma}{d\Omega}\right]^0_{gg}Z^{-1}\exp(-\beta\delta E) , \tag{20}$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{gu}=\left[\frac{d\sigma}{d\Omega}\right]^0_{ug}Z^{-1}\exp(-\beta\delta E) . \tag{21}$$

The prefactors in Eqs. (20) and (21) are given by Eqs. (18) and (19), respectively. We may imagine the following experimental scenario: (i) The experiment designed to observe the higher-energy transitions cannot simultaneously resolve the ground-state splitting. (ii) The temperature is sufficiently high that the two ground-state components are roughly equally populated, but sufficiently low that the excited states are empty. (iii) The first excited-state splitting is larger than the ground-state splitting and resolvable in the experiment satisfying (i) and (ii). Under these conditions, the cross section for a transition from the unresolved ground-state doublet to either the even or the odd component of the excited-state doublet is given, to good approximation, by the relation

$$\frac{d\sigma}{d\Omega}=\frac{1}{2}\frac{k_F}{k_I}|a|^2\langle |\tilde{F}(\vec{q})|^2\rangle . \tag{22}$$

The quantity $\tilde{F}(\vec{q})$, which appears in Eqs. (18), (19), and (22), is given by the expression

$$\tilde{F}(\vec{q})=\int d^3x\, e^{-i\vec{q}\cdot\vec{x}} f^{ex*}(\vec{x})f(\vec{x}) , \tag{23}$$

where $f^{ex}(\vec{x})$ is the excited state and $f(\vec{x})$, the ground state of the unperturbed local-well potential. [Within the three-dimensional oscillator model, the quantum numbers for f_1^{ex} are $(n_{||}=1, n_{\perp 1}=0, n_{\perp 2}=0)$.] Quite generally, since the inner product (f^{ex},f) vanishes, it follows that $\tilde{F}(\vec{q})\to 0$ as $q\to 0$. Thus, even when $F(\vec{q})$ can be ignored $\tilde{F}(\vec{q})$ cannot.

To the extent that a small-$\vec{q}$ expansion is legitimate,

$$\tilde{F}(\vec{q})=-i\vec{q}\cdot\vec{D}-Q^{\mu\nu}q_\mu q_\nu+\cdots , \tag{24}$$

where

$$\vec{D}=\int d^3x\, f^{ex*}(\vec{x})\vec{x}f(\vec{x}) , \tag{25}$$

and $\overleftrightarrow{Q}^{\mu\nu}$ is the transition quadrapole tensor. In general $\vec{D}_1$ does not vanish even when parity is a good symmetry of the one-well potential, since f_1^{ex} and f can be expected to be of opposite parity. Next, I assume the following: (i) Parity is a good single-well symmetry. (ii) The first single-well excitation is nondegenerate. (iii) The wave functions factor

$$\begin{aligned} f(\vec{x})&=f_\perp(\vec{x}_\perp)f_{||}(\xi) ,\\ f^{ex}(\vec{x})&=f_\perp(\vec{x}_\perp)f_{||}^{ex}(\xi) , \end{aligned} \tag{26}$$

where $\xi=\vec{x}\cdot\vec{r}/d$ and $\vec{x}_\perp$ is a two-dimensional vector satisfying $\vec{x}_\perp\cdot\vec{r}=0$. Then,

$$\vec{D}=\frac{\vec{r}}{d}\int d\xi f_{||}^{ex*}(\xi)\xi f_{||}(\xi) . \tag{27}$$

This reduction to a one-dimensional form also follows when the parity assumption (i) is replaced by a somewhat weaker assumption of reflection symmetry in two mutually perpendicular planes intersecting through the line of centers. In either case Eqs. (24) and (27) together imply that to lowest order in $\vec{q}$, for transitions to the first excited state,

$$\langle|\tilde{F}(\vec{q})|^2\rangle=\langle(\vec{q}\cdot\vec{r}/d)^2\rangle|\vec{D}|^2 , \tag{28}$$

where $\vec{D}$ is given by Eq. (27).

