(which I am sorry I called it) but a suggestion as to the interpretation of the structure of the line, being the smallest hyperfine structure and isotope shift that would give a pattern of blends conforming with his observed Ba I structure, taking no account of Arroe's inferred Ba I isotope shifts but giving shifts qualitatively somewhat similar to Arroe's observations in Ba II. He agrees that it is preferable to find an interpretation consistent with both Jackson's and Arroe's experiments, as he is satisfied that my inference is. He points out that, moreover, my inferred component at -3.1 mK provides a very satisfactory explanation of the observed increase in the extent of his main component, at intermediate intensity, to -3.5 mK (reference 3, page 951).

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Molecular Beam Resonances in Oscillatory Fields of Nonuniform Amplitudes and Phases*

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Molecular beam resonances are discussed for molecules subjected to various combinations of nonuniform fixed and oscillatory fields. The transition probability equations are reduced to forms which are suitable for digital computer calculations. A UNIVAC computer program for the calculation of the shapes of the resonances has been developed which is applicable to systems involving simultaneous transitions between two or three different energy levels and to cases where the magnitudes of the fixed fields, the amplitudes of the oscillatory fields, and the phases of the oscillatory fields vary arbitrarily throughout the transition region. The calculation is applicable to systems perturbed at as many as nine different frequencies simultaneously and to arbitrarily determined molecular velocity distributions. Curves are shown for molecular beam resonances with two, three, and four separated oscillatory fields and for resonances with a gradually applied single oscillatory field. The effects of phase variation along the beam in distorting a separated oscillatory field resonance are discussed.

I. INTRODUCTION

IN his original molecular beam resonance proposal, Rabi[1] considered only a single uniform oscillatory field region. Several years ago Ramsey[2] pointed out that this was not the only method of applying the oscillatory field since resonance curves of a different and often more useful character could be obtained if the amplitude and phase of the oscillating field were varied along the path of the beam. However, the only arrangement which he discussed in detail was that of his separated oscillatory field method in which the oscillatory field is confined to small initial and final regions, with no oscillating field in between. It was shown that the separated oscillatory field method often provided much narrower resonances than a single oscillatory field and that the resonance was less affected by Doppler broadening. Other, possible configurations of oscillatory fields were not discussed because of the difficulty in calculating the shapes of the resonances for more complicated field configurations. In the present paper general methods are presented for the calculation of the shapes of molecular beam resonances under a wide variety of circumstances. Results of calculations of the shapes of the resonances for various field configurations are described.

II. PROBABILITY AMPLITUDE EQUATIONS

Consider a system with three eigenstates p, q, and r of the Hamiltonian $\mathcal{H}_0$. Let the system be acted upon by the additional time-dependent perturbation V and let $\langle p|t\rangle$ represent the transformation function between the eigenvector $|p\rangle$ of the pth eigenstate of $\mathcal{H}_0$ and the general time-dependent state vector $|t\rangle$ of the system with $\mathcal{H}=\mathcal{H}_0+V$. Then by a simple generalization to three energy levels of the well-known[3] two-level relations, the three appropriate differential equations are

$$i\hbar\frac{d}{dt}\langle p|t\rangle=\langle p|\mathcal{H}_0|p\rangle\langle p|t\rangle+\langle p|V|p\rangle\langle p|t\rangle+\langle p|V|q\rangle\langle q|t\rangle+\langle p|V|r\rangle\langle r|t\rangle, \qquad (1)_{\text{cyc}}$$

together with the two equations obtained by cyclic permutations of p, q, and r. Here and subsequently, the subscript "cyc" behind the equation number indicates that the equation represents the three equations obtainable by cyclic permutations of p, q, and r.

Equation (1) is exact but it is excessively general for integration since no limitations on the forms of $\mathcal{H}_0$ and V have been made. A wide variety of relevant problems

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[1] I. I. Babi *et al.*, Phys. Rev. **53**, 318 (1938); and **55**, 728 (1939).

[2] N. F. Ramsey, Phys. Rev. **76**, 996 (1949); **78**, 695 (1950); and **84**, 506 (1951).

