[51]B. Bederson, Phys. Today 22 (No. 11), 87 (1969).
[52]J. Bjorken and E. A. Paschos, Phys. Rev. 185, 1975 (1969).
[53]U. Heinzmann, J. Kessler, and J. Lorenz, Phys. Rev. Letters 25, 1325 (1970).
[54]H. R. Kratz, Phys. Rev. 75, 1844 (1949).
[55]C. E. Moore, in *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949), Vol. I, p. 227.
[56]S. Sambursky, Z. Physik 49, 731 (1928).
[57]F. Waibel, Z. Physik 53, 459 (1929).
[58]M. Beutell, Ann. Physik 36, 533 (1939).
[59]G. S. Kvater and T. G. Meister, Vestnik. Leningrad. Univ. 9, 137 (1952); *Optical Transition Probabilities* (National Science Foundation, Israel Program for Scientific Translations, Jerusalem, 1962), p. 191.
[60]P. M. Stone, Phys. Rev. 127, 1151 (1962).
[61]L. Agnew, Bull. Am. Phys. Soc. 11, 327 (1966).
[62]B. Warner, Monthly Notices Roy. Astron. Soc. 139, 115 (1968).
[63]C. Füchtbauer and W. Hofmann, Ann. Physik 43, 96 (1914).
[64]H. Bartels, Ann. Physik 65, 143 (1921).
[65]D. S. Roshdestvenski, Trans. Opt. Inst. Petrograd II 13, 1 (1921).
[66]F. Rasetti, Nuovo Cimento 1, 115 (1924).
[67]H. Kohn and H. Jakob, Physik. Z. 27, 819 (1926).
[68]C. Füchtbauer and H. Maier, Physik. Z. 27, 853 (1926).
[69]A. Filippov, Z. Physik 36, 477 (1926).
[70]C. F. Hagenow and A. L. Hughes, Phys. Rev. 30, 284 (1927).
[71]H. Jakob, Ann. Physik 86, 449 (1928).
[72]C. Füchtbauer and H. W. Wolff, Ann. Physik 3, 359 (1929).
[73]W. Bleeker, Z. Physik 52, 808 (1929).
[74]R. Minkowski and W. Mühlenbruch, Z. Physik 63, 198 (1930).
[75]W. Schütz, Z. Physik 64, 682 (1930).
[76]H. Kohn and H. J. Hübner, Physik. Z. 34, 278 (1933); H. J. Hübner, Ann. Physik 17, 781 (1933).
[77]H. Stroke (private communication).

PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Further Calculations on Multiple-Quantum Transitions*

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We develop a detailed theory to calculate multiple-quantum transition probabilities. It is shown that the quantum electrodynamical (QED) approach must be used in order to explain quantitatively the experimental observations of Kusch. The anomalous behavior of shifts in resonance frequency and saturation of widths of transition probabilities can be explained on the basis of a QED renormalization principle. In this paper, we work out the detailed calculations for the case of a double-quantum transition quantitatively. The agreement between QED calculation and Kusch's observation is remarkable. We conclude that the renormalization principle of QED is important even for low-frequency and finite-intensity fields.

I. INTRODUCTION

In an earlier paper[1] a quantum electrodynamic (QED) theory of induced transitions in atoms and molecules was developed and shown to be distinct from the semiclassical theory when the inducing field is not weak. In this paper the methods developed are applied in detail to the experiments of Kusch[2] resulting in excellent agreement between theory and observation. No such agreement can be obtained by applying the semiclassical theory.

Kusch used a five-level system, so that a theoretical discussion requires the use of higher orders in perturbation theory. When orders higher than the lowest nontrivial order are included, it is necessary to include renormalization effects produced by forward scattering processes just as in higher-order radiative correction calculations it is necessary to take wave-function renormalization produced by virtual-photon processes into account.[3] In Sec. II this renormalization procedure is developed, and in Sec. III it is applied to a double-quantum transition observed by Kusch, yielding both the lineshift and the linewidth as functions of inducing field strength. The results are compared with observation and with the semiclassical results obtained by Salwen.[4] In Sec. IV some comments on the method and its relation to the Majorana formula[5] are given.

