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COLLEGE OF ENGINEERING
Department of Nuclear Engineering

Technical Report

INVESTIGATION OF ATOMIC MOTION IN LIQUIDS USING THE MÖSSBAUER EFFECT

John F. Ullrich

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INTRODUCTION

The purpose of this paper is to investigate the use of the Mössbauer effect in studying atomic motion in liquid systems. In particular, the feasibility of performing an actual experiment is investigated.

The interest in studying the dynamics of atomic motion in liquids is of both a pure and applied nature. The results are of interest to the pure scientist because of the present lack of knowledge of the forces governing the interaction between atoms in the liquid state. This is due in part both to the lack of good experimental information because of the difficulty of performing interesting experiments to study the dynamics of atomic motion in liquids and to the complexity of doing any theoretical study of liquids. The results are of interest to the applied scientist because of the effects that can result from atomic motion. To the reactor physicist using liquid fuels or moderators, the effects of the atomic motion on the cross sections is no new problem.

In recent years, much experimental work has been carried out using neutron scattering techniques to study liquids. Even though essentially providing the same information about liquids, the Mössbauer effect seems to have several advantages over neutron scattering. First, the Mössbauer cross section can be expressed in terms of Van Hove's self correlation function¹ whereas for neutron scattering the cross section contains both the self correlation function and the pair correlation function. This makes the analysis of experimental results much easier. The Mössbauer cross section contains only the self correlation function due to the fact that the atom involved is

excited to an intermediate state and hence retains its identity while undergoing motion. Second, the resolution of Mössbauer experiments is much greater than that of neutron scattering experiments. Typically the resolution of a Mössbauer experiment might be of the order of 10^{-12} whereas a thermal neutron scattering experiment might be of the order of 10^{-1} . Third, the Mössbauer experiments are much easier to perform than neutron scattering experiments. The only real disadvantage to the Mössbauer technique is the fact that the momentum transfer is fixed whereas in neutron scattering experiments the momentum transfer is a variable.

Sections I and II of this paper are not really necessary for the development proposed since the usual starting point for calculations of the Mössbauer cross section is the cross section at the end of Section II. However, since the details of the derivation of this cross section are not presented in the literature, the development is instructive. In Section I, the transition probability is obtained from the time evolution operator for transitions through an intermediate state which does not have a well defined energy.² In Section II the Mössbauer scattering cross section is obtained for an arbitrary system of interacting particles.

The scattering cross section is extended further in Section III with recourse to the formalism developed by Van Hove¹ wherein the cross section is related to the atomic motion in the system by means of the self correlation function. The result is then applied to a particular experimental situation in which a Mössbauer source nuclide in the solid state is moved with respect to an identical absorber in the liquid state and the gamma ray

transmission through the absorber is observed as a function of the relative velocity. This so-called self-absorption cross section then is the experimentally measured cross section.

In Section IV, two models are proposed for the classical self diffusion function. The first is the continuous diffusion model of Vineyard.³ This model treats the atomic motion as that of continuously diffusing atoms. The second model is the quasi-crystalline model of Singwi and Sjölander.⁴ This model assumes liquid behavior is much like that of solids on a short time scale where the atoms undergo oscillations in a localized region before undergoing diffusion. The self-absorption cross section is determined for both of these models.

Section V is devoted to consideration of a real experiment using the Mössbauer nuclide Kr^{83} . This particular nuclide is chosen because of the interest in performing the experiment in a simple monatomic fluid. A numerical estimate of the resonance self-absorption is obtained and the possibility of carrying out the experiment is discussed.

SECTION I

DEVELOPMENT OF THE TRANSITION PROBABILITY

In order to develop a cross section describing the process of interest, it is first necessary to develop the probability for transition between the initial and final states. This section is devoted to the development of that transition probability.

Formally, the transition probability can be written in terms of a time evolution operator as

$$T_{n'n} = |U_{n'n}(t)|^2/t \quad (1.1)$$

where under certain circumstances $T_{n'n}$ can be interpreted as the probability per unit time for small times of transition from state n to state n' . $U_{n'n}(t)$ is the time evolution operator for the system and is given by

$$U_{n'n}(t) = (e^{-iH t/\hbar})_{n'n} \quad (1.2)$$

where H , the Hamiltonian for the entire system, can be written as

$$H = H_0 + V \quad (1.3)$$

The Hamiltonian is separated such that the eigenvalue problem

$$H_0 |n\rangle = E_n |n\rangle \quad (1.4)$$

can be solved. Hence the states of the system, n and n' , are eigenfunctions of H_0 .

The familiar second order perturbation theory technique cannot be used to obtain $U_{n'n}(t)$ since the intermediate state of the system does not have a well defined energy due to its finite lifetime. Hence the time evolution operator must be obtained in a different manner.

To begin with, a new function, $G(z)$, the Laplace transform of $U(t)$, is introduced, or

$$\begin{aligned}
 G(z) &= \int_0^{\infty} e^{-t/\hbar} z U(t) \frac{dt}{\hbar} \\
 &= \int_0^{\infty} e^{-t/\hbar} z e^{-i t/\hbar} H \frac{dt}{\hbar} \\
 &= \int_0^{\infty} e^{-t/\hbar(z+iH)} \frac{dt}{\hbar} \tag{1.5}
 \end{aligned}$$

or

$$G(z) = \frac{1}{z+iH} \tag{1.6}$$

and

$$G_{n'n}(z) = \left(\frac{1}{z+iH} \right)_{n'n} \tag{1.7}$$

$U(t)$ is then the inverse Laplace transform of $G(z)$, so it can be written

$$U(t) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar} z G(z) dz \tag{1.8}$$

and

$$U_{n'n}(t) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar} z \left(\frac{1}{z+iH} \right)_{n'n} dz \tag{1.9}$$

$U_{n'n}(t)$ is the function ultimately desired to calculate the transition probability. To obtain this, it is first necessary to obtain (1.7) so that (1.9) may be used to calculate $U_{n'n}(t)$. Now from (1.6) and (1.3),

$$G(z) = (z+iH_0+iV)^{-1}$$

so

$$(z+iH_0+iV)G(z) = 1$$

In matrix form

$$\sum_{n''} (z+iH_0+iV)_{n'n''} G_{n''n}(z) = \delta_{n'n} . \quad (1.10)$$

It is necessary to obtain both the diagonal and off diagonal elements of G . First, to obtain the diagonal elements of G , consider $n' = n$ in (1.10).

Thus

$$\sum_{n''} (z+iH_0+iV)_{n'n''} G_{n''n'} = 1 . \quad (1.11)$$

Splitting the sum in (1.11) into two parts, for $n'' = n'$ and $n'' \neq n'$,

$$(z+iH_0+iV)_{n'n'} G_{n'n'} + \sum_{n'' \neq n'} (z+iH_0+iV)_{n'n''} G_{n''n'} = 1 . \quad (1.12)$$

Now define a new function Q relating the off diagonal elements of G to the diagonal elements of G , or

$$G_{n''n'} = G_{n''n} Q_{n''n'} G_{n'n'} \quad (1.13)$$

so (1.12) becomes

$$(z+iH_0+iV)_{n'n'} G_{n'n'} + \sum_{n'' \neq n'} (z+iH_0+iV)_{n'n''} G_{n''n} Q_{n''n'} G_{n'n'} = 1 . \quad (1.14)$$

However, z is diagonalized in the representation as well as H_0 , as defined in (1.4), so

$$\left(z+iE_{n'}+iV_{n'n'} + i \sum_{n'' \neq n'} V_{n'n''} G_{n''n''} Q_{n''n'} \right) G_{n'n'} = 1 . \quad (1.15)$$

Define a new function $\gamma_{n'}$, by

$$\frac{i\hbar}{2} \gamma_{n'} = iV_{n'n'} + i \sum_{n'' \neq n'} V_{n'n''} G_{n''n''} Q_{n''n'} \quad (1.16)$$

and

$$\left(z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'} \right) G_{n'n'} = 1$$

or

$$G_{n'n'} = \frac{1}{z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'}} . \quad (1.17)$$

Next, to obtain the off diagonal elements of G , consider $n' \neq n$ in (1.10). Dividing the sum in (1.10) into two parts, for $n'' = n'$ and $n'' \neq n'$,

$$(z+iH_0+iV)_{n'n'} G_{n'n'} + \sum_{n'' \neq n'} (z+iH_0+iV)_{n'n''} G_{n''n'} = 0$$

or

$$(z+iE_{n'}+iV_{n'n'}) G_{n'n'} + i \sum_{n'' \neq n'} V_{n'n''} G_{n''n'} = 0 . \quad (1.18)$$

Dividing the sum in the last term in (1.18) into two parts, for $n'' = n$ and $n'' \neq n$,

$$(z+iE_{n'}+iV_{n'n'}) G_{n'n'} + iV_{n'n} G_{nn} + i \sum_{n'' \neq n', n} V_{n'n''} G_{n''n'} = 0 .$$

Using (1.13),

$$(z+iE_{n'}+iV_{n'n'})G_{n'n'}Q_{n'n}G_{nn}+iV_{n'n}G_{nn}+i\sum_{n''\neq n',n}V_{n'n}G_{n''n}Q_{n''n}G_{nn}=0. \quad (1.19)$$

Using (1.15) in (1.19)

$$\left(1-i\sum_{n''\neq n'}V_{n'n}G_{n''n}Q_{n''n}G_{n'n'}\right)Q_{n'n}+iV_{n'n}+i\sum_{n''\neq n',n}V_{n'n}G_{n''n}Q_{n''n}=0.$$

Hence

$$Q_{n'n}=-iV_{n'n}-i\sum_{n''\neq n',n}V_{n'n}G_{n''n}Q_{n''n}+i\sum_{n''\neq n'}V_{n'n}G_{n''n}Q_{n''n}G_{n'n'}Q_{n'n} \quad (1.20)$$

and the off diagonal elements of Q are related to the diagonal elements of G.

To this point the calculation is exact, however to proceed further, some approximations must be made. To obtain the diagonal elements of G from (1.17), (1.16) must be used to obtain $\gamma_{n'}$. Now

$$\frac{i\hbar}{2}\gamma_{n'}=iV_{n'n'}+i\sum_{n''\neq n'}V_{n'n}G_{n''n}Q_{n''n'}. \quad (1.21)$$

Using (1.17) in (1.21),

$$\frac{i\hbar}{2}\gamma_{n'}=iV_{n'n'}+i\sum_{n''\neq n'}\frac{V_{n'n}Q_{n''n'}}{z+iE_{n''}+\frac{i\hbar}{2}\gamma_{n''}}.$$

To solve this equation for $\gamma_{n'}$, an iterative procedure is used. As the first iterate, take $\gamma_{n''}=0$ so

$$\frac{i\hbar}{2}\gamma_{n'}\simeq iV_{n'n'}+i\sum_{n''\neq n'}\frac{V_{n'n}Q_{n''n'}}{z+iE_{n''}}. \quad (1.22)$$

Now, to obtain the off diagonal elements of Q from (1.20), consider only the terms with powers of V through V^2 . To a first approximation the diagonal elements of G are independent of V so (1.20) becomes

$$Q_{n',n} = -iV_{n',n} - i \sum_{n'' \neq n', n} V_{n',n''} G_{n''n''} Q_{n''n''} + \mathcal{O}(V^3) .$$

To solve this equation for $Q_{n',n}$, an iterative procedure is used. As the first iterate, take $Q_{n''n''} = -iV_{n''n''}$ so

$$Q_{n',n} \simeq -iV_{n',n} - \sum_{n'' \neq n', n} V_{n',n''} G_{n''n''} V_{n''n''} . \quad (1.23)$$

Also using the first iterate for $Q_{n''n''}$, in (1.22)

$$\frac{i\hbar}{2} \gamma_{n'} \simeq iV_{n'n'} + \sum_{n'' \neq n'} \frac{V_{n'n''} V_{n''n'}}{z + iE_{n''}} . \quad (1.24)$$

This then is the first approximation to $\gamma_{n'}$ which also gives a first approximation to the diagonal elements of G in (1.17). Using the approximation to the diagonal elements of G in (1.23)

$$Q_{n',n} \simeq -iV_{n',n} - \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{z + iE_{n''} + \frac{i\hbar}{2} \gamma_{n''}} . \quad (1.25)$$

Since the off diagonal elements of G are related to the off diagonal elements of Q by (1.13)

$$G_{n'n} = G_{n'n'} Q_{n'n} G_{nn}$$

and with the use of (1.17) and (1.25)

$$\begin{aligned}
G_{n'n} &= \left(\frac{1}{z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'}} \right) \left(-iV_{n'n} - \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{z+iE_{n''} + \frac{i\hbar}{2} \gamma_{n''}} \right) \left(\frac{1}{z+iE_n + \frac{i\hbar}{2} \gamma_n} \right) \\
&= \frac{-iV_{n'n}}{\left(z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'} \right) \left(z+iE_n + \frac{i\hbar}{2} \gamma_n \right)} \\
&\quad - \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{\left(z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'} \right) \left(z+iE_{n''} + \frac{i\hbar}{2} \gamma_{n''} \right) \left(z+iE_n + \frac{i\hbar}{2} \gamma_n \right)} \\
&= G_{n'n}^{(1)} + G_{n'n}^{(2)} \tag{1.26}
\end{aligned}$$

$G_{n'n}^{(1)}$ takes account of all direct processes between the initial and final states. $G_{n'n}^{(2)}$ accounts for transitions between the initial and final states which pass through an intermediate state. Nuclear resonance scattering and absorption are processes passing through an intermediate state. Hence, only $G_{n'n}^{(2)}$ is necessary in calculating the transition probability for these particular processes.

To obtain the time evolution operator, use (1.9) so

$$\begin{aligned}
U_{n'n}^{(2)}(t) &= \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} G_{n'n}^{(2)}(z) dz \\
&= \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{\left(z+iE_{n'} + \frac{i\hbar}{2} \gamma_{n'} \right) \left(z+iE_{n''} + \frac{i\hbar}{2} \gamma_{n''} \right) \left(z+iE_n + \frac{i\hbar}{2} \gamma_n \right)} dz .
\end{aligned} \tag{1.27}$$

For the Mössbauer effect, the initial and final states of the nucleus are ground states with essentially infinite lifetimes. Under this condition,

and assuming no contributions to γ from the center of mass motion of the nucleus, $\gamma_{n'} = \gamma_n = 0$ and (1.27) becomes

$$U_{n'n}^{(2)}(t) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{(z+iE_{n'}) (z+iE_{n''} + \frac{i\hbar}{2} \gamma_{n''}) (z+iE_n)} dz \quad (1.28)$$

Equation (1.28) is the inverse Laplace transform of a product of two functions or

$$U_{n'n}^{(2)}(t) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} \bar{f}_{n'n}(z) \bar{g}_{n'n}(z) dz \quad (1.29)$$

where

$$\bar{f}_{n'n}(z) = \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{(z+iE_{n''} + \frac{i\hbar}{2} \gamma_{n''})} \quad (1.30)$$

$$\bar{g}_{n'n}(z) = \frac{1}{(z+iE_{n'}) (z+iE_n)} \quad (1.31)$$

Equation (1.31) can be rewritten as

$$\begin{aligned} \bar{g}_{n'n}(z) &= \frac{i}{E_{n'} - E_n} \left[\frac{1}{z+iE_{n'}} - \frac{1}{z+iE_n} \right] \\ &= \frac{i}{E_{n'} - E_n} \left[\bar{g}_{n'n}^{-(1)}(z) - \bar{g}_{n'n}^{-(2)}(z) \right] \end{aligned}$$

Hence (1.29) becomes

$$\begin{aligned} U_{n'n}^{(2)}(t) &= \left(\frac{i}{E_{n'} - E_n} \right) \left\{ \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} \bar{f}_{n'n}(z) \bar{g}_{n'n}^{-(1)}(z) dz \right. \\ &\quad \left. - \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{+t/\hbar z} \bar{f}_{n'n}(z) \bar{g}_{n'n}^{-(2)}(z) dz \right\} \quad (1.32) \end{aligned}$$

By applying the Laplace transform convolution theorem which can be written as⁵

$$\mathcal{L}^{-1}[\mathcal{L}[f]\mathcal{L}[g]] = \int_0^t f(u)g(t-u)du$$

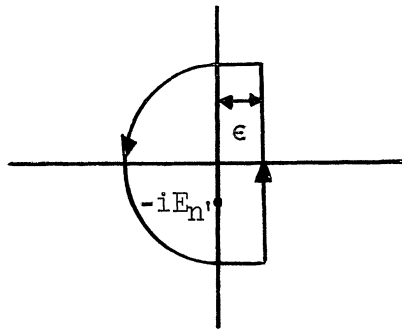
(1.32) becomes

$$U_{n'n}^{(2)}(t) = \left(\frac{i}{E_{n'} - E_n} \right) \left\{ \int_0^t f_{n'n}(u) g_{n'n}^{(1)}(t-u) du / \hbar - \int_0^t f_{n'n}(u) g_{n'n}^{(2)}(t-u) du / \hbar \right\} . \quad (1.33)$$

Taking the inverse Laplace transform of $g_{n'n}^{(1)}(z)$,

$$g_{n'n}^{(1)}(t-u) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} \frac{e^{(t-u)/\hbar z}}{z+iE_{n'}} dz .$$

To evaluate this, take the contour integral on the following path:



Hence,

$$g_{n'n}^{(1)}(t-u) = \frac{i}{2\pi i} \left[\oint \frac{e^{(t-u)/\hbar z}}{z+iE_{n'}} dz - \oint \frac{e^{(t-u)/\hbar z}}{z+iE_{n'}} dz \right] .$$

This path was chosen so that the real part of $(t-u)/\hbar z$ is negative for $t > u$.