Because of experimental interest, I obtain a general expression for the ratio Λ of the differential cross section for scattering from the unresolved doublet ground state to either component of the excited two-well doublet, divided by the sum of the differential cross sections for inelastic scattering among the components of the ground-state doublet. The numerator is given by Eq. (22) for the experimental scenario described earlier. To the extent that deviations from unity of the ratio (k_F/k_I) can be ignored for transitions *within the ground-state doublet,* the sum in the denominator is equal to the zero-temperature inelastic cross section, as given by Eq. (8). (The relative values of the lower-energy cross sections in $NbO_{0.013}H_{0.016}$ are known from the distinct high-resolution experiments described earlier.[6,7]) With no further approximation, in particular, for *arbitrary* momentum transfers, which need *not* be small, I find the following general expression for Λ:

$$\Lambda=\frac{1}{2}\frac{k_F'}{k_I'}\langle|\tilde{F}(\vec{q}')|^2\rangle\Big/\left\langle|F(\vec{q})|^2\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle . \tag{29}$$

The primes on various momenta designate the values associated with these quantities which are appropriate for the higher-energy experiments and reflect the fact that the kinematic boundaries are not identical in the two experiments.

Whereas Eq. (29), together with the results of the lower-energy experiments and a model of the two-well potential, can be used to estimate the differential cross sections for the higher-energy experiments under quite general assumptions, for reasons of simplicity, I shall estimate them under the following special assumptions: (i) $\vec{q}'$ and $\vec{q}$ are parallel, i.e., $\vec{q}'=\rho\vec{q}$ where ρ is some constant. (ii) $\vec{q}$ and $\vec{q}'$ are allowed to become small in the sense that expansions of the quantities $F(\vec{q})$, $\tilde{F}(\vec{q}')$, and $\sin^2(\vec{q}\cdot\vec{r}/2)$ are meaningful. Then, to lowest order in q, for transitions to the first excited state,

$$\Lambda=\frac{1}{2}\rho^2(k_F'/k_I')|\vec{D}|^2/l^2 , \tag{30}$$

where $l=d/2$ and, from Eq. (23), for real f^{ex},

$$|\vec{D}|=\int d\xi f_{||}^{ex}(\xi)\xi f_{||}(\xi) . \tag{31}$$

Equation (31) is in the form of a one-dimensional integral. Specializing further to the harmonic oscillator, $|\vec{D}|=(1/2\alpha)^{1/2}$ where, reintroducing $\hbar$, $\alpha=m^*\omega/\hbar$, with m^* the renormalized effective mass of the proton. In the two-well problem considered by Sussmann,[8] $\alpha l^2=V_0/(\hbar\omega/2)$ where V_0 is the barrier height at $\xi=0$, where the two parabolas intersect, and $\hbar\omega/2$ is the zero-point energy of each effective one-dimensional oscillator. It follows that

$$|\vec{D}|^2/l^2=\hbar\omega/(4V_0) , \tag{32}$$

whence, from Eq. (30), omitting the primes on k_I and k_F, for the first excitation,

$$\Lambda=(\rho^2/8)(k_F/k_I)(\hbar\omega/V_0) , \tag{33}$$

where k_F and k_I are related by energy conservation. It is evident that the oscillator model parameters enter the expression for Λ only through the ratio γ, where

$$\gamma=\hbar\omega/V_0 . \tag{34}$$

To the extent that V_0 represents the actual barrier height of a realistic (renormalized) potential, it is clear that the tight-binding approach adopted here applies to the first-excited oscillator states only if $\gamma<\frac{2}{3}$. I shall treat γ as a parameter to be determined by comparison with experiment of the cross-section ratio defined by Λ with the theoretical expression, once corrections for well asymmetry have been taken into account in the next section. For

ease of reference in later discussions, it is convenient to rewrite Eq. (33) in the form

$$\Lambda_S=(\rho^2/8)(k_F/k_I)\gamma\ , \tag{35}$$

where the subscript S has been added to signify the result obtained for symmetric wells. The result for Λ when well asymmetry is taken into account is readily expressed in terms of Λ_S and the mixing angle θ defined in Sec. I.