[3] N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1955), pp. 119 and 127.

can be included if $\mathcal{H}_0$ and V are restricted to forms which provide Hermitian matrix elements such that

$$\begin{aligned}
&\langle p|\mathcal{H}_0|p\rangle/\hbar=a_p,\\
&\langle p|V|q\rangle/\hbar=b_r\exp[i(\omega_{br}t+\delta_{br})]\\
&\qquad\qquad+c_r\exp[i(\omega_{cr}t+\delta_{cr})],\\
&\langle p|V|r\rangle/\hbar=b_q\exp[i(-\omega_{bq}t-\delta_{bq})]\\
&\qquad\qquad+c_q\exp[i(-\omega_{cq}t-\delta_{cq})],\\
&\langle p|V|p\rangle/\hbar=d_p\cos(\omega_{dp}t+\delta_{dq}),
\end{aligned}\qquad(2)_{\text{cyc}}$$

where a_p, b_p, c_p, d_p, δ_{cp}, δ_{dp}, etc. are real constants that are not explicit functions of the time, although they may vary in magnitude along the path of the beam. For example, if the amplitude of b_r vanishes everywhere except at the beginning and end of the transition region, the condition corresponds to that of the separated oscillatory field method. The quantities ω_{cp}, etc., correspond to the various frequencies of the perturbations and are assumed to be unaltered throughout the transition region.

If Eq. (2) is substituted into Eq. (1) the required three complex simultaneous differential equations for $\langle p|t\rangle$ are obtained. Alternatively these three complex differential equations could be reduced to six equations for the real and imaginary parts respectively of each $\langle p|t\rangle$. For only two energy levels, for a constant oscillatory field amplitude, and for a single perturbing frequency, these equations have known integrals,[3] but this is not true for the more general cases considered here.

III. REDUCTION TO ITERABLE FORM

In principle, the combination of Eqs. (1) and (2) together with a knowledge of a_p, etc., and of the initial conditions $\langle p|0\rangle$, etc., provide equations that could be numerically integrated to yield the desired transition probabilities. In practice, however, such a straightforward numerical integration procedure is not useful; in a typical experiment the molecules are subject to frequencies of 10^7 cycles per second for 0.01 second so a million or more successive steps would be required for a direct numerical integration with a moderate number of steps per cycle; such an integration would have to be completed for several different velocities before a single theoretical point on a resonance curve could be obtained.

However, for most significant problems the oscillatory frequencies of the perturbations are much greater than the rates at which the perturbation and probability amplitudes change as the molecules go through the transition region. Consequently, for an interval of time Δ including a considerable number of cycles, the coefficients in Eqs. (1) and (2) may be treated as approximately constant. Under such conditions expressions for the integrals can be obtained in terms of well-known functions.

The results of the above integration over time Δ may be written as

$$\begin{aligned}
\langle p|t+\Delta\rangle_R={}&F(a_p,d_p,\omega_{dp},t,\Delta)\langle p|t\rangle_R\\
&+[G(a_p,a_q,b_r,\omega_{br},\delta_{br},t,\Delta)\\
&+G(a_p,a_q,c_r,\omega_{cr},\delta_{cr},t,\Delta)]\langle q|t\rangle_R\\
&+[G(a_p,\,a_r,\,b_q,\,-\omega_{bq},\,-\delta_{bq},\,t,\,\Delta)\\
&+G(a_p,\,a_r,\,c_q,\,-\omega_{cq},\,-\delta_{cq},\,t,\,\Delta)]\langle r|t\rangle_R\\
&+H(a_p,d_p,\omega_{dp},\delta_{dp},t,\Delta)\langle p|t\rangle_I\\
&+[I(a_p,a_q,b_r,\omega_{br},\delta_{br},t,\Delta)\\
&+I(a_p,a_q,c_r,\omega_{cr},\delta_{cr},t,\Delta)]\langle q|t\rangle_I\\
&+[I(a_p,\,a_r,\,b_q,\,-\omega_{bq},\,-\delta_{bq},\,t,\,\Delta)\\
&+I(a_p,a_r,c_q,\,-\omega_{cq},\,-\delta_{cq},\,t,\,\Delta)]\langle r|t\rangle_I,\quad(3)_{\text{cyc}};\\
\langle p|t+\Delta\rangle_I={}&-H(a_p,d_p,\omega_{dp},\delta_{dp},t,\Delta)\langle p|t\rangle_R\\
&-[I(a_p,a_q,b_r,\omega_{br},\delta_{br},t,\Delta)\\
&+I(a_p,a_q,c_r,\omega_{cr},\delta_{cr},t,\Delta)]\langle q|t\rangle_R\\
&-[I(a_p,\,a_r,\,b_q,\,-\omega_{bq},\,-\delta_{bq},\,t,\,\Delta)\\
&+I(a_p,\,a_r,\,c_q,\,-\omega_{cq},\,-\delta_{cq},\,t,\,\Delta)]\langle r|t\rangle_R\\
&+F(a_p,d_p,\omega_{dp},\delta_{dp},t,\Delta)\langle p|t\rangle_I\\
&+[G(a_p,a_q,b_r,\omega_{br},\delta_{br},t,\Delta)\\
&+G(a_p,a_q,c_\imath,\omega_{cr},\delta_{cr},t,\Delta)]\langle q|t\rangle_I\\
&+[G(a_p,\,a_r,\,b_q,\,-\omega_{bq},\,-\delta_{bq},\,t,\,\Delta)\\
&+G(a_p,\,a_r,\,c_q,\,-\omega_{cq},\,-\delta_{cq},\,t,\,\Delta)]\langle r|t\rangle_I,
\end{aligned}$$