Thus for $|z|$ large, the second term will go to zero and

$$g_{n'n}^{(1)}(t-u) = \frac{1}{2\pi i} \oint \frac{e^{(t-u)/\hbar z}}{z+iE_{n'}} .$$

Evaluating the integral by residues

$$g_{n'n}^{(1)}(t-u) = \frac{1}{2\pi i} \left[2\pi i \operatorname{Res} \left(\frac{e^{(t-u)/\hbar z}}{z+iE_{n'}} , -iE_{n'} \right) \right]$$

$$g_{n'n}^{(1)}(t-u) = e^{-iE_{n'}(t-u)/\hbar} \quad t > u . \quad (1.34)$$

The integral for $g_{n'n}^{(2)}(t-u)$ can be carried out in a similar manner and

$$g_{n'n}^{(2)}(t-u) = e^{-iE_n(t-u)/\hbar} \quad t > u . \quad (1.35)$$

Using (1.34) and (1.35) in (1.33),

$$U_{n'n}^{(2)}(t) = \left(\frac{i}{E_{n'} - E_n} \right) \left\{ \int_0^t f_{n'n}(u) e^{-iE_{n'}(t-u)/\hbar} \frac{du}{\hbar} \right. \\ \left. - \int_0^t f_{n'n}(u) e^{-iE_n(t-u)/\hbar} \frac{du}{\hbar} \right\}$$

$$= \left(\frac{i}{E_{n'} - E_n} \right) \left\{ e^{-iE_{n'} t/\hbar} \int_0^t f_{n'n}(u) e^{iE_{n'} u/\hbar} \frac{du}{\hbar} \right. \\ \left. - e^{-iE_n t/\hbar} \int_0^t f_{n'n}(u) e^{iE_n u/\hbar} \frac{du}{\hbar} \right\} . \quad (1.36)$$

If (1.36) is taken in the limit as $t \rightarrow \infty$, the integrals simply become the Laplace transforms of $f_{n'n}(u)$ which are already known from (1.30). Physically this limit corresponds to observation of the process at large times (large with respect to the decay time of the intermediate state) when the process has been completed. Taking this limit

$$\lim_{t \rightarrow \infty} U_{n'n}^{(2)}(t) = \lim_{t \rightarrow \infty} \left(\frac{i}{E_{n'} - E_n} \right) \left\{ e^{-iE_{n'} t/\hbar} f_{n'n}(-iE_{n'}) - e^{-iE_n t/\hbar} f_{n'n}(-iE_n) \right\} . \quad (1.37)$$

Taking this same limit for the transition probability in (1.1) and using (1.37)

$$\begin{aligned}
T_{n'n} &= \lim_{t \rightarrow \infty} \frac{|U_{n'n}^{(2)}(t)|^2}{t} \\
&= \lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} \left| e^{-iE_{n'} t/\hbar} \bar{f}_{n'n}(-iE_{n'}) - e^{-iE_n t/\hbar} \bar{f}_{n'n}(-iE_n) \right|^2 .
\end{aligned} \tag{1.38}$$

Expanding $\bar{f}_{n'n}(-iE_{n'})$ about $-iE_n$ in a Taylor series

$$\bar{f}_{n'n}(-iE_{n'}) = \bar{f}_{n'n}(-iE_n) + (-iE_{n'} + iE_n) \bar{f}'_{n'n}(-iE_n) + \dots \tag{1.39}$$

Using (1.39) in (1.38)

$$\begin{aligned}
T_{n'n} &= \lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} \left| \bar{f}_{n'n}(-iE_n) (e^{-iE_{n'} t/\hbar} - e^{-iE_n t/\hbar}) \right. \\
&\quad \left. + (-iE_{n'} + iE_n) \bar{f}'_{n'n}(-iE_n) e^{-iE_n t/\hbar} + \dots \right|^2 .
\end{aligned} \tag{1.40}$$

Taking the absolute square in (1.40)

$$\begin{aligned}
T_{n'n} &= \lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} \left\{ |\bar{f}_{n'n}(-iE_n)|^2 |e^{-iE_{n'} t/\hbar} - e^{-iE_n t/\hbar}|^2 \right. \\
&\quad + \bar{f}_{n'n}(-iE_n) (e^{-iE_{n'} t/\hbar} - e^{-iE_n t/\hbar}) (-iE_{n'} + iE_n) \bar{f}'_{n'n}(-iE_n) e^{-iE_n t/\hbar} \\
&\quad \left. + (E_{n'} - E_n)^2 |\bar{f}'_{n'n}(-iE_n)|^2 + \dots \right\} .
\end{aligned} \tag{1.41}$$

Considering (1.41) in the limit as $t \rightarrow \infty$, the third term on the right as well as all other terms of higher order derivatives and cross terms will go to zero since these terms $\sim 1/t$. The second term $\sim 1/t(E_{n'} - E_n)$ which goes to zero for $t \rightarrow \infty$ except when $E_{n'} = E_n$. However, when $E_{n'} = E_n$, the term will again go to zero because of the first exponential factor. Hence the only

term which does not vanish in the limit as $t \rightarrow \infty$ is the first, so

$$T_{n'n} = \lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} |\bar{f}_{n'n}(-iE_n)|^2 |e^{-iE_{n'} t/\hbar} - e^{-iE_n t/\hbar}|^2 \quad (1.42)$$

Using (1.30) in (1.42)

$$T_{n'n} = \lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} \left| \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{(-iE_n + iE_{n''} + \frac{i\hbar}{2} \gamma_{n''}(-iE_n))} \right|^2$$

(x) $|e^{-iE_{n'} t/\hbar} - e^{-iE_n t/\hbar}|^2$

$$T_{n'n} = \left| \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{(-iE_n + iE_{n''} + \frac{i\hbar}{2} \gamma_{n''}(-iE_n))} \right|^2$$

(x) $\lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} |e^{-i(E_{n'} - E_n) t/\hbar} - 1|^2 \quad (1.43)$

Letting $\omega_{n'n} = E_{n'} - E_n/\hbar$,

$$\lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} |e^{-i(E_{n'} - E_n) t/\hbar} - 1|^2 = \lim_{t \rightarrow \infty} \frac{1}{\hbar^2 \omega_{n'n}^2} |\cos \omega_{n'n} t - i \sin \omega_{n'n} t - 1|^2$$

$$= \lim_{t \rightarrow \infty} \frac{1}{\hbar^2 \omega_{n'n}^2} (2 - 2 \cos \omega_{n'n} t)$$

$$= \lim_{t \rightarrow \infty} \frac{1}{\hbar^2 \omega_{n'n}^2} \cdot 4 \sin^2 \frac{\omega_{n'n} t}{2} \quad (1.44)$$

The Dirac delta function can be written in the Fourier representation as

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk \quad (1.44.5)$$

$$= \frac{1}{2\pi} \left[\int_0^{\infty} e^{ikx} dk + \int_0^{\infty} e^{-ikx} dk \right]$$

$$\begin{aligned}
\delta(x) &= \frac{1}{\pi} \lim_{t \rightarrow \infty} \int_0^t \cos kx \, dk \\
&= \frac{1}{\pi x} \lim_{t \rightarrow \infty} \sin tx \quad (1.45)
\end{aligned}$$

Making use of the delta function in (1.44)

$$\begin{aligned}
\lim_{t \rightarrow \infty} \frac{1}{t(E_{n'} - E_n)^2} |e^{-i(E_{n'} - E_n) t/\hbar} - 1|^2 &= \frac{2\pi}{\hbar^2} \lim_{t \rightarrow \infty} \left(\frac{1}{\pi \frac{\omega_{n'n}}{2}} \sin \frac{\omega_{n'n}}{2} t \right) \left(\frac{\sin \frac{\omega_{n'n}}{2} t}{\omega_{n'n} t} \right) \\
&= \frac{2\pi}{\hbar^2} \delta\left(\frac{\omega_{n'n}}{2}\right) \frac{1}{2} .
\end{aligned}$$

This can be written as a delta function in energy since

$$\delta\left(\frac{\omega_{n'n}}{2}\right) d\left(\frac{\omega_{n'n}}{2}\right) = \delta(E_{n'} - E_n) d(E_{n'})$$

or

$$\delta\left(\frac{\omega_{n'n}}{2}\right) = 2\hbar \delta(E_{n'} - E_n) .$$

Thus (1.43) becomes

$$T_{n'n} = \frac{2\pi}{\hbar} \left| \sum_{n'' \neq n', n} \frac{V_{n'n''} V_{n''n}}{(iE_{n''} - iE_n + \frac{i\hbar}{2} \gamma_{n''}(-iE_n))} \right|^2 \delta(E_{n'} - E_n) \quad (1.46)$$

where $i\hbar/2 \gamma_{n''}(-iE_n)$ is given by (1.24) as

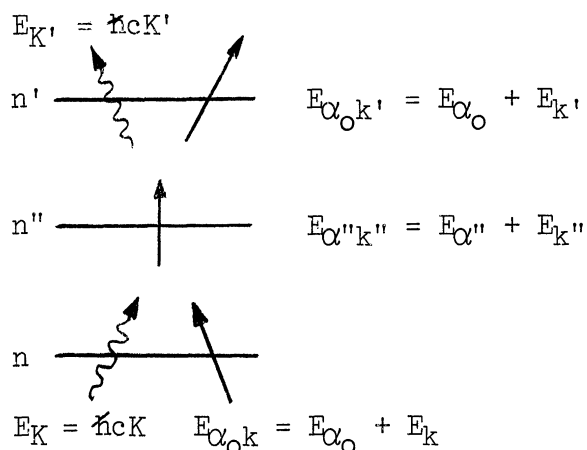
$$\begin{aligned}
\frac{i\hbar}{2} \gamma_{n''}(-iE_n) &\simeq iV_{n'n''} + \sum_{n''' \neq n''} \frac{V_{n'n''} V_{n''n'''}}{-iE_n + iE_{n''}} \\
\frac{i\hbar}{2} \gamma_{n''}(-iE_n) &= iV_{n'n''} + i \sum_{n''' \neq n'} \frac{V_{n'n''} V_{n''n'''}}{E_n - E_{n''}} . \quad (1.47)
\end{aligned}$$

Equations (1.46) and (1.47) will serve as the starting point for calculations of the cross section for nuclear resonance scattering and absorption.

SECTION II

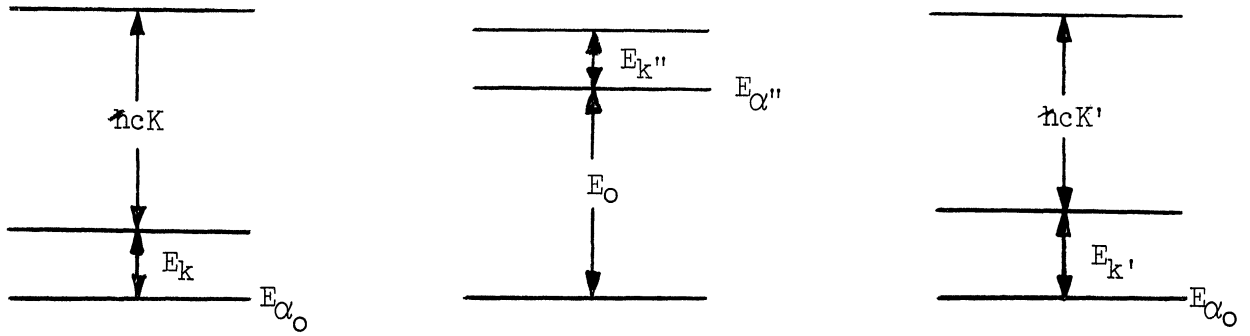
CROSS SECTION FOR NUCLEAR RESONANCE SCATTERING

In this section, the results of Section I will be applied to the calculation of the cross section for nuclear resonance scattering. Schematically, the initial, intermediate, and final states of the process can be represented as follows:



The initial state consists of a photon of momentum $\hbar \underline{K}$ and a nucleus in a state $\alpha_0 k$ where α_0 is a set of numbers characterizing the nucleus in the ground state and k is a set of numbers characterizing the state of the center of mass motion of the nucleus. The intermediate state consists of a nucleus in a state $\alpha'' k''$ where α'' is a set of numbers characterizing the excited state of the nucleus and k'' is again the state of the center of mass motion. In the final state there is a photon of momentum $\hbar \underline{K}'$ and a nucleus again in the ground state α_0 with k' the state of the center of mass motion.

On an energy scale, the three states appear as follows:



To proceed to any calculation, it is first necessary to write the Hamiltonian for the system. For nuclear resonance scattering, the non-relativistic Hamiltonian for the entire system can be written

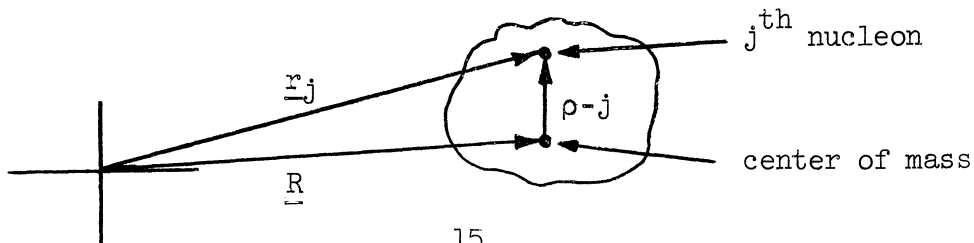
$$H = \int d^3r \frac{E^2 + H^2}{8\pi} + \sum_j \frac{\left(\underline{p}_j - \frac{e_j}{c} \underline{A}(\underline{r}_j) \right)^2}{2m_j} + H^{S'} + H^{N'} \quad (2.1)$$

where: $\int d^3r \frac{E^2 + H^2}{8\pi}$ is the energy of the free electromagnetic field; $\frac{(\underline{p}_j - e_j/c \underline{A}(\underline{r}_j))^2}{2m_j}$ is the kinetic energy of the j^{th} nucleon in the electromagnetic field; $H^{S'}$ describes the interaction between the nuclei in the crystal; and $H^{N'}$ describes the interaction between the nucleons in each nucleus.

The second term in (2.1) can be rewritten as follows:

$$\sum_j \frac{\left(\underline{p}_j - \frac{e_j}{c} \underline{A}(\underline{r}_j) \right)^2}{2m_j} = \sum_j \left\{ \frac{p_j^2}{2m_j} - \frac{e_j}{2m_j c} (\underline{p}_j \cdot \underline{A}(\underline{r}_j) + \underline{A}(\underline{r}_j) \cdot \underline{p}_j) + \frac{e_j^2}{2m_j c^2} A^2(\underline{r}_j) \right\}. \quad (2.2)$$

The coordinates describing the individual nucleons can be written in terms of a center of mass coordinate and a relative coordinate, or



Hence

$$\underline{r}_j = \underline{\rho}_j + \underline{R} \quad (2.3)$$

and also by taking derivatives

$$\dot{\underline{r}}_j = \dot{\underline{\rho}}_j + \dot{\underline{R}}$$

so

$$m_j \dot{\underline{r}}_j = m_j \dot{\underline{\rho}}_j + m_j \dot{\underline{R}}$$

which can be written

$$\underline{p}_j = \underline{\pi}_j + m_j \dot{\underline{R}} \quad (2.4)$$

where $\underline{p}_j \equiv m_j \dot{\underline{r}}_j$ and $\underline{\pi}_j \equiv m_j \dot{\underline{\rho}}_j$. Using (2.4) in the first term in (2.2)

$$\begin{aligned} \sum_j \frac{p_j^2}{2m_j} &= \sum_j \frac{(\underline{\pi}_j + m_j \dot{\underline{R}})^2}{2m_j} \\ &= \sum_j \left(\frac{\pi_j^2}{2m_j} + \frac{1}{2} m_j \dot{\underline{R}}^2 + \underline{\pi}_j \cdot \dot{\underline{R}} \right) . \end{aligned}$$

Now the total mass of the nucleus $M = \sum_j m_j$ and $\underline{P} \equiv M \dot{\underline{R}}$ so

$$\sum_j \frac{p_j^2}{2m_j} = \sum_j \frac{\pi_j^2}{2m_j} + \frac{P^2}{2M} + \sum_j \underline{\pi}_j \cdot \dot{\underline{R}} .$$

The center of mass coordinate is defined by

$$\underline{R} = \frac{\sum_j m_j \underline{r}_j}{M}$$

so $\sum_j \underline{\pi}_j$ is by definition equal to zero, and

$$\sum_j \frac{p_j^2}{2m_j} = \sum_j \frac{\pi_j^2}{2m_j} + \frac{P^2}{2M} . \quad (2.5)$$

Using (2.5) in (2.2)

$$\sum_j \frac{\left(\underline{p}_j - \frac{e_j}{c} \underline{A}(\underline{r}_j) \right)^2}{2m_j} = \sum_j \frac{\pi_j^2}{2m_j} + \frac{P^2}{2M} - \sum_j \frac{e_j}{2m_j c} (\underline{p}_j \cdot \underline{A}(\underline{r}_j) + \underline{A}(\underline{r}_j) \cdot \underline{p}_j) \\ + \sum_j \frac{e_j^2}{2m_j c^2} A^2(\underline{r}_j) .$$

Since the vector potential \underline{A} is gauge invariant, we can choose \underline{A} such that $\underline{\nabla} \cdot \underline{A} = 0$. Hence the operators \underline{p}_j and \underline{A} will commute under scalar multiplication. The term quadratic in the vector potential describes two photon processes. For nuclear resonance scattering with an intermediate state, the excitation and decay are just single photon processes, hence there are no non-vanishing contributions from the term quadratic in the vector potential between the initial and intermediate and intermediate and final states. Neglecting this term, (2.1) becomes

$$H = \int d^3r \frac{E^2 + H^2}{8\pi} + \frac{P^2}{2M} + H^{S'} + \sum_j \frac{\pi_j^2}{2m_j} + H^{N'} \\ - \sum_j \frac{e_j}{m_j c} \underline{A}(\underline{r}_j) \cdot \underline{p}_j .$$

Define:

$$H^S \equiv \frac{P^2}{2M} + H^{S'} \quad - \text{the Hamiltonian for the system;}$$

$$H^N \equiv \sum_j \frac{\pi_j^2}{2m_j} + H^{N'} \quad - \text{the Hamiltonian for the nucleus;}$$

$$H^\gamma \equiv \int d^3r \frac{E^2 + H^2}{8\pi} \quad - \text{the Hamiltonian for the electromagnetic field;}$$

and

$$H = H^\gamma + H^S + H^N - \sum_j \frac{e_j}{m_j c} \underline{A}(\underline{r}_j) \cdot \underline{p}_j . \quad (2.6)$$

To use the formalism of Section I, H must be separated into H_0 and V where H_0 is chosen such that $H_0|n\rangle = E_n|n\rangle$ can be solved. Since H^S , H^N , and H^γ satisfy the following eigenvalue problems

$$H^S|k\rangle = E_k|k\rangle \quad (2.7)$$

$$H^N|\alpha\rangle = E_\alpha|\alpha\rangle \quad (2.8)$$

$$H^\gamma|\eta_K\rangle = \eta_K \hbar c K |\eta_K\rangle \quad (2.9)$$

choose

$$H_0 = H^S + H^N + H^\gamma \quad (2.10)$$

Since the Hamiltonian H_0 is written as the sum of three terms (2.10) which act on coordinates independently, the eigenfunctions of H_0 can be written as the product of the eigenfunctions of (2.7), (2.8), and (2.9) and

$$H_0|\alpha k \eta_K\rangle = (E_\alpha + E_k + \eta_K \hbar c K) |\alpha k \eta_K\rangle \quad .$$

Hence,

$$V = - \sum_j \frac{e_j}{m_j c} \underline{A}(\underline{r}_j) \cdot \underline{p}_j \quad (2.11)$$

To calculate the matrix elements of V , the quantum mechanical operator corresponding to \underline{A} must be used. One such representation for \underline{A} can be obtained by expanding in terms of plane waves normalized in a large box of volume L^3 . The coefficients are chosen so that \underline{A} satisfies the free space Maxwell equations and the gauge condition $\underline{\nabla} \cdot \underline{A} = 0$. With this expansion

$$\underline{A}(\underline{r}_j) = \sum_{\lambda \kappa} \sqrt{\frac{2\pi \hbar c}{L^3 \kappa}} E^{-i\kappa \cdot \underline{r}_j} (a_\lambda^\dagger(\kappa) \underline{\epsilon}_\lambda(\kappa) + a_\lambda(-\kappa) \underline{\epsilon}_\lambda(-\kappa)) \quad (2.12)$$

where $a_\lambda^\dagger(\kappa)$ acts as a creation operator and $a_\lambda(-\kappa)$ acts as an annihilation operator or

$$a_{\lambda}^{\dagger}(\underline{\kappa}) |0_{K'\lambda'}\rangle = \delta_{\kappa K'} \delta_{\lambda \lambda'} |1_{K'\lambda'}\rangle$$

$$a_{\lambda}(-\underline{\kappa}) |1_{K'\lambda'}\rangle = \delta_{\kappa K'} \delta_{\lambda \lambda'} |0_{K'\lambda'}\rangle$$

and $\underline{\epsilon}_{\lambda}(\underline{\kappa})$ and $\underline{\epsilon}_{\lambda}(-\underline{\kappa})$ are unit polarization vectors with polarization state λ . The polarization vectors for the two polarization states form a triplet of orthogonal vectors with $\hat{\underline{\kappa}}$, or

$$\underline{\epsilon}_1(\underline{\kappa}) \cdot \underline{\kappa} = \underline{\epsilon}_2(\underline{\kappa}) \cdot \underline{\kappa} = \underline{\epsilon}_1(\underline{\kappa}) \cdot \underline{\epsilon}_2(\underline{\kappa}) = 0 .$$