Before considering the effects of well asymmetry in detail, several remarks concerning the validity and application of Eq. (35) are in order. (i) It was obtained by letting $\vec{q}'$ and $\vec{q}$ become small such that their ratio remains constant and equal to ρ. In the actual experiments, intensity considerations require maximizing both q' and q. It seems reasonable to select a value for ρ which lies close to its actual value under realistic conditions and then let $\vec{q}\to 0$. (ii) The errors introduced in making the small-$\vec{q}$ expansion in both the numerator and denominator of the expression for Λ given by Eq. (29) tend to cancel in taking the ratio. (iii) Since V_0 is, by definition, the barrier height in the idealized potential where it represents the height of a cusp at the intersection of two parabolas, whereas the actual potential should be smooth at $\xi=0$, the above bounds on γ do not have a precise physical meaning. Nonetheless, in order of magnitude, if $\gamma<1$, then the theory developed here applies and imposes constraints on the model as a whole. (iv) Since, for fixed k_I and k_F, there exists a minimum value for the magnitude of $\vec{q}'$, namely k_I-k_F, then for fixed value of ρ, there exists a minimum physical value of q, namely $(k_I-k_F)/\rho$. This latter value may or may not be sufficiently small as to allow small-$\vec{q}$ expansions. However, this circumstance need not be the cause for undue concern. We may simply regard the small-$\vec{q}$ limit as a process of analytic continuation and proceed to take the formal limit $\vec{q}\to 0$. This limit exists and is given by Eq. (30), which ultimately reduces to Eq. (35).

III. ASYMMETRIC WELLS

A. Ground-state doublet

If, as a consequence of, say, strains, the well minima within each two-center complex are displaced with respect to each other by varying amounts, 2ϵ, then, quite generally, the Hamiltonian matrix can be written in the form

$$H=\begin{bmatrix} H_{11}-\epsilon & H_{12} \\ H_{12} & H_{11}+\epsilon \end{bmatrix}. \tag{36}$$

H is real as a consequence of time-reversal invariance. Explicit formulas for the independent elements H_{11} and H_{12} exist if one adopts the effective one-dimensional harmonic-oscillator model.[8] For the present discussion it suffices to note that the mixing angle θ in Eq. (1) satisfies the relation

$$\sin^2 2\theta=J^2/(J^2+\epsilon^2)\ , \tag{37}$$

where $J=|H_{12}-H_{11}\Delta_{12}(0)|$ when overlap is included. Then, at 0 K $(d\sigma/d\Omega)^0_{\rm in}$ is given by the right side of Eq. (8) multiplied by the factor $\langle\sin^2 2\theta\rangle_{\rm av}$. The average over mixing angle is to be taken with respect to some assumed probability distribution $P(\epsilon)$ for the displacement of the well bottoms. At finite temperatures, the same thermal factors Z^{-1} and $Z^{-1}\exp(-\beta\delta E)$ enter for neutron energy loss and gain, respectively, as did for the case of the symmetric wells. Moreover, the cross-section ratio R as defined in Sec. II A is given by the result of multiplying Eq. (13) by this same factor. That is,

$$R=\langle\sin^2 2\theta\rangle_{\rm av}\frac{\left\langle |F(\vec{q})|^2\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle}{\langle |F(\vec{q})|^2\rangle}\ . \tag{38}$$

If $P(\epsilon)$ is characterized by a half-width ϵ_0 that is large compared with J, then it follows from Eq. (37) that

$$\langle\sin^2 2\theta\rangle_{\rm av}\simeq J/\epsilon_0\ . \tag{39}$$

If, furthermore, one can ignore anisotropy in $F(\vec{q})$, then Eq. (38) reduces to the approximate relation

$$R\simeq\frac{J}{\epsilon_0}\left\langle\sin^2\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right\rangle. \tag{40}$$

As noted in the Introduction, Wipf *et al.*[6] arrive at the result (40) by assuming that $P(\epsilon)$ is Lorentzian and employ the (assumed) smallness of $\langle\sin^2 2\theta\rangle_{\rm av}$ to explain their experimental result, $R=O(1\%)$. I shall next consider the effect of the asymmetric displacement of the wells on the transitions to the excited states.

B. Excited-state transitions

I assume that the tunnel splittings are sufficiently small compared with the separation between the ground-state and excited-state doublets that the lowest (4×4) Hamiltonian matrix is block diagonal in two (2×2) matrices. Both (2×2) matrices are of a form given by Eq. (36). Both sets of approximate eigenstates are of a form given by Eq. (1) and the excited-state mixing angle ϕ satisfies an equation similar to Eq. (37)

$$\sin^2 2\phi=\tilde{J}^2/(\tilde{J}^2+\epsilon^2)\ , \tag{41}$$

where $\tilde{J}=|\tilde{H}_{12}-\tilde{H}_{11}\tilde{\Delta}_{12}(0)|$ in an obvious notation.