II. RENORMALIZATION BY FORWARD SCATTERING

The Green's function for an electron moving in a static potential $V(\vec{r})$ and in a radiation field with one mode excited satisfies the Schwinger-Dyson equation given in I, namely,

$$G(x,x') = S_F(x,x') - i\int d^4x''d^4x''' S_F(x,x'') \times M(x'',x''')G(x''',x') , \quad (1)$$

where $S_F(x,x')$ is the propagator in the static field

alone and where $M(x'', x''')$ is the mass operator resulting from forward scattering in the excited radiation field mode as described in I. In lowest order the expression for the Green's function is

$$G(x, x') = \sum_n \psi_n(\vec{r})\bar{\psi}_n(\vec{r}) \int_{-\infty}^{\infty} \frac{d\Omega}{2\pi i} e^{i\Omega(t-t')} \times [\Omega + E_n + H_{n,n}(-\Omega)]^{-1} , \quad (2)$$

where $H_{n,n}(-\Omega)$ is the Fourier transform of a diagonal matrix element of the mass operator. When $H_{n,n}(-\Omega)$ can be considered to depend weakly on Ω so that this dependence is ignorable in evaluating the integral in (2), then as $t' \to t$, $G(x, x') \to \delta(\vec{r} - \vec{r}')$ as is necessary for a Green's function. When, however, $H_{n,n}(-\Omega)$ cannot be treated as slowly varying it is necessary to take this variation into account and to introduce a renormalization constant Z_n on the right-hand side of Eq. (2) to cancel this out.

To accomplish the renormalization it is necessary to separate two effects of the radiation field: the shift of energy levels due to nonresonant terms, analogous to the Bloch-Siegert shift; the production of transitions and level widths due to resonant terms. This split is analogous to the splitting of self-energy integrals into principal part (nonresonant) and δ-function (resonant) parts.[6] Thus

$$H_{n,n}(-\Omega) = H'_{n,n}(-\Omega) + \tilde{H}_{n,n}(-\Omega) . \quad (3)$$

We define a propagator $G'(x, x')$ in analogy with Eq. (2) using only the nonresonant part H',

$$G'(x, x') = \sum_n Z_n^{-1} \psi_n(\vec{r}) \bar{\psi}_n(\vec{r}') \int_{-\infty}^{\infty} \frac{d\Omega}{2\pi i} e^{i\Omega(t-t')} \times [\Omega + E_n + H'_{n,n}(-\Omega)]^{-1} . \quad (4)$$

The shifted energy levels are determined by the poles of the integrand,

$$-\tilde{E}_n + E_n + H'_{n,n}(\tilde{E}_n) = 0 , \quad (5)$$

and the renormalization constants Z_n are given by

$$Z_n = \left(\int_{-\infty}^{\infty} \frac{d\Omega}{2\pi i} [\Omega + E_n + H'_{n,n}(-\Omega)]^{-1} \right)^{-1} \approx 1 + \left. \frac{\partial H'_{n,n}(-\Omega)}{\partial \Omega} \right|_{\Omega = -\tilde{E}_n} . \quad (6)$$

The renormalized Green's function $\tilde{G}(x, x')$ then satisfies the equation

$$\tilde{G}(x, x') = \sum \tilde{\psi}_n(\vec{r}) \bar{\tilde{\psi}}_n(\vec{r}') \int_{-\infty}^{\infty} \frac{d\Omega}{2\pi i} e^{i\Omega(t-t')} \times [\Omega + \tilde{E}_n + \tilde{H}_{n,n}(-\Omega)]^{-1} , \quad (7)$$

with the renormalized wave functions $\tilde{\psi} = Z_n^{-1/2}\psi$

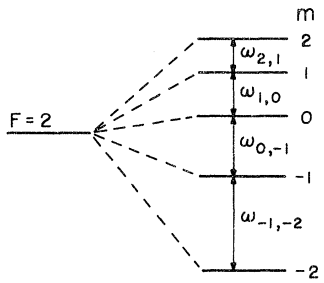

FIG. 1. Level scheme of a five-level atom.

and shifted energies alone appearing. This Green's function has the proper behavior as $t' \to t$ because the resonant term $H_{n,n}(-\Omega)$ has the form

$$\tilde{H}_{n,n}(-\Omega) = -C_n^2/(\Omega + a_n) ,$$

and insertion of this in Eq. (7) with $t = t'$ yields the required δ function since the $\tilde{\psi}_n$ are normalized. The renormalized Green's function now is used to calculate transition probabilities as in I, this prescription meaning that all measurable effects are to be described in terms of renormalized quantities only, no "radiation-free" quantities remaining in the expressions.