With (2.12), (2.11) now becomes

$$V = - \sum_j \frac{e_j}{m_j c} \sum_{\lambda \kappa} \sqrt{\frac{2\pi \hbar c}{L^3 \kappa}} e^{-i\underline{\kappa} \cdot \underline{r}_j} \underline{\xi}_{\lambda}(\underline{\kappa}) \cdot \underline{p}_j \quad (2.13)$$

where

$$\underline{\xi}_{\lambda}(\underline{\kappa}) = a_{\lambda}^{\dagger}(\underline{\kappa}) \underline{\epsilon}_{\lambda}(\underline{\kappa}) + a_{\lambda}(-\underline{\kappa}) \underline{\epsilon}_{\lambda}(-\underline{\kappa}) .$$

Using (2.3) and (2.4) in (2.13)

$$\begin{aligned} V &= - \sum_j \frac{e_j}{m_j c} \sum_{\lambda \kappa} \sqrt{\frac{2\pi \hbar c}{L^3 \kappa}} e^{-i\underline{\kappa} \cdot \underline{\rho}_j} e^{-i\underline{\kappa} \cdot \underline{R}} \underline{\xi}_{\lambda}(\underline{\kappa}) \cdot \left(\underline{\pi}_j + \frac{m_j}{M} \underline{P} \right) \\ &= - \sum_{\lambda \kappa} \sqrt{\frac{2\pi \hbar c}{L^3 \kappa}} e^{-i\underline{\kappa} \cdot \underline{R}} \left[\sum_j \frac{e_j}{m_j c} e^{-i\underline{\kappa} \cdot \underline{\rho}_j} \underline{\xi}_{\lambda}(\underline{\kappa}) \cdot \underline{\pi}_j \right. \\ &\quad \left. + \underline{\xi}_{\lambda}(\underline{\kappa}) \cdot \underline{P} \sum_j \frac{e_j}{M c} e^{-i\underline{\kappa} \cdot \underline{\rho}_j} \right] . \end{aligned} \quad (2.14)$$

The first term in (2.14) contains only relative coordinates and represents the effect of the internal motion of the nucleus. The second term represents the radiative effects due to the center of mass motion of the entire nucleus. It has been demonstrated by Frauenfelder⁶ that the matrix elements of the first term are of the order of 10^5 greater than the matrix elements of the second term. Hence, the second term can be neglected and

$$V \simeq -\sum_{\lambda \kappa} \sqrt{\frac{2\pi\hbar c}{L^3 \kappa}} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_j \frac{e_j}{m_j c} e^{-i\mathbf{k}\cdot\mathbf{r}_j} \underline{\underline{\epsilon}}_{\lambda}(\underline{\underline{\kappa}}) \cdot \underline{\underline{\pi}}_j \quad (2.15)$$

For the nuclear resonance scattering the transition probability can be written as in (1.46), so

$$T_{\alpha_0 k' K' \lambda', \alpha_0 k K \lambda} \simeq \frac{2\pi}{\hbar} \left| \sum_{\alpha'' k'' = \alpha_0 k', \alpha_0 k} \frac{V_{\alpha_0 k' K' \lambda', \alpha'' k''} V_{\alpha'' k'', \alpha_0 k K \lambda}}{E_{\alpha''} + E_{k''} - E_{\alpha_0} - E_k - \hbar c K} + \frac{\hbar}{2} \gamma_{\alpha'' k''} \right| \quad (2.16)$$

(x) $\delta(E/\alpha_0 + E_k + \hbar c K' - E/\alpha_0 - E_k - \hbar c K)$

and $\gamma_{\alpha'' k''}$ can be written as in (1.47), or

$$\frac{\hbar}{2} \gamma_{\alpha'' k''} \simeq V_{\alpha'' k'', \alpha'' k''} + \sum_{n''' = \alpha'' k''} \frac{V_{\alpha'' k'', n'''} V_{n''', \alpha'' k''}}{(E_{\alpha_0} + E_k + \hbar c K - E_{n'''})} \quad (2.17)$$

To evaluate the transition probability, it is first necessary to evaluate the function $\gamma_{\alpha'' k''}$. This function can be written as the sum of two terms; a real term $S_{\alpha'' k''}$ which contributes a shift in energy and an imaginary term $-i/2 \Gamma_{\alpha'' k''}$ which contributes a certain energy width. It is this width term which is of interest in the present problem. So

$$\frac{\hbar}{2} \gamma_{\alpha'' k''} = S_{\alpha'' k''} - \frac{i}{2} \Gamma_{\alpha'' k''} \quad (2.18)$$

To obtain the width function, consider the evaluation of the second term in (2.17).

There will be one contribution from this term for states n''' like the initial or the final states since it is known that (2.15) will have non-vanishing matrix elements for this transition. Hence

$$\begin{aligned}
\Sigma^\gamma &= \sum_{\substack{n'' = \alpha''k'' \\ n'' \text{ like initial state}}} \frac{V_{\alpha''k'', n''} V_{n'', \alpha''k''}}{(E_{\alpha_0} + E_k + \hbar c K - E_{n''})} \\
&= \sum_{\alpha''k''\lambda''} \frac{|V_{\alpha''k'', \alpha''k''K''\lambda''}|^2}{(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - \hbar c K'')} \quad . \quad (2.22)
\end{aligned}$$

The sum over K'' in (2.22) can be extended to an integral over d^3K'' by noting that if the argument is slowly varying with respect to K'' , then

$$\sum_{K'' \in \Delta^3 K''} 1 \rightarrow \frac{L^3 d^3 K''}{(2\pi)^3}$$

so

$$\begin{aligned}
\Sigma^\gamma &= \sum_{\alpha''k''\lambda''} \int \frac{L^3 d^3 K''}{(2\pi)^3} \frac{|V_{\alpha''k'', \alpha''k''K''\lambda''}|^2}{(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - \hbar c K'')} \\
&= \frac{L^3}{(2\pi)^3} \sum_{\alpha''k''\lambda''} \int d\Omega_{K''} \int_0^{K'' \max} \frac{K''^2 |V_{\alpha''k'', \alpha''k''K''\lambda''}|^2 dK''}{(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - \hbar c K'')} \quad (2.23)
\end{aligned}$$

Now let $E_{K''} = \hbar c K''$ so $dK'' = 1/\hbar c dE_{K''}$. Thus (2.23) becomes

$$\Sigma^\gamma = \frac{L^3}{(2\pi\hbar c)^3} \sum_{\alpha''k''\lambda''} \int d\Omega_{K''} \int_0^{E_{K''} \max} \frac{E_{K''}^2 |V_{\alpha''k'', \alpha''k''K''\lambda''}|^2 dE_{K''}}{(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''}) - E_{K''}} \quad (2.24)$$

The integral over $E_{K''}$ is of the form

*The integral over K'' is from 0 to $K'' \max$. where

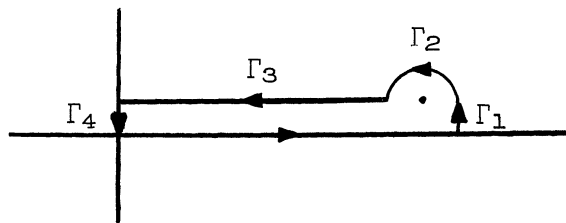
$$K'' \max = \frac{1}{\hbar c} (E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''}) \quad .$$

$$\int_0^a \frac{f(x)}{a-x} dx .$$

To obtain the real and imaginary parts corresponding to the shift and width function it is necessary to consider

$$\int_0^a \frac{f(x)}{a-x} dx = \lim_{\epsilon \rightarrow 0} \int_0^a \frac{f(x)}{a-x+i\epsilon} dx . \quad (2.25)$$

This corresponds to keeping the small real part of z in evaluating the inverse Laplace transform in (1.34) rather than taking the limit at $\epsilon \rightarrow 0$. The integral in (2.25) can be performed by taking the contour integral on the following path



and

$$\begin{aligned} \int_0^{a+\epsilon} \frac{f(x)}{a+i\epsilon-x} dx &= \oint \frac{f(z)}{a+i\epsilon-z} dz - \int_{\Gamma_1} \frac{f(z)}{a+i\epsilon-z} dz - \int_{\Gamma_2} \frac{f(z)}{a+i\epsilon-z} dz \\ &\quad - \int_{\Gamma_3} \frac{f(z)}{a+i\epsilon-z} dz - \int_{\Gamma_4} \frac{f(z)}{a+i\epsilon-z} dz . \end{aligned}$$

Now in the limit as $\epsilon \rightarrow 0$ both the integrals over Γ_1 and Γ_4 will go to zero. The integral over Γ_2 is just $\pi i (\text{Res } f(z)/a+i\epsilon-z; a+i\epsilon)^7$ and the integral over Γ_3 is the principal value of

$$\int_a^0 \frac{f(z)}{a-z} dz = - \mathcal{P} \int_0^a \frac{f(z)}{a-z} dz .$$

The integral around the complete path evaluated by residues is

$$2\pi i \left(\text{Res} \frac{f(z)}{a+i\epsilon-z}; a+i\epsilon \right)$$

so

$$\begin{aligned} \int_0^a \frac{f(x)}{a-x} dx &= \lim_{\epsilon \rightarrow 0} \int_0^{a+\epsilon} \frac{f(x)}{a+i\epsilon-x} dx \\ &= 2\pi i f(a) - 0 - \pi i f(a) + \mathcal{P} \int_0^a \frac{f(x)}{a-x} dx - 0 \\ &= \mathcal{P} \int_0^a \frac{f(x)}{a-x} dx + \pi i f(a) . \end{aligned} \quad (2.26)$$

Using (2.26), (2.24) can be written as

$$\begin{aligned} \Sigma^\gamma &= \frac{L^3}{(2\pi\hbar c)^3} \sum_{\alpha''k''\lambda''} \int d\Omega_{K''} \left[\mathcal{P} \int_0^{E_{K''}^{\max}} \frac{E_{K''}^2 |V_{\alpha''k''}, \alpha''k''\lambda''|^2 dE_{K''}}{(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - E_{K''}) - E_{K''}} \right. \\ &\quad \left. + \pi i \int_0^{E_{K''}^{\max}} E_{K''}^2 |V_{\alpha''k''}, \alpha''k''\lambda''|^2 \delta(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - E_{K''}) dE_{K''} \right] . \end{aligned} \quad (2.27)$$

The first term in (2.27) is real and can be associated as part of the shift function in (2.18). The second term in (2.27) is imaginary and can be identified as the width function associated with this particular process (n'' like initial states). Hence the width function for the gamma decay process can be written as

$$\begin{aligned} -\frac{i}{2} \Gamma_{\alpha''k''}^\gamma &= \frac{L^3}{(2\pi\hbar c)^3} \pi i \sum_{\alpha''k''\lambda''} \int_0^{E_{K''}^{\max}} d\Omega_{K''} E_{K''}^2 |V_{\alpha''k''}, \alpha''k''\lambda''|^2 \\ &\quad (x) \delta(E_{\alpha_0} + E_k + \hbar c K - E_{\alpha''} - E_{k''} - E_{K''}) dE_{K''} . \end{aligned} \quad (2.28)$$

The matrix elements of V can be calculated using (2.15), or

$$V_{\alpha''k'', \alpha'''k'''K'''\lambda'''} = \left\langle \alpha''k'' \left| - \sum_{\lambda} \sqrt{\frac{2\pi\hbar c}{L^3 \kappa}} e^{-i\kappa \cdot R} \sum_j \frac{e_j}{m_j c} e^{-i\kappa \cdot \rho_j} \right. \right. \\ \left. \left. (x) (a_{\lambda}^{\dagger}(\kappa) \underline{\epsilon}_{\lambda}(\kappa) + a_{\lambda}(-\kappa) \underline{\epsilon}_{\lambda}(-\kappa)) \cdot \underline{\pi}_j \right| \alpha'''k'''K'''\lambda''' \right\rangle . \quad (2.29)$$

Only the annihilation operator has non-vanishing matrix elements between the states $1_{K''\lambda''}$ and $0_{K'''\lambda'''}$ and

$$\left\langle 0_{K'''\lambda'''} \left| a_{\lambda}(-\kappa) \underline{\epsilon}_{\lambda}(-\kappa) \right| 1_{K''\lambda''} \right\rangle = \underline{\epsilon}_{\lambda}(-\kappa) \delta_{\kappa K''} \delta_{\lambda \lambda''} . \quad (2.30)$$

Making use of the delta functions, (2.29) reduces to

$$V_{\alpha''k'', \alpha'''k'''K'''\lambda'''} = \left\langle \alpha''k'' \left| - \sqrt{\frac{2\pi\hbar c}{L^3 K''}} e^{-iK'' \cdot R} \sum_j \frac{e_j}{m_j c} e^{-iK'' \cdot \rho_j} \underline{\epsilon}_{\lambda''}(-K'') \cdot \underline{\pi}_j \right| \alpha'''k''' \right\rangle . \quad (2.31)$$

(2.31) can be written as the product of two matrix elements. The only part of the interaction Hamiltonian which acts on the states of the center of mass motion is $e^{-iK'' \cdot R}$, so (2.31) yields

$$V_{\alpha''k'', \alpha'''k'''K'''\lambda'''} = \left\langle \alpha'' \left| - \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} e^{-iK'' \cdot \rho_j} \underline{\epsilon}_{\lambda''}(-K'') \cdot \underline{\pi}_j \right| \alpha''' \right\rangle \\ (x) \left\langle k'' \left| e^{-iK'' \cdot R} \right| k''' \right\rangle \quad (2.32)$$

With (2.32), (2.28) can be evaluated since

$$-\frac{i}{2} \Gamma^{\gamma} \alpha''k'' = \frac{L^3}{(2\pi\hbar c)^3} \pi i \sum_{\alpha'''k'''K'''\lambda'''} \int d\Omega_{K''} \int_0^{E_{K''}^{\max}} dE_{K''} E_{K''}^2 \left| \left\langle k'' \left| e^{+iK'' \cdot R} \right| k''' \right\rangle \right|^2 \\ (x) \left| \left\langle \alpha'' \left| - \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} e^{-iK'' \cdot \rho_j} \underline{\epsilon}_{\lambda''}(-K'') \cdot \underline{\pi}_j \right| \alpha''' \right\rangle \right|^2 \delta(E_{\alpha''} + E_{K''} + \hbar c K - E_{\alpha'''} - E_{K'''} - E_{\lambda'''}). \quad (2.32.5)$$

$E_k - E_{k''}$ is small compared to the photon energy $\hbar cK$, so neglecting the energy of the center of mass motion, the only term which depends on k'' is the square of the matrix element. Here the sum over k'' can be performed easily using the closure property since

$$\begin{aligned} \sum_{k''} \left| \left\langle k'' \left| e^{-i\mathbf{K}'' \cdot \mathbf{R}} \right| k'' \right\rangle \right|^2 &= \sum_{k''} \left\langle k'' \left| e^{-i\mathbf{K}'' \cdot \mathbf{R}} \right| k'' \right\rangle \left\langle k'' \left| e^{+i\mathbf{K}'' \cdot \mathbf{R}} \right| k'' \right\rangle \\ &= \left\langle k'' \left| e^{-i\mathbf{K}'' \cdot \mathbf{R}} e^{+i\mathbf{K}'' \cdot \mathbf{R}} \right| k'' \right\rangle \\ &= 1 \quad . \end{aligned} \tag{2.33}$$

To this point, nothing has been said about the set of numbers describing the internal state of the nucleus. It is known that two good quantum numbers are the total angular momentum of the nucleus j and the projection of the angular momentum m . It is also known that the nuclear state is a state of definite parity π . Hence the set of numbers α should include j , m and π in addition to other quantum numbers τ descriptive of the nuclear state.

Now

$$\begin{aligned} H^N |\tau j m \pi\rangle &= E_{\tau j} |\tau j m \pi\rangle \\ J^2 |\tau j m \pi\rangle &= j(j+1) |\tau j m \pi\rangle \\ M |\tau j m \pi\rangle &= m |\tau j m \pi\rangle \\ P |\tau j m \pi\rangle &= \pi |\tau j m \pi\rangle \quad . \end{aligned}$$

In considering the Mössbauer effect, certain generalizations can be made concerning these quantum numbers. The effect is limited to nuclei having low lying isomeric states (less than 200 keV) because the source must be a gamma emitted by the decay of an excited state to the ground state, the excited state must have sufficient abundance, the decay must be predominantly

by gamma emission, and most important, the effect is governed by a factor $e^{-fE_0^2}$, the Lamb-Mössbauer factor, where f is a function of other lattice and experimental parameters. In addition to an upper limit to the energy of the excited state, there are limits on the lifetimes of the excited state. Lifetimes greater than 10^{-5} sec produce lines too narrow to be observed with the resolution of conventional equipment. The lower limit on lifetimes for experimentally useful line widths is about 10^{-11} sec. If these limits are compared to the lifetimes as a function of gamma energy predicted for electric and magnetic multipole radiation,⁸ it is apparent that nuclei decaying by magnetic dipole radiation would fit the requirements for Mössbauer nuclides. The selection rules for magnetic dipole transitions are $\Delta j \leq 1$, $\Delta \pi = N_0$, $j_G + j_E \neq 0$; and if several known Mössbauer nuclides are considered, it appears that the radiative transitions satisfy the magnetic dipole radiation selection rules.

NUCLIDE	EXCITATION ENERGY	EXCITED STATE	GROUND STATE	Δj	$\Delta \pi$	$j_G + j_E$
Fe ⁵⁷	14.4 keV	3/2-	1/2-	1	N_0	2
Kr ⁸³	9.3 keV	7/2+	9/2+	1	N_0	8
Sn ¹¹⁹	24.0 keV	3/2+	1/2+	1	N_0	2
Ir ¹⁹¹	129.0 keV	5/2+	3/2+	1	N_0	4

These same transitions, however, also satisfy the selection rules for electric quadrupole radiation where $\Delta j \leq 2$, $\Delta \pi = N_0$, and $j_G + j_E \neq 0, 1$. In general though, the magnetic dipole transition is the predominant mode of decay,

as observed by the half lives, which are much shorter than those predicted for electric quadrupole transitions.