where

$$\begin{aligned}
&F(a,d,\omega,\delta,t,\Delta)\\
&\quad=\cos(a\Delta)-2d\cos[\omega(t+\Delta/2)+\delta]\\
&\qquad\qquad\times\sin(a\Delta)[\sin(\omega\Delta/2)]/\omega,\\
&G(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=2b\sin[\omega(t+\Delta/2)-(a_x+a_y)\Delta/2+\delta]\\
&\qquad\qquad\times\{\sin[(\omega-a_x+a_y)\Delta/2]\}/(\omega-a_y+a_x),\\
&H(a,d,\omega,\delta,t,\Delta)\\
&\quad=\sin(a\Delta)+2d\cos[\omega(t+\Delta/2)+\delta]\\
&\qquad\qquad\times\cos(a\Delta)[\sin(\omega\Delta/2)]/\omega,\\
&I(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=2b\cos[\omega(t+\Delta/2)-(a_x+a_y)\Delta/2+\delta]\\
&\qquad\qquad\times\{\sin[(\omega-a_y+a_x)\Delta/2]\}/(\omega-a_y+a_x).
\end{aligned}\qquad(4)$$

The subscripts R and I indicate real and imaginary components. The conditions for the validity of Eq. (3) are (a) that Δ must be sufficiently small for the quantities a_p, b_p, δ_{bp}, etc., not to change significantly throughout the time Δ, and (b) that Δ must be sufficiently small for the products of Δ times the perturbation coefficients b_p, c_p, d_p, etc., to be small compared to one. The last condition must be well satisfied since Eq. (3) is ordinarily used many successive times and errors may tend to accumulate.

IV. CALCULATIONS OF TRANSITION PROBABILITIES

The formulas of Eq. (3) which relate $\langle p|t+\Delta\rangle$ to $\langle p|t\rangle$, etc., may be used successively many times to go from the initial probability amplitudes $\langle p|0\rangle$'s to the final $\langle p|t\rangle$'s. Since this iterative procedure may have to be applied a hundred or more times to obtain a single transition probability for a single molecular velocity, it is best done with the aid of a high-speed digital computer. This problem has been programmed for such a computer and coded for the UNIVAC I. In the program, the twenty-one quantities a_p, b_p, c_p, d_p, δ_{bp}, δ_{cp}, δ_{dp}, etc., may vary along the beam path in an arbitrary fashion provided only that their values can be satisfactorily inferred by linear interpolation between values tabulated at twenty arbitrarily chosen points along the beam. For each resonance frequency, the transition probability can be calculated at up to twenty different molecular velocities and these can be averaged with arbitrarily chosen weights to provide an average over any desired probability distribution. Ordinarily an average over only five velocities is sufficient and for some purposes the use of a single velocity is adequate and much faster.

With no significant increase in computing time, the final occupation probabilities of all three states can be calculated separately. The extent to which these add up to unity provides a measure of the degree to which the validity conditions discussed at the end of the previous section are satisfied.