III. TWO-QUANTUM TRANSITION

The method just described is applied to the two-quantum transition observed by Kusch[2] in the five-level system provided by the K^{39} hyperfine ground state, namely, the $(2 \to 0)$ transition. The level scheme is shown in Fig. 1. According to I the transition amplitude is

$$C_{2\to 0}(t) = \int d^3r\, d^3r'\, d^3r''\, dt'\, dt''\, \theta(t'')\, \bar{\tilde{\psi}}_0(r) \times \tilde{G}(\vec{r}, \vec{r}'; t - t')\, ie(N/2\omega V)^{1/2} \times \hat{e}\, e^{i(\omega t' - \vec{k}\cdot\vec{r}')}\, \tilde{G}(\vec{r}', \vec{r}''; t' - t'') \times ie(N/2\omega V)^{1/2} \hat{e}\, e^{i(\omega t'' - \vec{k}\cdot\vec{r}'')}\, \bar{\tilde{\psi}}_2(\vec{r}'')\, e^{-i\tilde{E}_2 t''} . \quad (8)$$

Using Salwen's notation[4] we introduce

$$\omega_{n,m} = E_n - E_m , \quad \tilde{\omega}_{n,m} = \tilde{E}_n - \tilde{E}_m , \quad (9a)$$

$$\alpha(n; m) = (b/2\pi)\, \alpha(n, m) = (b/2\pi) \langle n | \hat{d} | m \rangle , \quad (9b)$$

where $\hat{d}$ is the dipole operator. The numerical values corresponding to Kusch's experiment are given in Table I. According to Kusch,[2]

$$b/2\pi = 175 B_0 , \quad (10)$$

with b in kilohertz and B_0 in gauss. B_0, the amplitude of the rf field, is related to N/V by

$$B_0^2 = N\hbar\omega/2V \ . \tag{11}$$

Further,

$$\tilde{f}_{n,n}(\Omega) = [\tilde{E}_n + \Omega + \tilde{H}_{n,n}(-\Omega)]^{-1} \ , \tag{12a}$$

$$\tilde{\alpha}(n;m) = Z_n^{-1/2} Z_m^{-1/2} \alpha(n;m) \ . \tag{12b}$$

In this notation, and using the dipole approximation, we get

$$C_{2\to 0}(t) = \tilde{\alpha}(0;1)\,\tilde{\alpha}(1;2)\,\frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{d\Omega e^{i\Omega t}}{\Omega + \tilde{E}_2 - 2\omega}\,\tilde{f}_{0,0}(\Omega)\tilde{f}_{1,1}(\Omega-\omega)$$

$$= \tilde{\alpha}(0;1)\,\tilde{\alpha}(1;2)\,e^{-i\tilde{E}_0 t}\,\frac{1}{2\pi i}\int_{-\infty}^{\infty} dz\,\frac{e^{izt}}{z + \tilde{\omega}_{2,0} - 2\omega}\,\tilde{f}_{0,0}(z-\tilde{E}_0)\tilde{f}_{1,1}(z-\tilde{E}_0-\omega) \ . \tag{13}$$

We are interested in this when $2\omega \simeq \tilde{\omega}_{2,0}$, which corresponds to the two quantum transition under study, or in the pole of the integrand near $z=0$. This determines the separation of $H_{n,n}$ into nonresonant and resonant parts as given in Eq. (3).