Now to continue with the calculation of (2.33), it can be noted that for state α'' like the initial state, α'' is a definite state of angular momentum j , parity π , and τ characteristic of the ground state. The sum over α'' then reduces to only a sum over m'' , the projection of the angular momentum and since $E_{\alpha''} = E_{\tau j} = E_{\alpha_0}$, (2.32.5) becomes

$$-\frac{i}{2} \Gamma_{\alpha''k}^{\gamma} = \frac{L^3}{(2\pi\hbar c)^3} \pi i \sum_{m''\lambda''} \int d\Omega_{K''} \int_0^{E_{K''\max}} E_{K''}^2 \delta(\hbar c K - E_{K''})$$

$$(x) \left| \left\langle \tau'' j'' m'' \pi'' \right| - \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} e^{-i\mathbf{K}'' \cdot \underline{\rho}_j} \underline{\epsilon}_{\lambda''}(-\mathbf{K}'') \cdot \underline{\pi}_j \left| \tau j m'' \pi \right\rangle \right|^2 dE_{K''}.$$

(2.34)

The matrix elements in (2.34) can be evaluated further by expanding the exponential $e^{-i\mathbf{K}'' \cdot \underline{\rho}_j}$, or

$$e^{-i\mathbf{K}'' \cdot \underline{\rho}_j} = 1 - i\mathbf{K}'' \cdot \underline{\rho}_j + \dots \quad (2.35)$$

This expansion is good through the first few terms since the argument is small where

$$\mathbf{K}'' \cdot \underline{\rho}_j \approx \frac{r}{\lambda} \sim \frac{10^{-12} \text{ cm}}{10^{-9} \text{ cm}} = 10^{-3}$$

where

r - nuclear radius

λ - photon wavelength

The first term in (2.35) corresponds to an electric dipole transition which has no non-vanishing matrix elements for the nuclei considered above since electric dipole transitions have the selection rule $\Delta\pi = \text{Yes}$. The second

term includes both magnetic dipole and electric quadrupole transitions. Thus the matrix elements for the magnetic dipole and electric quadrupole approximation are

$$\begin{aligned} & \left\langle \tau'' j'' m'' \pi'' \left| -\sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} e^{-i\mathbf{K}'' \cdot \underline{\rho}_j} \underline{\epsilon}_{\lambda''}(-\mathbf{K}'') \cdot \underline{\pi}_j \right| \tau j m \pi \right\rangle \\ & \simeq \left\langle \tau'' j'' m'' \pi'' \left| -\sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} (-i\mathbf{K}'' \cdot \underline{\rho}_j) (\underline{\epsilon}_{\lambda''}(-\mathbf{K}'') \cdot \underline{\pi}_j) \right| \tau j m \pi \right\rangle . \end{aligned} \quad (2.36)$$

The orbital angular momentum of the j^{th} particle in the nuclear system can be written $\underline{l}_j = \underline{\rho}_j \times \underline{\pi}_j$, hence

$$\begin{aligned} \mathbf{K}'' \times \underline{l}_j &= \mathbf{K}'' \times (\underline{\rho}_j \times \underline{\pi}_j) \\ &= (\mathbf{K}'' \cdot \underline{\pi}_j) \underline{\rho}_j - (\mathbf{K}'' \cdot \underline{\rho}_j) \underline{\pi}_j \\ &= \mathbf{K}'' \cdot (\underline{\pi}_j \underline{\rho}_j + \underline{\rho}_j \underline{\pi}_j) - 2\mathbf{K}'' \cdot \underline{\rho}_j \underline{\pi}_j \end{aligned}$$

or

$$(\mathbf{K}'' \cdot \underline{\rho}_j) \underline{\pi}_j = -\frac{1}{2} (\mathbf{K}'' \times \underline{l}_j) + \frac{1}{2} \mathbf{K}'' \cdot (\underline{\pi}_j \underline{\rho}_j + \underline{\rho}_j \underline{\pi}_j) . \quad (2.37)$$

The first term on the right in (2.37) corresponds to the magnetic dipole transition, the second to the electric quadrupole transition. It was mentioned above that the magnetic dipole transition is predominant. Hence, to a first approximation, only the magnetic dipole contribution is considered; however, it must be kept in mind that the electric quadrupole term can provide a significant contribution and must be considered for each nuclide.

Neglecting the electric quadrupole contribution

$$(\mathbf{K}'' \cdot \underline{\rho}_j) \underline{\pi}_j = -\frac{1}{2} (\mathbf{K}'' \times \underline{l}_j)$$

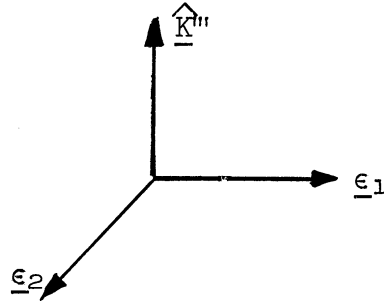
and (2.36) becomes

$$\begin{aligned}
& \left\langle \tau'' j'' m'' \pi'' \mid -\sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{m_j c} (\underline{\epsilon}_{\lambda''}(-\underline{K}'') \cdot \underline{\pi}_j) (-i \underline{K}'' \cdot \underline{\rho}_j) \mid \tau j m \pi \right\rangle \\
& \approx \left\langle \tau'' j'' m'' \pi'' \mid -i \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{2m_j c} \underline{\epsilon}_{\lambda''}(-\underline{K}'') \cdot (\underline{K}'' \times \underline{\ell}_j) \mid \tau j m \pi \right\rangle \\
& = \left\langle \tau'' j'' m'' \pi'' \mid -i \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \sum_j \frac{e_j}{2m_j c} \underline{\ell}_j \cdot (\underline{\epsilon}_{\lambda''}(-\underline{K}'') \times \underline{K}'') \mid \tau j m \pi \right\rangle . \quad (2.38)
\end{aligned}$$

The quantity $\sum_j \frac{e_j}{2m_j c} \underline{\ell}_j \equiv \underline{M}$, the total magnetic dipole moment of the nucleus, hence (2.38) can be reduced to

$$\left\langle \tau'' j'' m'' \pi'' \mid -i \sqrt{\frac{2\pi\hbar c}{L^3 K''}} \underline{M} \cdot (\underline{\epsilon}_{\lambda''}(-\underline{K}'') \times \underline{K}'') \mid \tau j m \pi \right\rangle . \quad (2.39)$$

Recall that $\underline{\epsilon}_1$, $\underline{\epsilon}_2$ and $\hat{\underline{K}}''$ form an orthogonal set of vectors so



Now,

$$\underline{\epsilon}_{\lambda''}(-\underline{K}'') \times \underline{K}'' = |\underline{K}''| \underline{\epsilon}_{\lambda''}(-\underline{K}'') \times \hat{\underline{K}}''$$

and since the unit vectors are orthogonal, the cross product of one polarization vector and $\hat{\underline{K}}''$ gives the other polarization vector so

$$\underline{\epsilon}_{\lambda''}(-\underline{K}'') \times \underline{K}'' = |\underline{K}''| \underline{\epsilon}_{\lambda''}(-\underline{K}'') (-1)^{\lambda''-1}$$

and (2.39) yields

$$\left\langle \tau'' j'' m'' \pi'' \mid -i \sqrt{\frac{2\pi\hbar c}{L^3 K''}} K'' (-1)^{\lambda''-1} \underline{M} \cdot \underline{\epsilon}_{\lambda''}(-\underline{K}'') \mid \tau j m \pi \right\rangle .$$

(2.34) can now be evaluated and

$$-\frac{i}{2} \Gamma_{\alpha''k''}^{\gamma} \approx \frac{L^3}{(2\pi\hbar c)^3} \pi i \sum_{m''\lambda''} \int d\Omega_{K''} \int_0^{E_{K''}^{\max}} E_{K''}^2 \delta(\hbar c K - E_{K''})$$

$$(x) \left| \left\langle \tau'' j'' m'' \pi'' \left| -i \sqrt{\frac{2\pi\hbar c}{L^3 K''}} K'' (-1)^{\lambda''-1} \underline{M} \cdot \underline{\epsilon}_{\lambda''}(-K'') \right| \tau j m \pi \right\rangle \right|^2 dE_{K''}$$

$$= \frac{i}{2} \cdot \frac{1}{2\pi} \cdot \frac{1}{(\hbar c)^3} \sum_{m''\lambda''} \int d\Omega_{K''} \int_0^{E_{K''}^{\max}} E_{K''}^3 \delta(\hbar c K - E_{K''})$$

$$(x) \left| \left\langle \tau'' j'' m'' \pi'' \left| \underline{M} \cdot \underline{\epsilon}_{\lambda''}(-K'') \right| \tau j m \pi \right\rangle \right|^2 dE_{K''} \quad . \quad (2.40)$$

Performing the integral over the delta function

$$-\frac{i}{2} \Gamma_{\alpha''k''}^{\gamma} = -\frac{i}{2} \cdot \frac{K^3}{2\pi} \sum_{m''\lambda''} \int d\Omega_{K''} \left| \left\langle \tau'' j'' m'' \pi'' \left| \underline{M} \cdot \underline{\epsilon}_{\lambda''}(-K'') \right| \tau j m \pi \right\rangle \right|^2 \quad . \quad (2.41)$$

Both \underline{M} and $\underline{\epsilon}_{\lambda''}(-K'')$ are vectors or first rank tensors which transform like the coordinates of a point in space. In the spherical basis, these transform like the first order spherical harmonics. These two tensors can be contracted to form the scalar product in the spherical basis as

$$\underline{M} \cdot \underline{\epsilon}_{\lambda''}(-K'') = \sum_{\mu=-1,0,+1} (-1)^{\mu} T_{1,-\mu}^{\epsilon_{\lambda''}} T_{1,\mu}^M \quad (2.42)$$

where $T_{1,-\mu}^{\epsilon_{\lambda''}}$ and $T_{1,\mu}^M$ are the representations of $\underline{\epsilon}$ and \underline{M} in the spherical basis.

Using (2.42) in (2.41)

$$-\frac{i}{2} \Gamma_{\alpha''k''}^{\gamma} = \frac{i}{2} \cdot \frac{K^3}{2\pi} \sum_{m''\lambda''} \int d\Omega_{K''} \left| \sum_{\mu} (-1)^{\mu} T_{1,-\mu}^{\epsilon_{\lambda''}} \left\langle \tau'' j'' m'' \pi'' \left| T_{1,\mu}^M \right| \tau j m \pi \right\rangle \right|^2 \quad (2.43)$$

Both the angular momentum eigenfunctions and $T_{1,\mu}^M$ have the same symmetry properties, hence the Wigner-Eckart theorem can be used to reduce the matrix elements⁹ to

$$\left\langle \tau'' j'' m'' \pi'' \left| T_{1, \mu}^M \right| \tau j m \pi \right\rangle = \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \left\langle \tau'' j'' \pi'' \left\| T_{1, \mu}^M \right\| \tau j \pi \right\rangle \quad (2.44)$$

where the coefficient is the Clebsch-Gordan coefficient and the matrix element is the reduced matrix element. Hence

$$-\frac{1}{2} \Gamma_{\alpha'' k''}^{\gamma} = \frac{1}{2} \cdot \frac{K^3}{2\pi} \left| \left\langle \tau'' j'' \pi'' \left\| T_{1, \mu}^M \right\| \tau j \pi \right\rangle \right|^2 \sum_{m'' \lambda'' \mu \mu'} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu' & m'' \end{pmatrix} \quad (2.45)$$

$$(x) \int d\Omega_{K''} (-1)^{\mu+\mu'} \begin{matrix} \epsilon_{\lambda''}^{\mu+\mu'} \\ T_{1, -\mu} \\ \epsilon_{\lambda''}^{\mu+\mu'} \end{matrix} \quad .$$

The integral over $\Omega_{K''}$ in (2.45) can be performed by noting that $T_{1, -\mu}^{\epsilon_{\lambda''}^{\mu+\mu'}}$ and $T_{1, -\mu'}^{\epsilon_{\lambda''}^{\mu+\mu'}}$ are proportional to first order spherical harmonics. In the cartesian system, with the basis vectors \underline{e}_2 , \underline{e}_1 and \hat{K}'' , the representations $T_{1, -\mu}^{\epsilon_{\lambda''}^{\mu+\mu'}}$ and $T_{1, -\mu'}^{\epsilon_{\lambda''}^{\mu+\mu'}}$ in the spherical basis are known. Now, consider a rotated coordinate system characterized by its Euler angles. The spherical harmonics in the rotated system can be related to those in the original system as

$$Y_1^{\mu}(\underline{\Omega}) = \sum_{\alpha} Y_1^{\alpha}(\underline{\Omega}') D_{\alpha\mu}^1 \quad (2.46)$$

where $D_{\alpha\mu}^1$ is the rotation matrix and is a function only of the Euler angles of the rotation. Now, $T_{1, -\mu}^{\epsilon}$ (and $T_{1, -\mu'}^{\epsilon}$) can be related to the spherical harmonics as

$$T_{1, 1}^{\epsilon} = -\frac{1}{\sqrt{2}} (\epsilon_x + i\epsilon_y) = -\frac{1}{\sqrt{2}} (\sin\theta \cos\phi + i \sin\theta \sin\phi) = -\frac{1}{\sqrt{2}} \sin\theta e^{i\phi} = \sqrt{\frac{4\pi}{3}} Y_1^1$$

$$T_{1, 0}^{\epsilon} = \epsilon_z = \cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^0$$

$$T_{1, -1}^{\epsilon} = \frac{1}{\sqrt{2}} (\epsilon_x - i\epsilon_y) = \frac{1}{\sqrt{2}} (\sin\theta \cos\phi - i \sin\theta \sin\phi) = \frac{1}{\sqrt{2}} \sin\theta e^{-i\phi} = \sqrt{\frac{4\pi}{3}} Y_1^{-1} .$$

Hence

$$T_{1,-\mu}^{\epsilon\lambda^m} = \sqrt{\frac{4\pi}{3}} Y_1^{-\mu}(\underline{\Omega}_{\lambda^m}) = \sqrt{\frac{4\pi}{3}} \sum_{\alpha} Y_1^{\alpha}(\underline{\Omega}'_{\lambda^m}) D_{\alpha,-\mu}^1$$

and the integral over Ω_{K^m} becomes

$$\int d\Omega_{K^m} (-1)^{\mu+\mu'} T_{1,-\mu}^{\epsilon\lambda^m} T_{1,-\mu'}^{\epsilon\lambda^{m'}*} = (-1)^{\mu+\mu'} \frac{4\pi}{3} \sum_{\alpha\alpha'} Y_1^{\alpha}(\underline{\Omega}'_{\lambda^m}) Y_1^{\alpha'*}(\underline{\Omega}'_{\lambda^{m'}}) \int d\Omega_{K^m} D_{\alpha,-\mu}^1 D_{\alpha',-\mu'}^{1*} .$$

This integral is carried out using the orthogonality of the rotation matrices and gives⁹

$$\int d\Omega_{K^m} (-1)^{\mu+\mu'} T_{1,-\mu}^{\epsilon\lambda^m} T_{1,-\mu'}^{\epsilon\lambda^{m'}*} = (-1)^{\mu+\mu'} \frac{4\pi}{3} \sum_{\alpha\alpha'} Y_1^{\alpha}(\underline{\Omega}'_{\lambda^m}) Y_1^{\alpha'*}(\underline{\Omega}'_{\lambda^{m'}}) \frac{4\pi}{3} \delta_{\alpha\alpha'} \delta_{\mu\mu'} . \quad (2.46.5)$$

So (2.45) reduces to

$$\begin{aligned} -\frac{i}{2} \Gamma_{a''k''}^{\gamma} &= \frac{i}{2} \frac{K^3}{2\pi} \left| \langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle \right|^2 \sum_{m'' \lambda'' \mu''} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu' & m'' \end{pmatrix} \\ &= \frac{i}{2} \frac{K^3}{2\pi} \left(\frac{4\pi}{3} \right)^2 \sum_{\alpha} Y_1^{\alpha}(\underline{\Omega}'_{\lambda^m}) Y_1^{\alpha*}(\underline{\Omega}'_{\lambda^{m'}}) (-1)^{\mu+\mu'} \delta_{\mu\mu'} \\ &= \frac{i}{2} \frac{K^3}{2\pi} \left(\frac{4\pi}{3} \right)^2 \left| \langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle \right|^2 \sum_{m'' \mu} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \\ &= \frac{i}{2} \frac{K^3}{2\pi} \sum_{\alpha\lambda^m} Y_1^{\alpha}(\underline{\Omega}'_{\lambda^m}) Y_1^{\alpha*}(\underline{\Omega}'_{\lambda^{m'}}) . \quad (2.47) \end{aligned}$$

The sum over λ''' and α can be performed by fixing λ''' and summing over α . $\lambda''' = 1$ corresponds to $Y_1^\alpha(\pi/2, \pi/2)$ and $\lambda''' = 2$ corresponds to $Y_1^\alpha(\pi/2, 0)$. The resultant is

$$\sum_{\lambda'''\alpha} Y_1^\alpha(\underline{\Omega}_{\lambda'''}^{\prime}) Y_1^{\alpha*}(\underline{\Omega}_{\lambda'''}^{\prime}) = 4 \cdot \frac{3}{8\pi} \quad (2.47.5)$$

and

$$-\frac{i}{2} \Gamma^\gamma \alpha'' k'' = \frac{i}{2} \frac{4K^3}{3} \left| \left\langle \tau'' j'' \pi'' \parallel T_1^M \parallel \tau j m \right\rangle \right|^2 \sum_{m''\mu} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix}.$$

The sum over m'', μ can be performed using the orthogonality of the Clebsch-Gordan coefficients¹⁰ and

$$\sum_{m''\mu} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m'' & \mu & m'' \end{pmatrix} = \frac{1}{2j''+1}.$$

so

$$-\frac{i}{2} \Gamma^\gamma \alpha'' k'' = \frac{i}{2} \frac{4K^3}{3(2j''+1)} \left| \left\langle \tau'' j'' \pi'' \parallel T_1^M \parallel \tau j \pi \right\rangle \right|^2. \quad (2.48)$$

This then is the width function for magnetic dipole radiation.

A second contribution to (2.18) arises from the internal conversion process. In this process, the energy of the excited state is transmitted directly to an atomic electron with the subsequent ejection of the electron from its bound orbit. This then becomes an atomic problem which we have not even considered in formulating the Hamiltonian for the entire system. The details of the calculation of the width function for the internal conversion process present a new problem and will not be considered in this paper; hence it is only noted that there is an additional contribution to the width

function $-\frac{i}{2} \Gamma^{\text{IC}}$. The usual procedure for treating this process is to relate the internal conversion width to the width for gamma emission by a function α , the internal conversion coefficient, or

$$-\frac{i}{2} \Gamma^{\text{IC}} = \alpha \left(-\frac{i}{2} \Gamma_{\alpha''k''}^{\gamma} \right)$$

where α is an experimentally measurable quantity.