In the following, I shall also assume the same experimental scenario as was assumed in discussing the excited-state transitions for symmetric wells in Sec. II B. To be definite, I consider the cross section for transitions from the unresolved ground-state doublet $|g\rangle, |u\rangle$ to the g excited state, where $|g\rangle$ and $|u\rangle$ are defined by Eq. (1) and, for general θ, are neither even nor odd under reflection in the midplane. Neglecting the overlap $\tilde{\Delta}(\vec{q})$, the corresponding T-matrix elements are

$$T_{gg}=a\left[\cos(\phi-\theta)\cos\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]+i\cos(\phi+\theta)\sin\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right]\tilde{F}(\vec{q}) , \quad (42)$$

$$T_{gu}=a\left[\sin(\phi-\theta)\cos\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]-i\sin(\phi+\theta)\sin\left[\frac{\vec{q}\cdot\vec{r}}{2}\right]\right]\tilde{F}(\vec{q}) . \quad (43)$$

Thus, the differential cross section for transitions from the unresolved ground-state doublet to the excited state $|g,E_{ex}\rangle$ is given by the relation

$$\frac{d\sigma}{d\Omega}=\frac{1}{2}\frac{k_F}{k_I}\langle\langle|T_{gg}|^2+|T_{gu}|^2\rangle\rangle_{av} . \quad (44)$$

From Eqs. (42) and (43) it follows that this cross section directly determines $\langle|\tilde{F}(\vec{q})|^2\rangle$, i.e.,

$$\frac{d\sigma}{d\Omega}=\frac{1}{2}\frac{k_F}{k_I}|a|^2\langle|\tilde{F}(\vec{q})|^2\rangle . \quad (45)$$

The expression for the cross section for transitions to the component $|uE_{ex}\rangle$ of the excited-state doublet is identical. Comparison of Eq. (45) with Eq. (22), Sec. II B, shows that *this cross section for the asymmetric wells is identical to the corresponding cross section for the symmetric wells, i.e., is independent of the mixing angles θ and ϕ, hence of the degree of asymmetry, ϵ.* Letting Π be the ratio of this invariant differential cross section to the similarly invariant sum of inelastic and elastic cross sections within the ground-state doublet, which can be shown to be given by Eq. (12), it follows that

$$\Pi=\frac{1}{2}\frac{k_F}{k_I}\langle|\tilde{F}(\vec{q}')|^2\rangle/\langle|F(\vec{q})|^2\rangle . \quad (46)$$

As defined, the cross-section ratios Π, Λ, and R are related,

$$\Pi=\Lambda R=\Lambda_S R_S , \quad (47)$$

where I have added the subscript S to denote the quantities Λ and R as determined for the *symmetric* well model in Sec. II. We have already seen that

$$R=\langle\sin^2 2\theta\rangle_{av}R_S . \quad (48)$$

Hence, as a consequence of Eq. (47), quite generally,

$$\Lambda=\Lambda_S/\langle\sin^2 2\theta\rangle_{av} , \quad (49)$$

where Λ_S is given by Eq. (29). Moreover, Λ_S is finite as $\vec{q}$ and $\vec{q}'$ approach zero at fixed ratio ρ, as was shown in Sec. II. Equation (46) can also be expanded in powers of q and q'. To lowest order,

$$\Pi=\frac{1}{2}\frac{k_F}{k_I}\langle(\vec{q}'\cdot\vec{r}/d)^2\rangle|\vec{D}|^2 . \quad (50)$$

Estimating the angular average by $\frac{1}{3}$,

$$\Pi\simeq\frac{1}{6}\frac{k_F}{k_I}|\vec{q}'|^2|\vec{D}|^2 . \quad (51)$$

If the excited-state doublet can be resolved, a measurement of Π yields a value for $|\vec{D}|$, provided an expansion in powers of $(q'D)^2/3$ is meaningful. Within the idealized oscillator model $|\vec{D}|=\gamma^{1/2}d/4$. Hence, by measuring Π, one can place restrictions on γ, provided lower-energy measurements associated with the ground-state doublet yield an independent measure of d.