Since we are considering double-quantum transition, it is sufficient to construct $H_{n,n}(-\Omega)$ up to the fourth-order forward scattering process. Following the method of I, we easily obtain, for a five-level system,

$$H_{\pm 2,\pm 2}(-\Omega) = -\left(\frac{|\alpha(\pm 2;\pm 1)|^2}{E_{\pm 1} + \Omega \pm \omega} + \frac{|\alpha(\pm 2;\pm 1)|^2 |\alpha(\pm 1;0)|^2}{[(E_{\pm 1} + \Omega + \omega)^2 (E_0 + \Omega \pm 2\omega)]}\right) , \tag{14a}$$

$$H_{\pm 1,\pm 1}(-\Omega) = -\left(\frac{|\alpha(\pm 1;0)|^2}{E_0 + \Omega \pm \omega} + \frac{|\alpha(\pm 2;\pm 1)|^2}{E_{\pm 2} + \Omega \pm \omega} + \frac{|\alpha(\pm 1;0)|^2 |\alpha(0;\mp 1)|^2}{[(E_0 + \Omega \pm \omega)^2 (E_{\mp 1} + \Omega \pm 2\omega)]}\right) , \tag{14b}$$

$$H_{0,0}(-\Omega) = -\left(\frac{|\alpha(0;\pm 1)|^2}{E_{\pm 1} + \Omega \pm \omega} + \frac{|\alpha(0;\pm 1)|^2 |\alpha(\pm 1;\pm 2)|^2}{[(E_{\pm 1} + \Omega \pm \omega)^2 (E_{\pm 2} + \Omega \pm 2\omega)]}\right) . \tag{14c}$$

Examining (14a) - (14c), we have

$$\tilde{H}_{0,0}(\tilde{E}_0 - z) = -\frac{|\tilde{\alpha}(0;1)|^2 |\tilde{\alpha}(2;1)^2}{[(z - \tilde{\omega}_{1,0} + \omega)^2 (z + \tilde{\omega}_{2,0} - 2\omega)]} \ , \tag{15a}$$

$$\tilde{H}_{1,1}(E_0 - \omega - z) = 0 \ . \tag{15b}$$

The remaining terms in (14b) and (14c) are nonsecular; they are used in the construction of the physical states ψ_0 and ψ_1. The bare state is renormalized similarly.

We then have

$$\tilde{f}_{1,1}(z - \tilde{E}_0 - \omega) = (z + \tilde{\omega}_{1,0} - \omega)^{-1} \approx (\tilde{\omega}_{1,0} - \omega)^{-1} \ , \tag{16}$$

and (13) becomes

$$C_{2\to 0}(t) = \frac{\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)}{\tilde{\omega}_{1,0} - \omega}\, e^{-i\tilde{E}_0 t}\,\frac{1}{2\pi i}\int_{-\infty}^{\infty} dz\,\frac{e^{itz}}{F(z)} \ , \tag{17}$$

where

$$F(z) = z(z + \tilde{\omega}_{2,0} - \omega) - \frac{|\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)|^2}{(z + \tilde{\omega}_{1,0} - \omega)^2} \ . \tag{18}$$

We further approximate (18) by

$$F(z) \approx z(z + \tilde{\omega}_{2,0} - \omega) - \frac{|\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)|^2}{(\tilde{\omega}_{1,0} - \omega)^2} \ . \tag{19}$$

With these approximations, (17) can be integrated to get

$$P_{2\to 0}(t) = |C_{2\to 0}(t)|^2 = \left|\frac{\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)}{\tilde{\omega}_{1,0} - \omega}\right|^2 \frac{\sin^2 ft}{f^2} \ , \tag{20}$$

where

$$f^2 = (\omega - \tfrac{1}{2}\tilde{\omega}_{2,0})^2 + \left|\frac{\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)}{\omega - \tilde{\omega}_{1,0}}\right|^2 \ . \tag{21}$$

We now calculate $\tilde{\omega}_{n,m}$ and $\tilde{\alpha}(n;m)$. We write

$$\tilde{E}_n = E_n + \Delta E_n = -\Omega \ . \tag{22}$$

According to the above discussions, we have

$$\Delta E_2 - \frac{|\alpha(2;0)|^2}{-\Delta E_2 + \omega - \omega_{2,1}} = 0 \ ,$$

$$\Delta E_1 - \frac{|\alpha(1;0)|^2}{-\Delta E_1 + \omega - \omega_{1,0}} - \frac{|\alpha(2;1)|^2}{-\Delta E_1 - \omega + \omega_{2,1}} = 0 \ , \tag{23}$$

TABLE I. The level structure for $(2 \to 0)$ transition.