V. SINGLE PERTURBATION FORMULATION

The above procedure is of course applicable to cases in which only a single oscillatory perturbation is applied and in which only two energy levels are concerned. Such a case would correspond to all b_p, c_p, d_p, etc., being equal to zero except for b_r, so that transitions occur only between levels p and q with a perturbation at the single frequence ω_{br}. However, such a procedure is wasteful of computation time since for this special case the following much more efficient program can be devised which is not dependent upon the validity restriction (b) at the end of Sec. III. Consequently, greater accuracy can be achieved with fewer iterative steps.

In the single perturbation case, advantage can be taken of the fact that Eq. (1) can be solved exactly if a_p, a_q, c_r, and δ_r are constant. These solutions can be used as the basis of the iteration; there is then no objection to large variations of $\langle p|t\rangle$ and $\langle q|t\rangle$ over the time Δ. From the standard form of these solutions,[3] it can be seen that all the procedures of the above sections remain applicable except that in Eq. (3) $F(a_p,d_p,\omega_{dp},\delta_{dp},t,\Delta)$ is replaced by $F'(a_p,a_q,b_r,\omega_{br},\delta_{br},t,\Delta)$ with a similar change being made for H, whereas G and I are merely replaced by G' and I' with the variables upon which they depend being unaltered. The G's and I's which depend on c_r may be omitted but that is not necessary since these functions vanish in any case for the assumed conditions. Equation (4) is replaced by the following new set of defining equations:

$$\begin{aligned}
&F'(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=\cos[(\omega-a_x-a_y)\Delta/2]\cos(A\Delta/2)+(\omega+a_x-a_y)\\
&\qquad\times\sin[(\omega-a_x-a_y)\Delta/2][\sin(A\Delta/2)]/A,\\
&G'(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=2b\sin[\omega(t+\Delta/2)\\
&\qquad-(a_x+a_y)\Delta/2+\delta][\sin(A\Delta/2)]/A,\\
&H'(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=-\sin[(\omega-a_x-a_y)\Delta/2]\cos(A\Delta/2)+(\omega+a_x-a_y)\\
&\qquad\times\cos[(\omega-a_x-a_y)\Delta/2][\sin(A\Delta/2)]/A,\\
&I'(a_x,a_y,b,\omega,\delta,t,\Delta)\\
&\quad=2b\cos[\omega(t+\Delta/2)\\
&\qquad-(a_x+a_y)\Delta/2+\delta][\sin(A\Delta/2)]/A,
\end{aligned}\tag{5}$$

where

$$A=[(a_y-a_x-\omega)^2+(2b)^2]^{\frac{1}{2}}.\tag{6}$$

Even though there may be a large change in probability amplitude in a single step, the above procedure is exact in so far as the perturbation can be represented in a stepwise fashion.

VI. MULTIPLE SEPARATED OSCILLATORY FIELDS

One application of the above methods is the calculation of the molecular beam resonance to be expected when more than two coherent separated oscillatory fields are employed.[3] Figure 1 shows the resonances to be expected with two, three, four, and an infinite number of successive oscillatory fields; the total length of the transition region is kept fixed. It will be noted that the resonance becomes slightly broader as the number of successive oscillatory fields is increased. However, the resonance then becomes more clearly differentiated from the neighboring subsidiary minima; under some circumstances, this can be valuable.

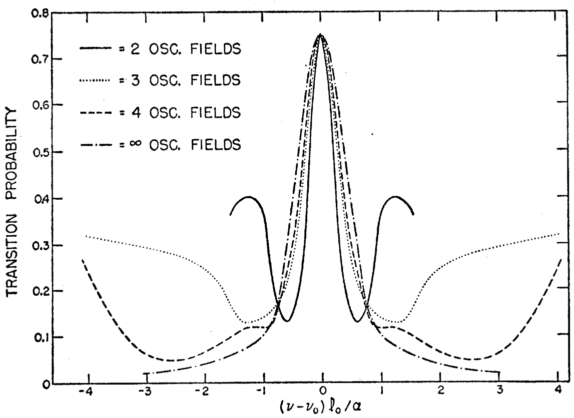

FIG. 1. Molecular beam resonances with various numbers of oscillatory fields. —— represents two separated fields, ··· three, --- four, and —·—·— infinitely many separated fields (the latter is equivalent to a single oscillatory field extending throughout the entire transition region).