If the lifetime of the crystal states (lattice relaxation time) is long compared to the lifetime of the nuclear excited state, there will be little contribution to the width function due to the crystal states. For our purposes, the lifetime of the crystal states will be assumed infinite so that there is no contribution to the width function. Assuming no additional contributions, the total width can be written

$$\begin{aligned} -\frac{i}{2} \Gamma &= -\frac{i}{2} \Gamma^{\gamma} - \frac{i}{2} \Gamma^{\text{IC}} \\ &= -\frac{i}{2} (1+\alpha) \Gamma^{\gamma} \end{aligned} \quad (2.48.5)$$

Returning to (2.16), the transition probability can be written

$$\begin{aligned} \tau_{jm' \pi k' K' \lambda', \tau_{jm \pi k K \lambda}} &\approx \frac{2\pi}{h} \left| \sum_{m''k''} \frac{V_{\tau_{jm' \pi k' K' \lambda'}, \tau''j''m''\pi''k''} V_{\tau''j''m''\pi''k'', \tau_{jm \pi k K \lambda}}}{\left(E_0 + E_{k''} - E_k - \hbar c K + S_{\alpha''k''} - \frac{i}{2} \Gamma \right)} \right|^2 \\ &(x) \delta(E_k, +\hbar c K' - E_k - \hbar c K) \quad . \end{aligned} \quad (2.49)$$

The cross section for nuclear resonance scattering can be written in terms of the transition probability (2.49). In particular, the cross section of interest is $\sigma_S(K)$ since the only parameter which can be controlled is the

incident photon energy.* To obtain this cross section, the transition probability must be summed over m', k', K' and λ' and averaged over m, k and λ and divided by the incident beam intensity, or

$$\sigma_s(\underline{K}) = \frac{2\pi}{\hbar} \cdot \frac{L^3}{c} \sum_{m'k'K'\lambda'mk\lambda} P_m P_k P_\lambda T_{\tau_{jm'} \pi k' K' \lambda', \tau_{jm} \pi k K \lambda} \cdot$$

The probability of the angular momentum having a projection m is just $1/2j+1$ and the probability of the radiation having a particular polarization state λ is just $1/2$, so

$$\sigma_s(\underline{K}) = \frac{\pi L^3}{\hbar c (2j+1)} \sum_{m'k'K'\lambda'mk\lambda} P_k T_{\tau_{jm'} \pi k' K' \lambda', \tau_{jm} \pi k K \lambda} \cdot$$

The sum over K' can be extended to an integral over $E_{K'}$, as done previously in evaluating the width function, so

$$\sigma_s(\underline{K}) = \frac{\pi L^3}{\hbar c (2j+1)} \cdot \frac{L^3}{(2\pi\hbar c)^3} \sum_{m'k'\lambda'mk\lambda} P_k \int d\Omega_{K'} \int_{E_K^2} dE_{K'} T_{\tau_{jm'} \pi k' K' \lambda', \tau_{jm} \pi k K \lambda} \quad (2.50)$$

The matrix elements in the transition probability (2.49) have already been evaluated in consideration of the width function, hence can just be written down as

$$V_{\tau_{jm'} \pi k' K' \lambda', \tau'' j'' m'' \pi'' k''} = i(-1)^{\lambda'} \sqrt{\frac{2\pi\hbar c K'}{L^3}} \langle k' | e^{-i\underline{K}' \cdot \underline{R}} | k'' \rangle$$

$$(x) \langle \tau_{jm'} \pi | \underline{M} \cdot \underline{\epsilon}_{\lambda'}(-\underline{K}') | \tau'' j'' m'' \pi'' \rangle \quad (2.51)$$

*If a true scattering experiment were performed, the cross section of interest would be $\sigma_s(\underline{K}, \underline{\Omega}_{K'}) d\Omega_{K'}$; however, the present interest in nuclear resonance scattering is only as a removal process.

and

$$V_{\tau''j''m''\pi''k'', \tau_{jm}\pi k K \lambda} = i(-1)^\lambda \sqrt{\frac{2\pi\hbar c K}{L^3}} \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle$$

$$(x) \langle \tau''j''m''\pi'' | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}) | \tau_{jm}\pi \rangle . \quad (2.52)$$

With (2.49), (2.51), and (2.52), (2.50) becomes

$$\sigma_s(\underline{K}) = \frac{E_K}{2(2j+1)(\hbar c)^4} \sum_{m'k'\lambda'mk\lambda} P_k \int d\Omega_{K'} \int dE_{K'} E_{K'}^3$$

$$(x) \left| \frac{\sum_{m''k''} \langle k' | e^{-i\underline{K}' \cdot \underline{R}} | k'' \rangle \langle \tau_{jm'}\pi | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}') | \tau''j''m''\pi'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle \langle \tau''j''m''\pi'' | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}) | \tau_{jm}\pi \rangle}{E_0 + E_{k''} - E_k - \hbar c K + S - \frac{i}{2} \Gamma} \right|^2$$

$$(x) \delta(E_{K'} + E_{K'} - E_k - \hbar c K) . \quad (2.53)$$

$E_{K'}, -E_k$ is small compared to $\hbar c K$, so by neglecting $E_{K'}$ and E_k in the delta function and performing the integral over $E_{K'}$,

$$\sigma_s(\underline{K}) = \frac{K^4}{2(2j+1)} \sum_{m'k'\lambda'mk\lambda} P_k \int d\Omega_{K'}$$

$$(x) \left| \frac{\sum_{m''k''} \langle k' | e^{-i\underline{K}' \cdot \underline{R}} | k'' \rangle \langle \tau_{jm'}\pi | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}') | \tau''j''m''\pi'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle \langle \tau''j''m''\pi'' | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}) | \tau_{jm}\pi \rangle}{E_0 + E_{k''} - E_k - \hbar c K + S - \frac{i}{2} \Gamma} \right|^2 . \quad (2.54)$$

The square of the sum in (2.54) can be written as the sum of the squares for m''^9 and k'' if it is assumed that the states k'' are not degenerate, so

$$\sigma_s(\underline{K}) = \frac{K^4}{2(2j+1)} \sum_{kk''} P_k \sum_{m'k'\lambda'm\lambda m''} \int d\Omega_{K'}$$

$$(x) \frac{|\langle k' | e^{-i\underline{K}' \cdot \underline{R}} | k'' \rangle \langle \tau_{jm'}\pi | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}') | \tau''j''m''\pi'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle \langle \tau''j''m''\pi'' | \underline{M} \cdot \underline{\epsilon}_\lambda(-\underline{K}) | \tau_{jm}\pi \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar c K + S)^2 + \frac{\Gamma^2}{4}} .$$

The sum over final states k' can be performed since

$$\begin{aligned} \sum_{k'} |\langle k' | e^{-i\mathbf{K}' \cdot \mathbf{R}} | k'' \rangle|^2 &= \sum_{k'} \langle k'' | e^{i\mathbf{K}' \cdot \mathbf{R}} | k' \rangle \langle k' | e^{-i\mathbf{K}' \cdot \mathbf{R}} | k'' \rangle \\ &= \langle k'' | e^{i\mathbf{K}' \cdot \mathbf{R}} e^{-i\mathbf{K}' \cdot \mathbf{R}} | k'' \rangle \\ &= 1 \quad . \end{aligned}$$

and

$$\begin{aligned} \sigma_S(\underline{K}) &= \frac{K^4}{2(2j+1)} \sum_{kk''} P_k \sum_{m' \lambda' m'' m \lambda} \int d\Omega_{K'} \\ (x) \quad & \frac{|\langle \tau j m' \pi | \underline{M} \cdot \underline{\epsilon}_{\lambda'}(-\underline{K}') | \tau'' j'' m'' \pi'' \rangle \langle k'' | e^{-i\mathbf{K}' \cdot \mathbf{R}} | k \rangle \langle \tau'' j'' m'' \pi'' | \underline{M} \cdot \underline{\epsilon}_{\lambda}(-\underline{K}) | \tau j m \pi \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar c K + S)^2 + \frac{\Gamma^2}{4}} \\ &= \frac{K^4}{2(2j+1)} \sum_{kk''} P_k \frac{|\langle k'' | e^{-i\mathbf{K}' \cdot \mathbf{R}} | k \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar c K + S)^2 + \frac{\Gamma^2}{4}} \\ (x) \quad & \sum_{m' \lambda' m'' m \lambda} \int d\Omega_{K'} |\langle \tau j m' \pi | \underline{M} \cdot \underline{\epsilon}_{\lambda'}(-\underline{K}') | \tau'' j'' m'' \pi'' \rangle \langle \tau'' j'' m'' \pi'' | \underline{M} \cdot \underline{\epsilon}_{\lambda}(-\underline{K}) | \tau j m \pi \rangle|^2. \end{aligned} \tag{2.55}$$

Now, expanding $\underline{M} \cdot \underline{\epsilon}$ in the spherical basis as done in (2.42), the last term in (2.55) becomes

$$\begin{aligned} & \sum_{m' \lambda' m'' m \lambda} \int d\Omega_{K'} |\langle \tau j m' \pi | \underline{M} \cdot \underline{\epsilon}_{\lambda'}(-\underline{K}') | \tau'' j'' m'' \pi'' \rangle \langle \tau'' j'' m'' \pi'' | \underline{M} \cdot \underline{\epsilon}_{\lambda}(-\underline{K}) | \tau j m \pi \rangle|^2 \\ &= \sum_{m' \lambda' m'' m \lambda} \int d\Omega_{K'} |\sum_{\mu} (-1)^{\mu} T_{1,-\mu}^{\epsilon \lambda'} \langle \tau j m' \pi | T_{1,\mu}^M | \tau'' j'' m'' \pi'' \rangle| \\ (x) \quad & \sum_{\eta} (-1)^{\eta} T_{1,-\eta}^{\epsilon \lambda} \langle \tau'' j'' m'' \pi'' | T_{1,\eta}^M | \tau j m \pi \rangle|^2. \end{aligned} \tag{2.56}$$

Using the Wigner-Eckart theorem as done previously in (2.44) and taking the square of the matrix elements, (2.56) reduces to

$$\begin{aligned}
& |\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \\
& \quad (x) \sum_{m' \lambda' m'' m \lambda} \int d\Omega_{K'} \sum_{\mu \mu'} (-1)^{\mu+\mu'} T_{1,-\mu}^{\epsilon \lambda'} T_{1,-\mu'}^{\epsilon \lambda'} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu & m' \end{pmatrix} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu' & m' \end{pmatrix} \\
& \quad (x) \sum_{\eta \eta'} (-1)^{\eta+\eta'} T_{1,-\eta}^{\epsilon \lambda} T_{1,-\eta'}^{\epsilon \lambda} \begin{pmatrix} j & 1 & j'' \\ m & \eta & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m & \eta' & m'' \end{pmatrix}. \quad (2.57)
\end{aligned}$$

The only terms which depend on the direction of K' are $T_{1,-\mu}^{\epsilon \lambda'}$ and $T_{1,-\mu'}^{\epsilon \lambda'}$.

This integral has been performed in (2.46.5) so

$$\int d\Omega_{K'} (-1)^{\mu+\mu'} T_{1,-\mu}^{\epsilon \lambda'} T_{1,-\mu'}^{\epsilon \lambda'} = \left(\frac{4\pi}{3}\right)^2 \sum_{\alpha} Y_1(\underline{\Omega}_{\lambda'}) Y_1^{\alpha*}(\underline{\Omega}_{\lambda'}) (-1)^{\mu+\mu'} \delta_{\mu\mu'}.$$

Taking the sum over μ' and the sums over λ' and α as evaluated in (2.47.5), (2.57) becomes

$$\begin{aligned}
& |\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \cdot \frac{8\pi}{3} \\
& \quad (x) \sum_{m' m'' \mu m \lambda} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu & m' \end{pmatrix} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu & m' \end{pmatrix} \\
& \quad (x) \sum_{\eta \eta'} (-1)^{\eta+\eta'} T_{1,-\eta}^{\epsilon \lambda} T_{1,-\eta'}^{\epsilon \lambda} \begin{pmatrix} j & 1 & j'' \\ m & \eta & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m & \eta' & m'' \end{pmatrix}. \quad (2.58)
\end{aligned}$$

The sums over m' and μ can be performed using the orthogonality of the Clebsch-Gordan coefficients since

$$\sum_{m' \mu} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu & m' \end{pmatrix} \begin{pmatrix} j'' & 1 & j \\ m'' & \mu & m' \end{pmatrix} = \sum_{m' \mu} \begin{pmatrix} 1 & j & j'' \\ \mu & m' & m'' \end{pmatrix} \begin{pmatrix} 1 & j & j'' \\ \mu & m' & m'' \end{pmatrix} = \frac{1}{2j''+1}$$

and (2.58) reduces to

$$|\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \cdot \frac{8\pi}{3(2j''+1)}$$

$$(x) \sum_{m'' m \lambda \eta \eta'} (-1)^{\eta+\eta'} T_{1,-\eta}^{\epsilon\lambda} T_{1,-\eta'}^{\epsilon\lambda} \begin{pmatrix} j & 1 & j'' \\ m & \eta & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m & \eta' & m'' \end{pmatrix} \quad (2.59)$$

The sums over m and m'' can be performed by again using the orthogonality of the Clebsch-Gordan coefficients and

$$\sum_{m'' m} \begin{pmatrix} j & 1 & j'' \\ m & \eta & m'' \end{pmatrix} \begin{pmatrix} j & 1 & j'' \\ m & \eta' & m'' \end{pmatrix} = \sum_{m'' m} \begin{pmatrix} j'' & j & 1 \\ m'' & m & \eta \end{pmatrix} \begin{pmatrix} j'' & j & 1 \\ m'' & m & \eta' \end{pmatrix} = \frac{1}{3} \delta_{\eta\eta'}$$

Using this in (2.59)

$$|\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \cdot \frac{8\pi}{9(2j''+1)} \sum_{\lambda \eta} T_{1,-\eta}^{\epsilon\lambda} T_{1,-\eta}^{\epsilon\lambda} *$$

or in terms of the spherical harmonics

$$|\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \frac{32\pi^2}{27(2j''+1)} \sum_{\lambda \eta} Y_1^{-\eta}(\underline{\Omega}_\lambda) Y_1^{-\eta*}(\underline{\Omega}_\lambda) \quad (2.60)$$

The sums over λ and η can be performed as in (2.47.5) and (2.60) now becomes

$$|\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2 \frac{16\pi}{9(2j''+1)} \quad .$$

Hence, (2.55) can be written as

$$\sigma_s(\underline{K}) = \frac{16\pi K^4}{18(2j+1)(2j''+1)} |\langle \tau j \pi \| T_1^M \| \tau'' j'' \pi'' \rangle|^2 |\langle \tau'' j'' \pi'' \| T_1^M \| \tau j \pi \rangle|^2$$

$$(x) \sum_{kk''} P_k \frac{|\langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar c K + S)^2 + \frac{\Gamma^2}{4}} \quad (2.61)$$

Equation (2.61) can be written in terms of Γ^γ rather than the reduced matrix elements by making use of (2.48) so

$$\sigma_s(\underline{K}) = \frac{\pi\Gamma\gamma^2}{2K^2} \cdot \frac{2j''+1}{2j+1} \sum_{kk''} P_k \frac{|\langle k'' | e^{-i\underline{K}\cdot\underline{R}} | k \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar cK + S)^2 + \frac{\Gamma^2}{4}} . \quad (2.62)$$

Noting that $1/K^2 = \lambda^2$, (2.62) can be written in the more conventional form¹¹

$$\sigma_s(\underline{K}) = \frac{\Gamma^2}{4} \sigma_0 W(\underline{K}) \quad (2.63)$$

where

$$\sigma_0 = 2 \left(\frac{2j''+1}{2j+1} \right) \pi\lambda^2 \frac{\Gamma\gamma^2}{\Gamma^2} \quad (2.64)$$

is the cross section at resonance for nuclear scattering of a gamma ray and

$$W(\underline{K}) = \sum_{kk''} P_k \frac{|\langle k'' | e^{-i\underline{K}\cdot\underline{R}} | k \rangle|^2}{(E_0 + E_{k''} - E_k - \hbar cK + S)^2 + \frac{\Gamma^2}{4}} . \quad (2.65)$$

Equation (2.62) is the usual starting point for calculations of the Mössbauer effect. The development in this section is included not so much for verification of the cross section (which is well substantiated by experiment), but to investigate the assumptions made in order to obtain a better understanding of the limitations of the cross section.

SECTION III

APPLICATION TO AN EXPERIMENTAL STUDY OF DIFFUSIVE MOTION IN LIQUIDS

The cross section for nuclear resonance scattering formulated in Section II is perfectly applicable to nuclei in a system in the solid, liquid, or gas state since the state of the center of mass motion k is just the eigenfunction of the system Hamiltonian H^S which can be appropriately chosen to describe a system in either the solid, liquid, or gas state.

There are two possible approaches at this point. First, if the Hamiltonian H^S for the system was known, the eigenfunctions of the system k could be obtained by solving the eigenvalue problem $H^S|k\rangle = E_k|k\rangle$ and the matrix elements in (2.62) could be calculated directly.* For solids this approach is possible since under certain conditions the system Hamiltonian is well known. In fact, this is the usual procedure for calculation of the cross section for the Mössbauer cross section in solids.^{11,12} In the case of liquids, however, the Hamiltonian H^S for the system is not known, hence this approach cannot be used.

Since the force laws governing the interaction of atoms in a liquid are not known, the second approach must be used out of necessity. The approach is mainly an attempt to push the calculation as far as possible without including any explicit knowledge of the system Hamiltonian. This essentially involves introduction of the space-time self correlation function

*Although the procedure is straightforward, the mathematics may not be.

first treated by Van Hove.¹ All information concerning the space and time dependent behavior of the system is then included in this correlation function. Hence, rather than working from the system Hamiltonian, models for the system are considered in terms of this self correlation function. This section is devoted to the introduction of the self correlation function with the necessary formalism and to the calculation of the cross section for application of the Mössbauer effect to a particular experiment to study diffusive motion in liquids.

To this point, no mention has been made of the shift function S in (2.65). To a first approximation the shift can be considered a constant since the range of \underline{K} for which $W(\underline{K})$ is large is quite small. For our purposes the width function is of main interest, and the shift will be retained only to keep in mind that the Mössbauer peak ($k'' = k$) may not be centered at E_0 but at energy $E'_0 = E_0 + S$.