$n \to m$	Level separations $\omega_{n,m}$ (kHz)	Matrix elements $\alpha(n,m)$
$2 \to 1$	20 836	1.71
$1 \to 0$	22 670	2.28
$0 \to -1$	25 095	2.52
$-1 \to -2$	28 519	2.34

$$\Delta E_0 - \frac{|\alpha(1;0)|^2}{-\Delta E_0 - \omega + \omega_{1,0}} - \frac{|\alpha(0;-1)|^2}{-E_0 + \omega - \omega_{0,-1}} = 0 .$$

Since $\alpha(n;m) \propto \sqrt{N} \propto B_0$, the root ΔE_n must satisfy the condition

$$\Delta E_n \to 0 \quad \text{as } (N/V)^{1/2} \quad \text{or } B_0 \to 0 . \tag{24}$$

As a result, there can be one root of each of Eqs. (23).[7]

It is seen that the ω dependence of f^2 in (21) is quite involved. However, as was pointed out by Kusch,[2] the static magnetic field which causes the anomalous Zeeman splitting is not measured directly, but is calculated from the observed center of the line using the usual expression[8] under the assumption that the center of the line corresponds to the transition frequency at the constant magnetic field in which the line is observed, i.e., that the line frequency is not significantly affected by the rf field. Anticipating this fact, we may assume that $2\omega \simeq \omega_{2,0}$, namely, we neglect the ω dependence of ΔE_n and Z_n, as they depend weakly on ω.

The line shape is essentially determined by the factor f^{-2} in (21), we therefore study f^2 as a function of ω, the frequency tuning. Since (20) is valid only for 2ω near $\tilde{\omega}_{2,0}$, it is sufficient to approximate (21) by the following expression:

$$f^2 = (\omega - \tfrac{1}{2}\tilde{\omega}_{2,0})^2 + \left| \frac{\tilde{\alpha}(0;1)\tilde{\alpha}(2;1)}{\tilde{\omega}_{1,0} - \tfrac{1}{2}\tilde{\omega}_{2,0}} \right|^2 . \tag{25}$$

We see that $f^{-2}(\omega)$ as a function of ω is Lorentzian centered at $\tfrac{1}{2}\tilde{\omega}_{2,0}$ with a half-width given by

$$d_{2\to 0} = \left| \frac{\tilde{\alpha}(2;1)\tilde{\alpha}(1;0)}{\tilde{\omega}_{1,0} - \tfrac{1}{2}\tilde{\omega}_{2,0}} \right| . \tag{26}$$

The shift in resonance frequency relative to $\tfrac{1}{2}\omega_{2,0}$ is then

$$\delta\omega_{2,0} = \tfrac{1}{2}(\Delta E_2 - \Delta E_0) , \tag{27}$$

where (22) has been used.

In the low-intensity limit, B_0^2 or $N/V \to 0$, expressions (26) and (27) reduce to the semiclassical results of Salwen.[4] For we have

$$Z_n \to 1, \quad \tilde{\omega}_{n,m} \to \omega_{n,m} \qquad \text{as } N/V \to 0 ,$$

and the width reduces to

$$d_{2\to\vec{0}} \left| \frac{\alpha(0;1)\alpha(2;1)}{\omega_{1,0} - \tfrac{1}{2}\omega_{2,0}} \right| . \tag{28}$$

In the same limit, the first nonvanishing order is B_0^2, and the shift reduces to

$$\delta\omega_{2,0} \to \frac{1}{2}\left(\frac{|\alpha(1;0)|^2}{\omega_{1,0} - \tfrac{1}{2}\omega_{2,0}} + \frac{|\alpha(0;-1)|^2}{\tfrac{1}{2}\omega_{2,0} - \omega_{0,-1}} - \frac{|\alpha(2;1)|^2}{\tfrac{1}{2}\omega_{2,0} - \omega_{2,1}} \right) , \tag{29}$$

as can be easily seen from (23) in the first approximation to the roots.