VII. STRAY FIELDS WITH A SINGLE EXCESSIVE OSCILLATORY FIELD

Another application is the determination of the effect of stray oscillatory fields in narrowing a resonance when excessive oscillatory fields are used. Kusch[4] has observed that when excessive oscillatory fields are used in the single oscillatory field methods, the resonance is often narrower than would be expected. Salwen[5] has suggested that this may be due to stray oscillatory fields and he showed that such an effect can occur with an exponentially applied field.

This interpretation was confirmed by the application of the present program to a case where the oscillatory field was primarily at a constant amplitude four times the normal optimum. A comparison was then made between the resonance pattern when there was just the constant oscillatory field for a distance and no stray oscillatory field and the pattern with a stray field. The amplitude of the stray field was assumed to rise linearly from zero to optimum value in the first distance $\frac{3}{4}l$, to jump abruptly to four times optimum, and to stay there for a distance l before dropping abruptly to optimum value and then linearally falling to zero in the final distance $\frac{3}{4}l$. The assumed amplitude variation is shown in Fig. 2.

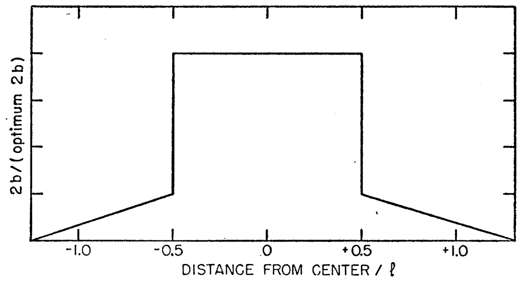

FIG. 2. Assumed variation of oscillatory perturbation amplitude along the transition region for the transition probability calculation whose results are shown in Fig. 3.

From Fig. 3 it can be seen that the apparently almost negligible stray field has a profound influence on the resonance shape and markedly narrows it. In some respects the stray field gives to the resonance many properties of the separated oscillatory field method.[3] The narrow dips on the far wings of the resonance were totally unexpected; they probably correspond to the similar dips whose occurrence in the separated oscillatory field method has been explained by Ramsey.[6]

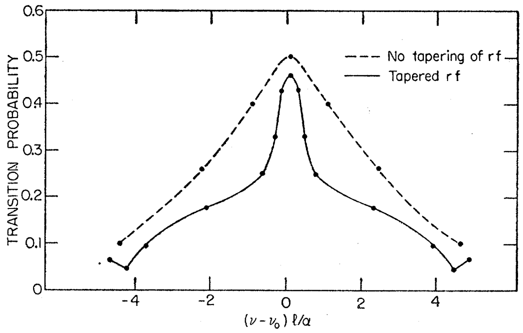

FIG. 3. Transition probability with excessive oscillatory field and stray field. —— represents the transition probability with stray fields as shown in Fig. 2; --- represents the transition probability with no stray fields.

VIII. RESONANCE SHIFTS FROM STRAY FIELDS OF DIFFERENT PHASES

Computations have also been carried out to investigate the effects of stray oscillatory fields in shifting the resonance frequency in the separated oscillatory field method. The results of the calculations are consistent with there being no shift as long as the stray fields are either in phase or 180° out of phase with the primary fields. However, if the stray fields in part have other phases by virtue either of a simple phase shift or of a rotation of the direction of the oscillatory field in space, the frequency of maximum transition probability may be shifted from the resonance frequency $\omega_0=(E_p-E_q)/h$.

The magnitude of such a shift may be estimated from the relations derived by Ramsey[7] for the effects of several oscillatory fields at different frequencies. These relations apply since the motion of the molecule through the region where the phase changes gives rise to an oscillatory field which is at a slightly different frequency as seen by the molecule. Such an oscillatory field not only gives rise to resonance transitions at its own apparent frequency, as in the Millman effect,[8] but also slightly shifts the position of the narrow resonance of the separated oscillatory field method.

If all the stray fields are at the same phase as all of the primary fields or of opposite phase, the resonance is distorted but it is not shifted since under this condition the perturbations at higher and lower frequencies are symmetrical about the oscillatory frequency so that the shifts cancel.

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