Whereas, as presented, the discussion in this subsection relates only to excitations to the first excited-state doublet, the results through Eq. (49) are quite general (if one includes possible degeneracy factors associated with motion transverse to $\vec{r}$) and apply to excitations from the ground-state doublet to the tunnel-split component of any excited-state doublet lying below the central barrier. (An additional factor of 2 enters if the excited-state doublet cannot be resolved.) Equations (50) and (51) are considerably more restricted, but can be generalized to include higher excitations, provided a change in parity occurs; otherwise $\vec{D}=0$. The subsequent expression for $|\vec{D}|$ is restricted to the first excitation.

IV. EXPERIMENTS ON NIOBIUM

The ground-state tunnel splittings have been observed in a polycrystalline sample of hydrogen- and oxygen-doped niobium[6] and also in single crystals, where the data are still preliminary.[7] Moreover, in the latter experiments, at least one excited peak has

been observed with $\hbar\omega = O(100\ \text{meV})$ and $k_F/k_I \simeq 0.16$. This peak is presumably to be associated with the (unresolved) first-excited-state doublet. The earlier lower-energy data, which were taken at $q = 2.5\ \text{Å}^{-1}$, have been fitted by the following parameter values: $\langle \sin^2 2\theta \rangle_{\text{av}} = 0.049$, $d \simeq 0.8$ Å.[6] Because the single-crystal data are still too preliminary to allow a detailed comparison with the theory developed here, I shall limit the discussion to a few brief remarks, which are based upon the limits for the value of Λ which I obtain in the small-q, q' limit, within the idealized oscillator model. The higher-energy peak has been observed with values of q' as high as $8\ \text{Å}^{-1}$. Therefore, incorporating the low-energy data, I have chosen $\rho = 3.2$ in Eq. (35), whence $\Lambda_S = 0.20\gamma$, and Eq. (49) reads $\Lambda = 0.20\gamma/\langle \sin^2 2\theta \rangle_{\text{av}} = 4.1\gamma$, where in the last equality the value 0.049 taken from the fits to the polycrystal data has been used. Recall that Λ is the ratio of the inelastic differential cross section of the high- to the low-energy experiments, assuming the first-excited-state doublet can be resolved. If this doublet is not resolved, the experimental ratio of inelastic cross sections should be compared with the quantity $2\Lambda = 8.2\gamma$. Since $\gamma = \hbar\omega/V_0$, if the first-excited state is tightly bound, it follows that $\gamma < \frac{2}{3}$. (If it is not tightly bound, the estimation procedure for Λ that was employed is invalid.) Experimentally, it may be possible to place lower bounds on γ, as well, since too small a value of γ would imply too many bound states. This, together with the experimental determination of the inelastic differential cross-section ratio, can test the validity of the small-$\vec{q}$ prediction for Λ, or possibly the model, itself, since it happens that Λ depends sensitively on the value of $\langle \sin^2 2\theta \rangle_{\text{av}}$ employed to fit the low-energy experiment. Unfortunately, because of the difficulties associated with the idealized oscillator model, as were discussed in Sec. II B, arguments based upon the precise value of γ lose some of their force. Also the small-$\vec{q}$ expansion introduces errors. Nevertheless, the results of the present analysis, together with the ongoing experiments,[7] may begin to impose some constraints on the model.

V. OUTLOOK

It is hoped that the general theory of neutron-induced transitions of a trapped proton from a tunnel split ground-state doublet to tightly-bound excited states developed here will find increasing application as the ongoing experiments on neutron scattering from hydrogen in metals come to completion and new experiments come on line.

Note added in proof. Since the high- and low-momentum transfer experiments are run under quite different conditions, quantitative comparison of the cross sections requires the solution of several difficult experimental problems in normalization. Hence, a reliable experimental estimate for the important quantity Λ has yet to be determined.[7]

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[11] That is, $a = (\frac{1}{4}|a_0|^2 + \frac{3}{4}|a_1|^2)\exp(-W)$, where $a_S = (m/\mu)a_S^F$, $S = 0,1$ a_0^F and a_1^F are the free-atom singlet and triplet low-energy s-wave nuclear scattering lengths and μ is the n-p reduced mass.