We now give a quantitative discussion of (26) and (27). We note that (26) can be written as

$$d_{2,0} = \frac{|\alpha(2;1)\alpha(1;0)|}{|(Z_0 Z_2)^{1/2} Z_1[\omega_{1,0} - \tfrac{1}{2}\omega_{2,0} - \Delta E_1 - \tfrac{1}{2}(\Delta E_2 + \Delta E_0)]|} , \tag{30}$$

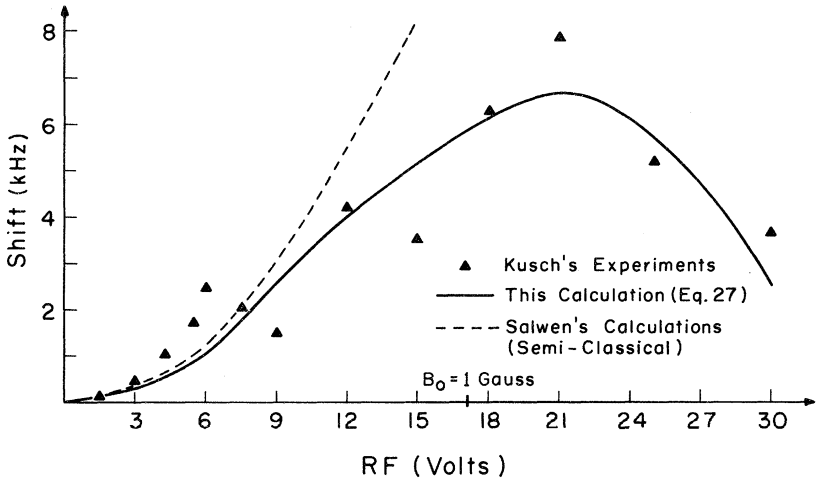

FIG. 2. Shift in resonance frequency of the line [2, 0] as a function of rf amplitude.

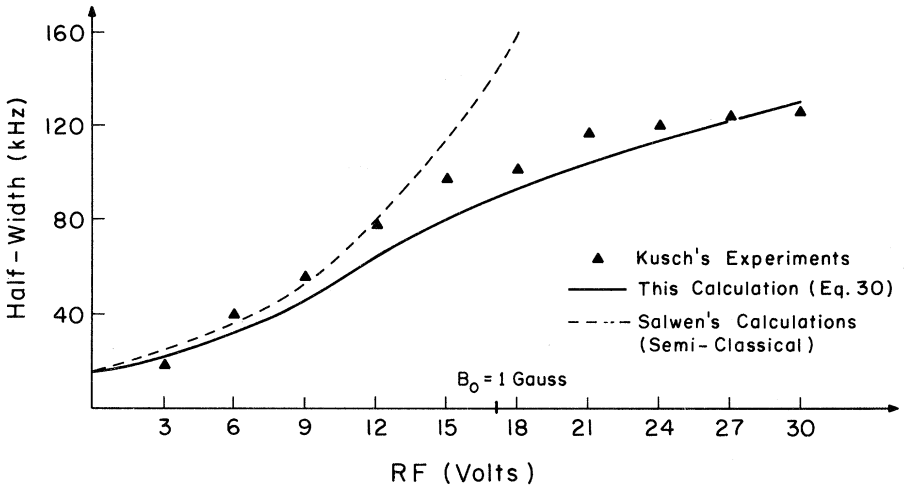

FIG. 3. Half-width of the line [2, 0] as a function of rf amplitude.

where

$$Z_2 = 1 + \frac{|\alpha(2;1)|^2}{(\frac{1}{2}\omega_{2,0} - \omega_{2,1})^2} ,$$

$$Z_1 = 1 + \frac{|\alpha(1;0)|^2}{(\frac{1}{2}\omega_{2,0} - \omega_{1,0})^2} + \frac{|\alpha(2;1)|^2}{(\frac{1}{2}\omega_{2,0} - \omega_{2,1})^2} , \quad (31)$$

$$Z_0 = 1 + \frac{|\alpha(0;1)|^2}{(\frac{1}{2}\omega_{2,0} - \omega_{1,0})^2} + \frac{|\alpha(0;-1)|^2}{(\frac{1}{2}\omega_{2,0} - \omega_{0,-1})^2}$$

in the first approximation.