Now, (2.63) can be rewritten as the integral over a delta function,

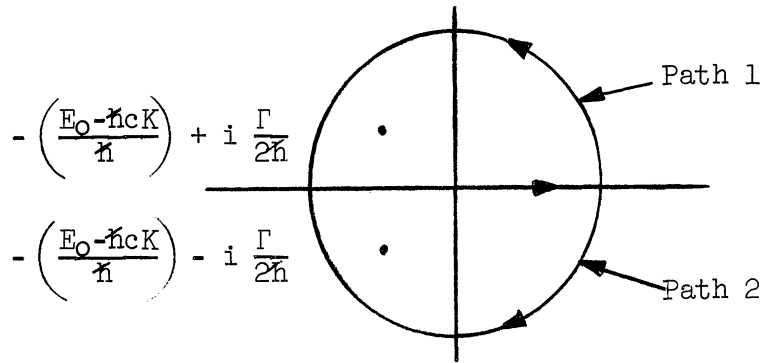
or

$$\sigma_S(\underline{K}) = \frac{\Gamma^2}{4} \sigma_0 \sum_{kk''} P_k \left| \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle \right|^2 \int_{-\infty}^{\infty} \frac{\delta\left(\rho - \frac{E_{k''} - E_k}{\hbar}\right) d\rho}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} \quad (3.1)$$

Using the Fourier representation of the delta function as in (1.44.5),

$$\begin{aligned}
\sigma_s(\underline{K}) &= \frac{\Gamma^2}{4} \frac{\sigma_0}{2\pi} \sum_{kk''} P_k |\langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle|^2 \int_{-\infty}^{\infty} d\rho \int_{-\infty}^{\infty} \frac{e^{-i\left(\rho - \frac{E_{k''} - E_k}{\hbar}\right)t} dt}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} \\
&= \frac{\Gamma^2}{4} \frac{\sigma_0}{2\pi} \int_{-\infty}^{\infty} dt \left\{ \sum_{kk''} P_k |\langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle|^2 e^{i\left(\frac{E_{k''} - E_k}{\hbar}\right)t} \right\} \\
(x) \int_{-\infty}^{\infty} \frac{e^{-i\rho t}}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} d\rho & \quad (3.2)
\end{aligned}$$

The integral over ρ can be performed by integrating in the complex plane on the following paths



For $t < 0$, path 1 is used since the real part of $-i\rho t$ goes to $-\infty$ when $\rho \rightarrow \infty$ and

$$\int_{-\infty}^{\infty} e^{-i\rho t} f(\rho) d\rho = \oint e^{-i\rho t} f(\rho) d\rho - \oint e^{-i\rho t} f(\rho) d\rho = \oint e^{-i\rho t} f(\rho) d\rho .$$

This can be evaluated by residues and

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{e^{-ipt} d\rho}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} &= \frac{2\pi i}{\hbar^2} \text{Res} \left[\frac{e^{-ipt}}{\left(\frac{E'_0 - \hbar c K}{\hbar} + \rho\right)^2 + \frac{\Gamma^2}{4\hbar^2}} ; -\left(\frac{E'_0 - \hbar c K}{\hbar}\right) + i \frac{\Gamma}{2\hbar} \right] \\
&= \frac{2\pi i}{\hbar^2} \frac{e^{\left(i\left(\frac{E'_0 - \hbar c K}{\hbar}\right) + \frac{\Gamma}{2\hbar}\right)t}}{i \frac{\Gamma}{\hbar}} \\
&= \frac{2\pi}{\hbar \Gamma} e^{i\left(\frac{E'_0 - \hbar c K}{\hbar}\right)t + \frac{\Gamma}{2\hbar} t} \quad t < 0 . \tag{3.3}
\end{aligned}$$

For $t > 0$, path 2 needs to be used so that the real part of $-ipt$ goes to $-\infty$ when $\rho \rightarrow \infty$. The integral can be evaluated in the same manner as for path 1, and

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{e^{-ipt} d\rho}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} &= -\frac{2\pi i}{\hbar^2} \text{Res} \left[\frac{e^{-ipt}}{\left(\frac{E'_0 - \hbar c K}{\hbar} + \rho\right)^2 + \frac{\Gamma^2}{4\hbar^2}} ; -\left(\frac{E'_0 - \hbar c K}{\hbar}\right) - i \frac{\Gamma}{2\hbar} \right] \\
&= -\frac{2\pi i}{\hbar^2} \frac{e^{\left(i\left(\frac{E'_0 - \hbar c K}{\hbar}\right) - \frac{\Gamma}{2\hbar}\right)t}}{-i \frac{\Gamma}{\hbar}} \\
&= \frac{2\pi}{\hbar \Gamma} e^{i\left(\frac{E'_0 - \hbar c K}{\hbar}\right)t - \frac{\Gamma}{2\hbar} t} \quad t > 0 . \tag{3.4}
\end{aligned}$$

Hence, combining (3.3) and (3.4), for all t

$$\int_{-\infty}^{\infty} \frac{e^{-ipt} d\rho}{(E'_0 - \hbar c K + \hbar \rho)^2 + \frac{\Gamma^2}{4}} = \frac{2\pi}{\hbar \Gamma} e^{i\left(\frac{E'_0 - \hbar c K}{\hbar}\right)t - \frac{\Gamma}{2\hbar} |t|} . \tag{3.5}$$

Using (3.5), (3.2) can be written

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} dt e^{i \left(\frac{E_0' - \hbar c K}{\hbar} \right) t - \frac{\Gamma}{2\hbar} |t|} e^{i(E_{k''} - E_k) t}$$

$$\begin{aligned} & \sum_{kk''} P_k |\langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle|^2 e^{i \left(\frac{E_{k''} - E_k}{\hbar} \right) t} \\ &= \sum_{kk''} P_k \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle^* \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle e^{i \left(\frac{E_{k''} - E_k}{\hbar} \right) t} \\ &= \sum_{kk''} P_k \langle k | e^{i\underline{K} \cdot \underline{R}} | k'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle e^{i \left(\frac{E_{k''} - E_k}{\hbar} \right) t} \quad (3.6.5) \end{aligned}$$

$$= \sum_{kk''} P_k \langle k | e^{i\underline{K} \cdot \underline{R} + i \frac{E_{k''} t}{\hbar}} | k'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R} - i \frac{E_k t}{\hbar}} | k \rangle \quad (3.7)$$

The last term in (3.6.5) can be taken into the matrix elements since it is just a number, which commutes. Since $E_{k''}$ and E_k satisfy the eigenvalue problem $H^S |k^\alpha\rangle = E_{k^\alpha} |k^\alpha\rangle$ and it is known that $f(H^S) |k^\alpha\rangle = f(E_{k^\alpha}) |k^\alpha\rangle$, then (3.7) becomes

$$\sum_{kk''} P_k \langle k | e^{i\underline{K} \cdot \underline{R} + i \frac{H^S t}{\hbar}} | k'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R} - i \frac{H^S t}{\hbar}} | k \rangle \quad (3.8)$$

Performing the sum over k'' by use of the completeness relation, (3.8) reduces to

$$\sum_k P_k \langle k | e^{i\mathbf{K} \cdot \mathbf{R} + i \frac{H^S t}{\hbar}} e^{-i\mathbf{K} \cdot \mathbf{R} - i \frac{H^S t}{\hbar}} | k \rangle . \quad (3.9)$$

To simplify the operator products in (3.9), the time dependent position coordinate $\underline{R}(t)$ is introduced. This satisfies the Heisenberg equation of motion

$$\frac{d\underline{R}(t)}{dt} = \frac{1}{i\hbar} [\underline{R}(t), H^S] \quad (3.10)$$

which has as solutions

$$\underline{R}(t) = e^{i \frac{H^S t}{\hbar}} \underline{R} e^{-i \frac{H^S t}{\hbar}} \quad (3.11)$$

so (3.9) becomes

$$\sum_k P_k \langle k | e^{i\mathbf{K} \cdot \underline{R}(0)} e^{-i\mathbf{K} \cdot \underline{R}(t)} | k \rangle .$$

Hence (3.6) has been reduced to

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} dt e^{i \left(\frac{E_0 - \hbar c K}{\hbar} \right) t - \frac{\Gamma}{2\hbar} |t|} \sum_k P_k \langle k | e^{i\mathbf{K} \cdot \underline{R}(0)} e^{-i\mathbf{K} \cdot \underline{R}(t)} | k \rangle . \quad (3.12)$$

Equation (3.12) can be related to the space-time self correlation function by the following identity:

$$\sum_{\underline{k}} P_{\underline{k}} \langle \underline{k} | e^{i\underline{K} \cdot \underline{R}(0)} e^{-i\underline{K} \cdot \underline{R}(t)} | \underline{k} \rangle \equiv \int e^{i\underline{K} \cdot \underline{r}} G_S(\underline{r}, t) d^3r \quad (3.13)$$

By inversion, $G_S(\underline{r}, t)$ is then given by

$$G_S(\underline{r}, t) = \frac{1}{(2\pi)^3} \int e^{-i\underline{K} \cdot \underline{r}} \sum_{\underline{k}} P_{\underline{k}} \langle \underline{k} | e^{i\underline{K} \cdot \underline{R}(0)} e^{-i\underline{K} \cdot \underline{R}(t)} | \underline{k} \rangle d^3K \quad (3.14)$$

Using (3.13), the cross section (3.12) can be written as

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \frac{\Gamma}{2\hbar} |t|} G_S(\underline{r}, t) d^3r dt \quad (3.15)$$

where $\hbar\omega = \hbar cK - E'_0$.

The function $G_S(\underline{r}, t)$ can be interpreted as describing the correlations between positions of one and the same particle at different times. Classically, $G_S(\underline{r}, t)$ can be defined as the probability that, given an atom at position $\underline{r} = 0$ at $t = 0$, the same atom is at position \underline{r} at time t . However, for small times, when the particle has moved only a distance of the order of the deBroglie wavelength, quantum effects are important and $G_S(\underline{r}, t)$ is complex. Van Hove has noted that only the real part of $G_S(\underline{r}, t)$ can be interpreted as the self diffusion function since the imaginary part is quantum mechanical in origin.

Several prescriptions have been used to relate the cross section $\sigma_S(\underline{K})$ to the self diffusion function. Vineyard³ suggested replacing $G_S(\underline{r}, t)$ by its classical limit (limit as $\hbar \rightarrow 0$). However, as Rosenbaum¹³ has shown, this approximation is not satisfactory since by setting $\hbar = 0$ in $G_S(\underline{r}, t)$, zero momentum transfer is implied. Also it is shown for an ideal monotomic gas that the classical limit of the scattering function

$S_S(\underline{K}, \omega)$, the Fourier transform of $G_S(\underline{r}, t)$, or

$$S_S(\underline{K}, \omega) = \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t)} G_S(\underline{r}, t) d^3r dt \quad (3.16)$$

does not equal the Fourier transform of the classical limit for the correlation function $G_S(\underline{r}, t)$. In addition, Schofield¹⁴ pointed out that the scattering function resulting from the above replacement does not satisfy the condition of detailed balance

$$S_S(\underline{K}, \omega) = e^{\hbar\omega/k_B T} S_S(-\underline{K}, -\omega) \quad (3.17)$$

which must be satisfied for a system in thermal equilibrium.

Schofield has suggested that $G_S(\underline{r}, t + i\hbar/2k_B T)$ should be considered as the self diffusion function rather than $G_S(\underline{r}, t)$. By using this prescription, the condition of detailed balance (3.17) will be satisfied. Hence rather than considering $\sigma_S(\underline{K})$ in terms of $G_S(\underline{r}, t)$, Schofield considers it in terms of the function $F_S(\underline{r}, t) = G_S(\underline{r}, t + i\hbar/2k_B T)$ which can be interpreted as the classical self diffusion function. To introduce this function, return to (3.6) and consider the last term

$$\sum_{kk''} P_k \left| \langle k'' | e^{-i\underline{K} \cdot \underline{R}} | k \rangle \right|^2 e^{i \left(\frac{E_{k''} - E_k}{\hbar} \right) t} .$$

For a system in thermodynamic equilibrium, the probability of the center of mass motion being a particular state k or k'' is

$$P_k = \frac{e^{-E_k/k_B T}}{\sum_{k'} e^{-E_{k'}/k_B T}} \quad \text{and} \quad P_{k''} = \frac{e^{-E_{k''}/k_B T}}{\sum_{k'} e^{-E_{k'}/k_B T}} .$$

Hence

$$P_k = P_{k''} \frac{e^{-E_k/k_B T}}{e^{-E_{k''}/k_B T}} = P_{k''} e^{(E_{k''} - E_k)/k_B T} . \quad (3.18)$$

Using (3.18), the last term in (3.6) can be written

$$\sum_{kk''} e^{\frac{(E_{k''}-E_k)}{2k_B T}} \sqrt{P_k} \sqrt{P_{k''}} |\langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}}{\hbar}} | k \rangle|^2 e^{i\left(\frac{E_{k''}-E_k}{\hbar}\right)t} .$$

Now also noting the fact that

$$\begin{aligned} & \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{kk''} e^{(E_{k''}-E_k)/2k_B T} \sqrt{P_k} \sqrt{P_{k''}} |\langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}}{\hbar}} | k \rangle|^2 e^{i\left(\frac{E_{k''}-E_k}{\hbar}\right)t} dt \\ &= \sum_{kk''} e^{\hbar\omega/2k_B T} \sqrt{P_k} \sqrt{P_{k''}} |\langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}}{\hbar}} | k \rangle|^2 \delta\left(\omega - \frac{E_{k''}-E_k}{\hbar}\right) \end{aligned}$$

(3.6) can be written as

$$\begin{aligned} \sigma_S(\underline{K}) &= \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t - \frac{\Gamma}{2\hbar} |t|} e^{\hbar\omega/2k_B T} \\ & \quad (x) \sum_{kk''} \sqrt{P_k} \sqrt{P_{k''}} |\langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}}{\hbar}} | k \rangle|^2 e^{i\left(\frac{E_{k''}-E_k}{\hbar}\right)t} . \end{aligned} \quad (3.19)$$

In the same manner as done previously, (3.19) can be written in terms of the time dependent position coordinate since

$$\begin{aligned} & |\langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}}{\hbar}} | k \rangle|^2 e^{i\left(\frac{E_{k''}-E_k}{\hbar}\right)t} \\ &= \langle k | e^{i\frac{\underline{K} \cdot \underline{R}(0)}{\hbar}} | k'' \rangle \langle k'' | e^{-i\frac{\underline{K} \cdot \underline{R}(t)}{\hbar}} | k \rangle \end{aligned}$$

so

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t - \frac{\Gamma}{2\hbar} |t|} e^{\hbar\omega/2k_B T}$$

$$(x) \sum_{kk''} \sqrt{P_k} \sqrt{P_{k''}} \langle k | e^{i\underline{K} \cdot \underline{R}(0)} | k'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}(t)} | k \rangle \quad (3.20)$$

Now, if the function $F_S(\underline{r}, t)$ is defined as

$$F_S(\underline{r}, t) \equiv \frac{1}{(2\pi)^3} \int e^{-i\underline{K} \cdot \underline{r}} \sum_{kk''} \sqrt{P_k} \sqrt{P_{k''}}$$

$$(x) \langle k | e^{i\underline{K} \cdot \underline{R}(0)} | k'' \rangle \langle k'' | e^{-i\underline{K} \cdot \underline{R}(t)} | k \rangle d^3K \quad (3.21)$$

(3.20) becomes

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} e^{\hbar\omega/2k_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \frac{\Gamma}{2\hbar} |t|} F_S(\underline{r}, t) d^3r dt \quad (3.22)$$

The identity $F_S(\underline{r}, t) = G_S(\underline{r}, t + i\hbar/2k_B T)$ can easily be verified by considering the replacement $t \rightarrow t + i\hbar/2k_B T$ in (3.14). By rewriting (3.14) with the help of (3.7), the replacement gives a term $e^{-\hbar\omega/2k_B T}$ and by substitution of $\sqrt{P_k}$ from (3.18) a term $e^{\hbar\omega/2k_B T}$ is obtained, verifying the identity.

It is known that the self correlation function in the case of a solid (cubic crystal lattice) and a gas has a Gaussian form

$$G_S(\underline{r}, t) = (2\pi \gamma(t))^{-3/2} e^{-r^2/2\gamma(t)} \quad (3.23)$$

where $\gamma(t)$ is the Gaussian width as a function of time. Van Hove¹ has shown in the case of an ideal gas that

$$\gamma(t) = -i \frac{\hbar t}{M} + \frac{k_B T t^2}{M} \quad (3.24)$$

and in the case of a monatomic cubic crystal that

$$\gamma(t) = \frac{\hbar^2}{M} \int_0^\infty \left[\coth\left(\frac{z}{2k_B T}\right) \left(1 - \cos \frac{zt}{\hbar}\right) - i \sin \frac{zt}{\hbar} \right] \frac{f(z)}{z} dz \quad (3.25)$$

where $f(z)$ is the normalized distribution of phonon energy levels.

The function $F_s(\underline{r}, t)$ will also have a Gaussian shape, or

$$F_s(\underline{r}, t) = (2\pi\rho(t))^{-3/2} e^{-r^2/2\rho(t)} \quad (3.26)$$

where $\rho(t)$ is the Gaussian width as a function of time and in the ideal gas and cubic crystal can be obtained from (3.24) and (3.25) simply by using the Schofield prescription since

$$\rho(t) = \gamma\left(t + \frac{i\hbar}{2k_B T}\right)$$

Hence, for the ideal gas

$$\rho(t) = \frac{\hbar^2}{4Mk_B T} + \frac{k_B T}{M} t^2 \quad (3.27)$$

and for the monatomic cubic crystal

$$\rho(t) = \frac{\hbar^2}{M} \int_0^\infty \frac{f(z)}{z} \left[\tanh \frac{z}{4k_B T} + \frac{1 - \cos \frac{zt}{\hbar}}{\sinh \frac{z}{2k_B T}} \right] dz \quad (3.28)$$

In the case of liquids, however, the Gaussian width function $\rho(t)$ is not known. In fact, it is not even known whether the self diffusion function $F_s(\underline{r}, t)$ is Gaussian at all times. However, it is reasonable to assume that the function is Gaussian since it is known that liquids have Gaussian behavior for both small times where the diffusing atom acts as a free particle and at large times where the atom acts as a diffusing particle. At small times then the behavior of a liquid is like that of the ideal gas with

the characteristic $\rho(t) \sim t^2$ behavior of the Gaussian width.* From the form of $\rho(t)$ for the ideal gas in (3.27), it is apparent that even at $t = 0$ there is a finite extension of the Gaussian since $\rho(0) = \hbar^2/4Mk_B T$. This is in agreement with what would be expected from consideration of the Heisenberg uncertainty principle. Since a liquid behaves much like the ideal gas at small times, it is not unreasonable to assume that the Gaussian for the liquid would also have the same finite extension at $t = 0$.¹⁵ With $\rho(0) = \hbar^2/4Mk_B T$ in $F_S(\underline{r}, 0)$,

$$\int e^{i\underline{K} \cdot \underline{r}} F_S(\underline{r}, 0) d^3r = e^{-\hbar^2 K^2 / 8Mk_B T}.$$

With this quantum mechanical correction applied to (3.22), $F_S(\underline{r}, t)$ can be considered as the classical self diffusion function $F_S^c(\underline{r}, t)$. Hence

$$\sigma_S(\underline{K}) = \frac{\sigma_0 \Gamma}{4\hbar} e^{\frac{\hbar\omega}{2k_B T} - \hbar^2 K^2 / 8Mk_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \Gamma/2\hbar |t|} F_S^c(\underline{r}, t) d^3r dt \quad (3.29)$$

describes the cross section in terms of the classical self diffusion function.**

The cross section for nuclear resonance scattering (3.29) has been pushed to the point where it is necessary to propose models to describe the classical self diffusion function $F_S^c(\underline{r}, t)$ for liquids. Two such models

*Vineyard³ has shown that the ideal gas, oscillator, and Debye lattice all have this form for small times.

**Rosenbaum¹³ derived (3.29) with considerably more rigor, which seems to verify the simple plausibility argument of Singwi and Sjölander. This also points up the fact that Schofield's prescription appears to be valid only in the limit of gamma rays with small momenta and heavy atom resonant scatterers.

will be considered in Section IV, however, before getting to that point it is necessary to consider the actual experimental situation in a little more detail and the quantity of interest in a measurement.

Although it is possible to perform resonant scattering experiments, these experiments suffer in intensity due to scattering into 4π solid angle. Instead, transmission experiments are performed in which the change in gamma ray intensity is observed along the axis of the incident gamma ray beam. The cross section measured in this way will include all processes which remove gamma rays from the incident beam. This includes the resonant scattering cross section which due to 4π scattering is essentially a removal process in a transmission experiment and internal conversion which is a gamma ray resonant absorption process.* Assuming these are the only two resonant processes, the removal cross section** can be written

$$\sigma_r(\underline{K}) = \sigma_s(\underline{K}) + \sigma_{IC}(\underline{K}) \quad .$$

The internal conversion cross section can be treated in the same way as the width function for internal conversion was treated in Section II and $\sigma_{IC}(\underline{K})$ is related to $\sigma_s(\underline{K})$ by the same function α , or

$$\sigma_{IC}(\underline{K}) = \alpha \sigma_s(\underline{K})$$

and

*Only resonant processes are of interest here. Non-resonant processes such as the photoelectric effect may be quite significant but are of interest only for the sake of intensity and not in the shape of the resonant cross section.

**The removal cross section is commonly referred to as the absorption cross section in the literature. This seems rather inappropriate to the nuclear engineer since the removal process also includes scattering.

$$\sigma_r(\underline{K}) = (1+\alpha) \sigma_s(\underline{K}) .$$

Hence,

$$\sigma_r(\underline{K}) = \frac{\sigma'_0 \Gamma}{4\hbar} e^{\hbar\omega/2k_B T - \hbar^2 K^2/8Mk_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \Gamma/2\hbar |t|} F_s^c(\underline{r}, t) d^3r dt \quad (3.30)$$

where $\sigma'_0 = \sigma_0(1+\alpha)$ and using (2.64) and (2.48.5)

$$\sigma'_0 = 2 \left(\frac{2j''+1}{2j+1} \right) \pi \lambda^2 \frac{\Gamma^\gamma}{\Gamma} \quad (3.31)$$

The usual Mössbauer experiment is carried out using as a source of gamma rays the decay of a nuclide identical to that of the absorber. This transition is one from an intermediate state to a ground state like that treated previously in consideration of the resonant scattering cross section in Section II. The gamma rays emitted in this transition will have an energy spectrum similar in form to the energy dependence of the resonant cross section. The cross section obtained from a transmission measurement will then be the overlap of the incident spectrum and the resonant absorption cross section. This cross section is usually referred to as the self-absorption cross section and for a thin absorber can be written as

$$\sigma' = \int_0^{\infty} \sigma_r(E) W_e(E) dE . \quad (3.32)$$

where

$$\sigma_r(E) = \frac{\sigma'_0 \Gamma}{4\hbar} e^{\hbar\omega/2k_B T - \hbar^2 K^2/8Mk_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \Gamma/2\hbar |t|} F_s^c(\underline{r}, t) d^3r dt \quad (3.33)$$

and $W_e(E)$ is the normalized probability for the emission of a gamma ray of energy E . $W_e(E)$ can be obtained in much the same manner as the cross section was derived in Section II, hence the details will not be included. The essential difference is the fact that the emission is a direct process between the intermediate and final states, thus involves use of $G_{n'n}^{(1)}$ rather than $G_{n'n}^{(2)}$. The result of the calculation is a form for $W_e(E)$ like that of (2.65) with the roles of k and k'' reversed, or

$$W_e(E) = C \sum_{kk''} P_k \frac{|\langle k | e^{-i\mathbf{K}\cdot\mathbf{R}} | k'' \rangle|^2}{(E'_0 + E_k - E_{k''} - E)^2 + \frac{\Gamma^2}{4}} \quad (3.34)$$

where the normalization constant C can be shown to have the value $\Gamma/2\pi$.¹⁶

The emission probability (3.34) can also be written in terms of the self correlation function $G_S(\underline{r}, t)$ using the procedure from the first part of this section. The result is

$$W_e(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \int e^{i(\mathbf{K}\cdot\mathbf{r} - \omega t) - \Gamma/2\hbar |t|} G_S(\underline{r}, t) d^3r dt \quad (3.35)$$

In the Mössbauer experiment of interest, the source will be in the solid state, hence (3.35) can be evaluated further using $G_S(\underline{r}, t)$ from (3.23) and $\gamma(t)$ from (3.25) for the monatomic cubic crystal. So

$$\begin{aligned} W_e(E) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \int e^{i(\mathbf{K}\cdot\mathbf{r} - \omega t) - \Gamma/2\hbar |t|} [2\pi\gamma(t)]^{-3/2} e^{-r^2/2\gamma(t)} d^3r dt \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} \int [2\pi\gamma(t)]^{-3/2} e^{i\mathbf{K}\cdot\mathbf{r}} e^{-r^2/2\gamma(t)} d^3r dt \quad (3.36) \end{aligned}$$

Performing the integral over d^3r in (3.36)

$$\begin{aligned}
 \int [2\pi\gamma(t)]^{-3/2} e^{i\mathbf{K}\cdot\mathbf{r}} e^{-r^2/2\gamma(t)} d^3r &= [2\pi\gamma(t)]^{-3/2} 2\pi \int_0^\infty r^2 e^{-r^2/2\gamma(t)} \int_{-1}^{+1} e^{iKr\mu} d\mu dr \\
 &= [2\pi\gamma(t)]^{-3/2} \frac{4\pi}{K} \int_0^\infty r e^{-r^2/2\gamma(t)} \sin Kr dr \\
 &= [2\pi\gamma(t)]^{-3/2} \frac{4\pi}{K} \left[-\sin Kr\gamma(t) e^{-r^2/2\gamma(t)} \Big|_0^\infty + \int_0^\infty \gamma(t) e^{-r^2/2\gamma(t)} K \cos Kr dr \right] \\
 &= [2\pi\gamma(t)]^{-3/2} 4\pi\gamma(t) \cdot \frac{\sqrt{\pi}}{2} \sqrt{2\gamma(t)} e^{-K^2/2\cdot\gamma(t)} \\
 &= e^{-K^2/2\cdot\gamma(t)} \tag{3.37}
 \end{aligned}$$

and so (3.36) becomes

$$W_e(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} e^{-K^2/2\cdot\gamma(t)} dt \quad . \tag{3.38}$$

Equation (3.38) can be rewritten in the form

$$\begin{aligned}
 W_e(E) &= \frac{1}{2\pi\hbar} \left[e^{-K^2/2\cdot\gamma(\infty)} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} dt \right. \\
 &\quad \left. + e^{-K^2/2\cdot\gamma(\infty)} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} \left\{ e^{K^2/2\cdot\gamma(\infty)} - K^2/2\cdot\gamma(t) - 1 \right\} dt \right] \\
 &\tag{3.39}
 \end{aligned}$$

where $\gamma(\infty)$ is $\gamma(t)$ evaluated at $t = \infty$. Expanding the term in the curly brackets in (3.39),

$$e^{K^2/2[\gamma(\infty) - \gamma(t)]} = 1 + \frac{K^2}{2} [\gamma(\infty) - \gamma(t)] + \frac{\left(\frac{K^2}{2}\right)^2 [\gamma(\infty) - \gamma(t)]^2}{2!} + \dots$$

so

$$\left\{ e^{K^2/2 \gamma(\infty)} - K^2/2 \gamma(t) - 1 \right\} = \sum_{n=1}^{\infty} \frac{\left(\frac{K^2}{2}\right)^n [\gamma(\infty) - \gamma(t)]^n}{n!} \quad (3.40)$$

With (3.40), (3.39) can be written

$$W_e(E) = \frac{1}{2\pi\hbar} e^{-2W} \left[\int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} dt + \sum_{n=1}^{\infty} \frac{\left(\frac{K^2}{2}\right)^n}{n!} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} [\gamma(\infty) - \gamma(t)]^n dt \right] \quad (3.41)$$

where $2W = K^2/2 \gamma(\infty)$ is the familiar Debye-Waller factor. The first integral in (3.41) can be performed and

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} dt &= 2 \int_0^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} dt \\ &= \frac{2}{-i\omega - \frac{\Gamma}{2\hbar}} [-1] \\ &= \frac{-2 \left(i\omega - \frac{\Gamma}{2\hbar} \right)}{\omega^2 + \left(\frac{\Gamma}{2\hbar} \right)^2} \\ &= \frac{\hbar\Gamma}{(E-E'_0)^2 + \frac{\Gamma^2}{4}} - i \frac{2\hbar^2\omega}{(E-E'_0)^2 + \frac{\Gamma^2}{4}} \quad (3.42) \end{aligned}$$

Taking the real part of the integral in (3.41),

$$W_e(E) = \frac{1}{2\pi\hbar} e^{-2W} \left[\frac{h\Gamma}{(E-E'_0)^2 + \frac{\Gamma^2}{4}} + \sum_{n=1}^{\infty} \frac{\left(\frac{K^2}{2}\right)^n}{n!} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t|} [\gamma(\infty) - \gamma(t)]^n dt \right] \quad (3.43)$$

The first term in (3.43) represents recoilless emission of gamma rays and is a line with natural width Γ . The remaining terms correspond to phonon exchange in the crystal. For our purposes, the phonon part can be neglected and only the Mössbauer pip (zero phonon line) considered, so

$$W_e(E) = \frac{\Gamma}{2\pi} e^{-2W} \frac{1}{(E-E'_0)^2 + \frac{\Gamma^2}{4}} \quad (3.44)$$

$2W$ can be evaluated using (3.25), or

$$\begin{aligned} 2W &= \frac{K^2}{2} \gamma(\infty) = \lim_{t \rightarrow \infty} \frac{\hbar^2 K^2}{2M} \int_0^{\infty} \left[\coth\left(\frac{z}{2k_B T}\right) \left(1 - \cos \frac{zt}{\hbar}\right) - i \sin \frac{zt}{\hbar} \right] \frac{f(z)}{z} dz \\ &= \frac{\hbar^2 K^2}{2M} \int_0^{\infty} \coth\left(\frac{z}{2k_B T}\right) \cdot \frac{f(z)}{z} dz \quad (3.45) \end{aligned}$$

Equation (3.45) cannot be evaluated further without knowledge of $f(z)$, the distribution of phonon energy levels in the crystal. In the Debye approximation, the crystal is assumed to have a phonon distribution $f(z) \sim z^2$ extending to an upper limit characteristic of the particular solid. The normalized distribution is given as

$$\begin{aligned}
f(z) &= 3z^2/(k_B\theta_D)^3 & z \leq k_B\theta_D \\
&= D & z > k_B\theta_D
\end{aligned}
\tag{3.46}$$

where θ_D is the characteristic Debye temperature. Using (3.46)

$$2W = \frac{\hbar^2 K^2}{2M} \int_0^{k_B\theta_D} \coth\left(\frac{z}{2k_B T}\right) \cdot \frac{3z}{(k_B\theta_D)^3} dz .$$

Letting $y \equiv z/k_B T$,

$$\begin{aligned}
2W &= \frac{\hbar^2 K^2}{2M} \cdot \frac{3}{k_B\theta_D} \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} y \coth\left(\frac{y}{2}\right) dy \\
&= \frac{\hbar^2 K^2}{2M} \cdot \frac{3}{k_B\theta_D} \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} y \left(\frac{e^y+1}{e^y-1}\right) dy \\
&= \frac{\hbar^2 K^2}{2M} \cdot \frac{3}{k_B\theta_D} \left(\frac{T}{\theta_D}\right)^2 \left[\int_0^{\theta_D/T} \frac{ye^y dy}{e^y-1} + \int_0^{\theta_D/T} \frac{y dy}{e^y-1} \right]
\end{aligned}$$

but

$$\int_0^{\theta_D/T} \frac{ye^y dy}{e^y-1} = \int_0^{\theta_D/T} \frac{y \cdot dy}{e^y-1} + \int_0^{\theta_D/T} y dy$$

so

$$\begin{aligned}
2W &= \frac{\hbar^2 K^2}{2M} \cdot \frac{3}{k_B\theta_D} \left(\frac{T}{\theta_D}\right)^2 \left[\frac{1}{2} \left(\frac{\theta_D}{T}\right)^2 + 2 \int_0^{\theta_D/T} \frac{y dy}{e^y-1} \right] \\
2W &= \frac{\hbar^2 K^2}{2M} \cdot \frac{6}{k_B\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{y dy}{e^y-1} \right]
\end{aligned}
\tag{3.47}$$

in the Debye approximation. The integral has been tabulated by Zener¹⁷ for different values of θ_D/T .

Using the result (3.44), the self-absorption cross section (3.32) can be written

$$\sigma' = \frac{\Gamma}{2\pi} e^{-2W} \int_0^{\infty} \sigma_r(E) \frac{dE}{(E-E'_0)^2 + \frac{\Gamma^2}{4}} \quad (3.48)$$

where $2W$ is assumed to be constant over the range of E for which σ_r is significant, or

$$2W \approx \frac{(E_0)^2}{2Mc^2} \cdot \frac{6}{k_B\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{y dy}{e^y - 1} \right]. \quad (3.49)$$

In a Mössbauer experiment, the source is moved with a velocity v with respect to the absorber. This provides a Doppler shift in energy of the emitted gamma ray equal to $S = v/c E_0$ where c is the velocity of light. The argument of $W_e(E)$ should then be $E+S$. This then gives the self-absorption cross section as a function of the source velocity, the quantity obtained from the measurements in a Mössbauer experiment. So

$$\sigma'(S) = \frac{\Gamma}{2\pi} e^{-2W} \int_0^{\infty} \sigma_r(E) \frac{dE}{(E+S-E'_0)^2 + \frac{\Gamma^2}{4}} \quad (3.50)$$

is the cross section which can be measured in a Mössbauer experiment in which the source is in the solid state and moved with a velocity v with respect to the absorber which is in the liquid state. The factor $2W$ is given by (3.49) under the assumptions and approximations previously mentioned and

$\sigma_r(E)$ is given by (3.33) where $F_S^C(\underline{r}, t)$ is the classical self diffusion function for which models can be proposed to describe the behavior of liquids.

SECTION IV

MODELS FOR DIFFUSIVE MOTION IN LIQUIDS

The approach to be followed in dealing with liquids is one of proposing particular models for the correlation function to obtain $\sigma_r(E)$. The cross section $\sigma'(S)$ obtained for this model of $\sigma_r(E)$ can then be either confirmed or disproved by direct experimental investigation. In this section two models will be proposed and the cross section $\sigma'(S)$ will be obtained for each.

A. CONTINUOUS DIFFUSION MODEL

The first model to be considered in describing atomic motion in liquids is the continuous diffusion model which was first treated by Vineyard³ in investigating the analogous topic, slow neutron scattering in liquids.

From Section III, the removal cross section is written in terms of the classical self diffusion function as

$$\sigma_r(E) = \frac{\sigma_0 \Gamma}{4\hbar} e^{\hbar\omega/2k_B T - \hbar^2 K^2/8Mk_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K} \cdot \underline{r} - \omega t) - \Gamma/2\hbar |t|} F_s^c(\underline{r}, t) d^3 r dt . \quad (4.1)$$

Since $F_s^c(\underline{r}, t)$ is taken to describe a diffusing atom (one that suffers random alterations of velocity in brief collisions occurring at random times), the function obeys the classical diffusion equation, or

$$D\nabla^2 F_S^C(\underline{r}, t) = \frac{\partial F_S^C(\underline{r}, t)}{\partial t} \quad (4.2)$$

where D is the self diffusion coefficient. Solving (4.2) for a point source at the origin at $t = 0$ gives

$$F_S^C(\underline{r}, t) = (4\pi D|t|)^{-3/2} e^{-r^2/4D|t|} \quad (4.3)$$

or in the notation of (3.26), a width function

$$\rho(t) = 2D|t| \quad .$$

Using (4.3) in (4.1), the cross section can be evaluated further, or

$$\sigma_r(E) = \frac{\sigma_0' \Gamma}{4\hbar} e^{\hbar\omega/2k_B T - \hbar^2 K^2/8Mk_B T} \int_{-\infty}^{\infty} \int e^{i(\underline{K}\cdot\underline{r} - \omega t) - \Gamma/2\hbar |t|} (4\pi D|t|)^{-3/2} e^{-r^2/4D|t|} d^3r dt \quad . \quad (4.4)$$

Performing the integral over d^3r as in (3.37)

$$\sigma_r(E) = \frac{\sigma_0' \Gamma}{4\hbar} e^{\hbar\omega/2k_B T - \hbar^2 K^2/8Mk_B T} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t| - K^2 D|t|} dt \quad . \quad (4.5)$$

In the region of the resonance $\hbar\omega = E - E_0 \ll 2k_B T$, so the first exponential is approximately equal to 1. The second exponential is analagous to the Debye-Waller factor for a solid, so let

$$2W_a = \frac{\hbar^2 K^2}{8Mk_B T} \quad (4.6)$$

and

$$\sigma_r(E) \approx \frac{\sigma_0' \Gamma}{4\hbar} e^{-2W_a} \int_{-\infty}^{\infty} e^{-i\omega t - \Gamma/2\hbar |t| - K^2 D|t|} dt \quad .$$

Performing the integral over t as in (3.42),

$$\sigma_r(E) = \frac{\sigma'_0 \Gamma}{4\hbar} e^{-2W_a} \frac{2 \left(\frac{\Gamma}{2\hbar} + K^2 D \right)}{\omega^2 + \left(\frac{\Gamma}{2\hbar} + K^2 D \right)^2}$$

$$\sigma_r(E) = \frac{\sigma'_0 \Gamma}{4} e^{-2W_a} \frac{(\Gamma + 2\hbar K^2 D)}{(E - E'_0)^2 + \frac{1}{4} (\Gamma + 2\hbar K^2 D)^2} \quad (4.7)$$

Now, using (3.50), the cross section $\sigma'(S)$ can be written

$$\sigma'(S) = \frac{\sigma'_0 \Gamma^2}{8\pi} e^{-2W} e^{-2W_a} \int_0^\infty \frac{(\Gamma + 2\hbar K^2 D) dE}{\left[(E - E'_0)^2 + \frac{1}{4} (\Gamma + 2\hbar K^2 D)^2 \right] \left[(E + S - E'_0)^2 + \frac{\Gamma^2}{4} \right]}$$

The broadening of the line in the cross section (4.7) is given by

$$\Delta\epsilon = 2\hbar K^2 D$$

which over the range of E for which $\sigma_r(E)$ is significant is approximately constant and equal to

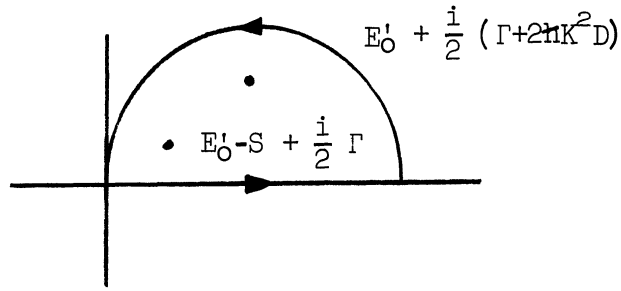
$$\Delta\epsilon \approx \frac{2E_0^2 D}{\hbar c^2} \quad (4.8)$$

so

$$\sigma'(S) \approx \frac{\sigma'_0 \Gamma^2}{8\pi} e^{-2W} e^{-2W_a} (\Gamma + 2\hbar K^2 D) \int_0^\infty \frac{dE}{\left[(E - E'_0)^2 + \frac{1}{4} (\Gamma + 2\hbar K^2 D)^2 \right] \left[(E + S - E'_0)^2 + \frac{\Gamma^2}{4} \right]}$$

(4.9)

The integral over E can be done by integrating in the complex plane on the following path



and

$$\int_0^{\infty} f(E) dE = \oint f(E) dE - \int f(E) dE .$$

The second integral goes to zero since $f(E)$ goes to zero for E far from the poles and the first integral can be evaluated by residues, so

$$\begin{aligned} \int_0^{\infty} f(E) dE &= 2\pi i \left[\text{Res } f(E); E'_0 + \frac{i}{2} (\Gamma + 2\alpha K^2 D) + \text{Res } f(E); E'_0 - S + \frac{i}{2} \Gamma \right] \\ &= 2\pi i \left[\frac{1}{i(\Gamma + 2\alpha K^2 D) \left[S + \frac{i}{2} (2\Gamma + 2\alpha K^2 D) \right] \left[S + \frac{i}{2} (2\alpha K^2 D) \right]} \right. \\ &\quad \left. + \frac{1}{i\Gamma \left[S - \frac{i}{2} (2\Gamma + 2\alpha K^2 D) \right] \left[S + \frac{i}{2} (2\alpha K^2 D) \right]} \right] . \end{aligned} \quad (4.10)$$

Expanding the two terms in (4.10) in partial fractions, two of the four terms obtained will cancel leaving

$$\begin{aligned} \int_0^{\infty} f(E) dE &= 2\pi i \left[\frac{1}{\Gamma(\Gamma + 2\alpha K^2 D)} \left\{ \frac{1}{S + \frac{i}{2} (2\Gamma + 2\alpha K^2 D)} - \frac{1}{S - \frac{i}{2} (2\Gamma + 2\alpha K^2 D)} \right\} \right] \\ &= \frac{4\pi(\Gamma + \alpha K^2 D)}{\Gamma(\Gamma + 2\alpha K^2 D)} \cdot \frac{1}{S^2 + (\Gamma + \alpha K^2 D)^2} . \end{aligned} \quad (4.11)$$

With (4.11), (4.9) can be written

$$\sigma'(s) = \frac{\sigma_0' \Gamma}{2} e^{-2W} e^{-2W_a} \frac{(\Gamma + \hbar K^2 D)}{s^2 + (\Gamma + \hbar K^2 D)^2} \quad (4.12)$$

Now consider the validity of this representation of the atomic motions in liquids. This form for the classical self diffusion function has a width which goes as $\rho(t) \sim t$; however, this representation is not valid at small times where it is known that $\rho(t) \sim t^2$ as discussed in Section III.

Hence, a second, more plausible description of the diffusing atom which would correct this poor representation at small times would be a Gaussian like (3.26) with a width function $\rho(t)$ which accounts for both limits, or

$$\begin{aligned} \rho(t) &= \frac{k_B T}{M} t^2 & t \ll \tau_D \\ &= 2Dt + C' & t \gg \tau_D \end{aligned} \quad (4.13)$$

where the small time limit is that of the ideal gas (3.27) and the large time limit is that of the diffusing atom where C' is a constant. The characteristic time τ_D is the Debye period which is related to the Debye temperature associated with a liquid (in analogy to a solid) by $\tau_D = 2\pi\hbar/k_B\theta_D$. The difficulty in this approach is the fact that there is no knowledge of the behavior at intermediate times.

Another approach to the problem is to consider $F_s^C(\underline{r}, t)$ with a Gaussian shape as in (3.26) with a width function obtained from the solution to the classical Langevin equation for Brownian motion, or

$$\rho(t) = 2D T_r \left(\frac{t}{T_r} - 1 + e^{-t/T_r} \right) \quad (4.14)$$

where T_r is the characteristic time and can be related to the diffusion coefficient by

$$T_r = \frac{MD}{k_B T} .$$

Equation (4.14) has the correct form for both small and large times; however, it is still not known whether (4.14) has the correct behavior at intermediate times. In fact, it is rather doubtful since the Langevin equation does not necessarily hold when there are strong correlation effects as in liquids. Singwi and Sjölander⁴ have shown that the results obtained using the solution to Langevin's equation differ from the results obtained using the solution to the classical diffusion equation (4.2) by only a small correction, with the leading terms identical.

B. QUASI-CRYSTALLINE MODEL

The second model to be considered in describing atomic motions in liquids is the quasi-crystalline model. This model was first treated by Singwi and Sjölander⁴ in an investigation of neutron scattering in water. In their model it is assumed that an atom performs an oscillatory motion about an equilibrium position for a mean time τ_0 before moving by a continuous diffusion process for a mean time τ_1 to a new equilibrium position, then repeating the process.

The grounds for describing liquids in this manner is partly founded on results of x-ray spectroscopy and neutron scattering measurements wherein a certain degree of order, much like that in a crystalline solid, seems to

exist in the liquid state for small times.

The quasi-crystalline model is derived by Singwi and Sjölander for a classical system and based on a probabilistic interpretation of the process, where:

The probability of finding a particle at position \underline{r} at time t when it is performing an oscillatory motion about an equilibrium position, starting from the origin at $t = 0$ is given by a Gaussian form as in (3.23) with a width function $\gamma(t)$ given by (3.25), the width function for a solid. Thus, it is assumed that the motion of the atom during the time τ_0 is like that which occurs in a solid;

The probability that a particle starting from a state of oscillatory motion at $t = 0$ remains in the same state at a later time t is given by e^{-t/τ_0} ;

The probability of finding a particle at position \underline{r} at time t when performing a diffusive motion between two equilibrium positions starting at the origin at $t = 0$ is given by (4.3), the solution to the classical diffusion equation with a diffusion coefficient defined by $D_1 = \ell^2/6\tau_1$ where ℓ^2 is the mean square displacement in time τ_1 , so ℓ is of the order of the interatomic spacing. Singwi and Sjölander indicate this form is quite satisfactory even with the poor representation at small times;

The probability that a particle starting from a state of diffusive motion at $t = 0$ remains in the same state at a later time t is given by e^{-t/τ_1} .

It is assumed in the derivation that there is no correlation between one jump and the next. For the case of interest in this paper, the more

general result is taken in the limit as $\tau_1 \rightarrow 0$, implying the jumps are instantaneous.

The results obtained by Singwi and Sjölander¹⁵ for the removal cross section $\sigma_r(E)$ for the quasi-crystalline model is

$$\sigma_r(E) = \frac{\sigma'_0 \Gamma}{4} e^{-2W_a} \frac{\Gamma + \frac{2\hbar}{\tau_0} \left(1 - e^{-2W_a/1+K^2 D \tau_0}\right)}{(E-E'_0)^2 + \frac{1}{4} \left(\Gamma + \frac{2\hbar}{\tau_0} \left[1 - e^{-2W_a/1+K^2 D \tau_0}\right]\right)^2} \quad (4.15)$$

where the diffusion coefficient is given by

$$D = \frac{R^2 + \ell^2}{6\tau_0} \quad (4.16)$$

with R^2 being the mean square radius of the fully developed thermal cloud of the oscillatory motion and e^{-2W_a} is the Debye-Waller factor for the quasi-crystalline liquid with $2W_a$ analagous to that for the solid in (3.49) and Θ_D being the Debye temperature for the quasi-crystalline liquid. Equation (3.49) can also be written as

$$2W_a = \frac{K^2}{6} \cdot R^2 \quad (4.17)$$

defining R^2 .

Using (4.15), the cross section $\sigma'(S)$ can be calculated from (3.50) in the same manner as for the continuous diffusion model. The result is

$$\sigma'(S) = \frac{\sigma'_0 \Gamma}{2} e^{-2W} e^{-2W_a} \frac{\Gamma + \frac{\hbar}{\tau} \left(1 - e^{-2W_a/1+K^2 D \tau_0}\right)}{S^2 + \left[\Gamma + \frac{\hbar}{\tau} \left(1 - e^{-2W_a/1+K^2 D \tau_0}\right)\right]^2} \quad (4.18)$$

Hence the broadening of the cross section $\sigma'(S)$ for the quasi-crystalline

model is given by

$$\Delta\epsilon = \frac{h}{\tau_0} \left(1 - e^{-2W_a / (1 + K^2 D \tau_0)} \right) . \quad (4.19)$$

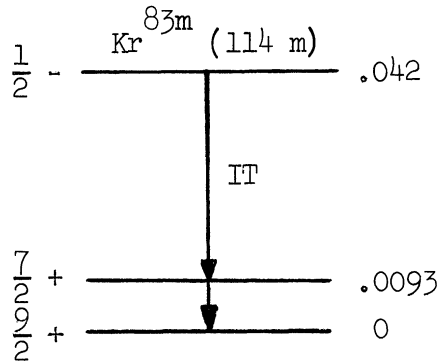
SECTION V

EXPERIMENTAL STUDY OF LIQUID KRYPTON

The purpose of this paper was to examine the possibility of performing a Mössbauer experiment to study atomic motions in liquids. Although the models discussed in Section IV are not the most sophisticated, they should serve to give a rough idea whether an experiment is feasible. This section is devoted to consideration of a particular Mössbauer nuclide, Kr^{83} , and the possibility of using it to study the dynamics of liquids. In particular, a numerical estimate of the maximum resonance self-absorption cross section is obtained using the results for the continuous diffusion model.

Kr^{83} was selected from the possible Mössbauer nuclides for this particular experiment for two reasons. First, the information obtained from an experiment would be of greatest interest for a simple monatomic fluid. For a monatomic fluid, the forces involved would be interatomic rather than intermolecular. Second, the nuclide must have certain characteristics to give a large Mössbauer effect. For the effect to be large, the Debye-Waller factor e^{-2W} must not be too small. From (3.49) it is apparent that this implies a nuclide with a low lying energy level E_0 , a large mass M , and high Debye temperature θ_D . Kr^{83} seems to fit these criteria quite well.

Now, consider the characteristics of the Kr^{83} gamma decay of interest. The decay scheme is as follows:



The half life of the 9.3 kev level has been measured as $\tau_{1/2} = 1.47 \pm .04 \times 10^{-7}$ seconds and the internal conversion coefficient has been measured as $\alpha = 11 \pm 2$.¹⁸

Some earlier Mössbauer work has been done using krypton in the solid state.¹⁹ In particular, krypton was used in clathrate compounds and the Debye temperature was determined to be $\Theta_D \sim 75^\circ\text{K}$. The melting point of krypton is 116.56°K and the boiling point is 120.26°K , so the ambient temperature of the liquid must be about 120°K . The solid could be held at liquid nitrogen temperature ($\sim 75^\circ\text{K}$) and the Debye-Waller factor is still fairly large.

Now the cross section $\sigma'(S)$ can be calculated from the data given since

$$\sigma'(S) = \frac{\sigma'_0 \Gamma}{2} e^{-2W} e^{-2W_a} \frac{(\Gamma + \hbar K^2 D)}{S^2 + (\Gamma + \hbar K^2 D)^2} \quad (5.1)$$

where

$$\sigma'_0 = 2\pi\lambda^2 \left(\frac{2j''+1}{2j+1} \right) \frac{\Gamma^\gamma}{\Gamma} \quad (5.2)$$

$$2W \approx \frac{E_0^2}{2Mc^2} \cdot \frac{6}{k_B \Theta_D} \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{y dy}{e^y - 1} \right] \quad (5.3)$$

and

$$2W_a = \frac{E_0^2}{8Mc^2 k_B T} \quad , \quad (5.4)$$

Equation (5.2) can be calculated if it is noted that $\lambda = 1/K$ so so $2\pi\lambda^2 = 2\pi h^2 c^2 / E_0^2$ and recalled that $\Gamma = \Gamma^\gamma(1+\alpha)$. Hence

$$\begin{aligned} \sigma'_0 &= \frac{h^2 c^2}{2\pi E_0^2} \left(\frac{2j''+1}{2j+1} \right) \cdot \frac{1}{1+\alpha} \\ \sigma'_0 &= \frac{(6.624 \times 10^{-27} \text{ erg-sec})^2 (3 \times 10^{10} \text{ cm/sec})^2}{2\pi (9.3 \times 10^3 \text{ ev})^2 (1.6 \times 10^{-12} \text{ erg/ev})^2} \left(\frac{8}{10} \right) \cdot \frac{1}{12} \\ \sigma'_0 &= 1.89 \times 10^{-18} \text{ cm}^2 \quad . \end{aligned} \quad (5.5)$$

The factor e^{-2W} can be calculated using (5.3) which can be rewritten as

$$2W \approx \frac{E_0^2}{2M_c^2} \cdot \frac{6T}{k_B \theta_D^2} \left[\frac{1}{4} \left(\frac{\theta_D}{T} \right) + \left(\frac{T}{\theta_D} \right) \int_0^{\theta_D/T} \frac{y \, dy}{e^y - 1} \right] .$$

The function $\frac{1}{x} \int_0^x \frac{\zeta \, d\zeta}{e^\zeta - 1} + \frac{x}{4}$ is tabulated by Zener. For this particular experiment, $x = \frac{\theta_D}{T} \approx 1$ and the function equals 1.028, so

$$2W = \frac{(9.3 \times 10^3 \text{ ev})^2 \cdot 6(75)(1.6 \times 10^{-12} \text{ erg/ev})}{2(83 \times 931.15 \times 10^6 \text{ ev})(1.38 \times 10^{-16} \text{ erg/}^\circ\text{K})(75)^2} [1.028]$$

$$2W = .533$$

or

$$e^{-2W} = .587 \quad . \quad (5.6)$$

The Debye-Waller factor for the liquid absorber can be calculated using (5.4) and

$$2W_a = \frac{E_0^2}{8Mc^2 k_B T}$$

$$2W_a = \frac{(9.3 \times 10^3 \text{ ev})^2 (1.6 \times 10^{-12} \text{ erg/ev})}{8(83 \times 931.15 \times 10^6 \text{ ev})(1.38 \times 10^{-16} \text{ erg/}^\circ\text{K})(120^\circ\text{K})}$$

$$2W_a = .0135$$

or

$$e^{-2W_a} \approx .9865 \quad (5.7)$$

The linewidth Γ is related to the lifetime of the excited state by the Heisenberg uncertainty relation $\tau \cdot \Gamma = \hbar$ where the mean life τ is related to the half life $\tau_{1/2}$ by $\tau = \tau_{1/2} / .693$ so

$$\Gamma = \frac{.693 \hbar}{2\pi \tau_{1/2}}$$

$$\Gamma = \frac{.693(6.624 \times 10^{-27} \text{ erg-sec})}{2\pi(1.47 \times 10^{-7} \text{ sec})(1.6 \times 10^{-12} \text{ erg/ev})}$$

$$\Gamma = 3.105 \times 10^{-9} \text{ ev} \quad (5.8)$$

The broadening in the cross section (5.1) due to the diffusive motion of the atoms in the absorber is given as

$$\Delta\epsilon = \hbar K^2 D = \frac{2\pi E_0^2 D}{\hbar c^2} \quad (5.9)$$

This broadening can be determined with knowledge of the diffusion coefficient D . The self-diffusion coefficient for liquid krypton has been measured by Naghizadeh and Rice²⁰ and for the temperature and pressure of 1 atm of interest here, $D \approx 1.5 \times 10^{-5} \text{ cm}^2/\text{sec}$. Hence the broadening (5.9) is equal to

$$\Delta\epsilon = \frac{2\pi(9.3 \times 10^3 \text{ev})^2(1.6 \times 10^{-12} \text{erg/ev})(1.5 \times 10^{-5} \text{cm}^2/\text{sec})}{(6.624 \times 10^{-27} \text{erg-sec})(3 \times 10^{10} \text{cm/sec})}$$

$$\Delta\epsilon = 2.19 \times 10^{-3} \text{ev} . \quad (5.10)$$

Using the results (5.5), (5.6), (5.7), (5.8) and (5.10), the cross section $\sigma'(S)$ can be calculated from (5.1). Since the broadening is much greater than the natural linewidth, Γ can be neglected in both the numerator and denominator so

$$\sigma'(S) \approx \frac{\sigma_0 \Gamma}{2} e^{-2W} e^{-2W_a} \frac{\hbar K^2 D}{S^2 + \hbar K^2 D}$$

$$\sigma'(S) = \frac{(1.89 \times 10^{-18})(3.105 \times 10^{-9})}{2} (.587)(.9865) \frac{(2.19 \times 10^{-3})}{S^2 + (2.19 \times 10^{-3})^2}$$

$$\sigma'(S) = \frac{3.72 \times 10^{-30}}{S^2 + (2.19 \times 10^{-3})^2} . \quad (5.11)$$

The maximum cross section occurs for $S = 0$, hence the maximum value of the cross section from (5.11) is

$$\sigma'(0) = \frac{3.72 \times 10^{-30}}{(2.19 \times 10^{-3})^2}$$

$$\sigma'(0) = .776 \text{ b.} \quad (5.12)$$

From this calculation it appears that an experiment is not feasible for two reasons. First, the cross section is very small compared to the non-resonant cross section for gamma ray removal (predominately by the photoelectric process at this low energy) which is about 6000 barns at 9.3 kev. Second, the broadening of the line (5.10) is much beyond the capabilities

of the conventional Mössbauer apparatus. In order to provide a Doppler shift equivalent to the width of the broadened line would require a velocity $v \sim 10^5$ cm/sec whereas to provide a shift equivalent to the natural linewidth requires only a velocity $v \sim 1$ cm/sec.

SECTION VI

CONCLUSION

It is apparent from Section V that an experiment to study atomic motion in liquid krypton is not possible. The difficulty with krypton is the fact that it behaves too much like a gas in the liquid state as is evidenced by the large diffusion coefficient. This causes an excessive broadening and subsequent decrease in the intensity.

A useful criterion then in investigating possibilities for studies of liquids using the Mössbauer effect is the ratio of the natural linewidth to the broadening term. To be useful for Mossbauer work, this ratio must be of the order of 1. Unfortunately, from a rather brief study of the possible Mössbauer nuclides, none seemed to fulfill this condition along with the conditions mentioned on page 71.

Another approach to the problem is to use the Mössbauer nuclide as a tracer element in studying the motion in the liquid in which it is dissolved. This technique has been used by two groups of experimenters, both studying the effect of the Mössbauer nuclide Fe^{57} in glycerol. In particular, they have studied the line broadening as a function of the temperature of the viscous fluid. Unfortunately the forces involved between molecules for this situation are very complicated and attempts to gain meaningful knowledge about the force laws for liquids would be nearly impossible. This is quite evident from the results reported by the two groups of experimenters. Craig

and Sutin²¹ using iron chloride dissolved in glycerol observe that the broadening seems to agree with the prediction of Vineyard's continuous diffusion model whereas Bunbury, et al,²² using iron sulfate dissolved in glycerol conclude that the broadening seems to indicate that a considerable part of the diffusion is by jumps.

Although it appears that the most informative experiment, which was investigated in this paper, is not possible using the Mössbauer effect, there is still a possibility of using the Mössbauer nuclide as a tracer to study the dynamics of liquids. At the present time, very little work has been done along this line and that which has been done is inconclusive, so there is room for additional experimentation.

SECTION VII

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