From Table I, we have

$$\tfrac{1}{2}\omega_{2,0} - \omega_{2,1} = \omega_{1,0} - \tfrac{1}{2}\omega_{2,0} = 917 \text{ kHz},$$

$$\omega_{0,1} - \tfrac{1}{2}\omega_{2,0} = 3342 \text{ kHz} .$$

Using (9b) and (10), we can calculate $d_{2\to0}$ and $\delta\omega_{2\to0}$ as functions of B_0, the rf amplitude. The results are shown in Figs. 2 and 3.

From the figures, we see that the numerical values calculated according to the QED formulas (27) and (30) agree with Kusch's experiment[2] very well. Note that in Fig. 3, we have added 18 kHz to the width arisen from the velocity distribution of the atoms, as was determined by Kusch.[2]

In concluding this section, we mention that the anomalous behavior of shift and width is entirely due to the renormalization effect envisaged in the present approach. It is therefore clear that for high-intensity rf fields the QED renormalization effect must be taken into account despite the low frequency.

IV. DISCUSSION

The behavior of line shift and linewidth as functions of intensity of the transition-inducing field has been shown to follow from the idea of renormalization applied to forward scattering. It seems impossible to incorporate this into a semiclassical theory in any simple way, so we must conclude that the semiclassical theory is not the appropriate limit of QED at high intensity when the frequencies are held fixed. The renormalization used here is finite because there is no integration over the photon momentum as there is when radiative corrections are involved, so there is no subtraction physics involved. We can look on this as an additional justification of the idea of renormalization.

When the levels involved are all equally spaced,[9] the nonresonant terms in the mass operator are not present and no renormalization is needed. In this case the result of Heitler-Ma perturbation theory, the Majorana formula discussed in I, is obtained. It is difficult however, to identify the transitions being produced under these circumstances by high-intensity incoming fields, so the experiment is best done using unequally spaced levels. When lines overlap it is difficult to separate $H_{n,n}$ into resonant and nonresonant parts and it is not clear how to proceed. The procedure is unambiguous for nonoverlapping lines.

In conclusion, we wish to point out that the present approach should be applied to the experiments quoted in a paper by Mizushima.[10] In a recent experiment by Mowat *et al.*,[11] the renormalization effect should also be taken into account, since the experimental data clearly indicate that the multilevel Bloch-Siegert shifts calculated are outside the experimental errors. We believe that the renormalization effect should be included in the masers and lasers experiments.

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[1]C. S. Chang and P. Stehle, Phys. Rev. A 4, 630 (1971), hereafter referred to as I.

[2]P. Kusch, Phys. Rev. 101, 627 (1956).

[3]F. E. Low, Phys. Rev. 88, 53 (1952).

[4]H. Salwen, Phys. Rev. 99, 1274 (1955); 101, 621 (1956).
[5]N. F. Ramsey, *Molecular Beams* (Oxford U.P., London, 1956), pp. 427–430.
[6]A. I. Akhiezer and V. B. Berestetzkii, *Quantum Electrodynamics* (Wiley, New York, 1965), pp. 758-764.
[7]Newton's method of finding the root can be applied if the resulting algebraic equation is of degree higher than 2.
[8]P. Kusch, J. Millman, and I. Rabi, Phys. Rev. 57, 765 (1940).
[9]This symmetry means that all levels are equally spaced and the matrix elements between any two adjacent levels are related to a simple two-level system by some Clebsch-Gordan coefficients.
[10]M. Mizushima, Phys. Rev. 133, A414 (1964).
[11]J. Mowat, C. Johnson, and H. Shugart, Phys. Rev. 3, 43 (1971).

PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Kinetic-Energy Expectation Values with Discontinuous Approximate Wave Functions*

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The Schlosser-Marcus stationary principle for discontinuous approximate wave functions is shown to be the "finite part" of the energy expectation value. The divergent terms in the expectation value of the kinetic energy are second order in the discontinuity, which explains why the energy expression obtained when they are omitted remains stationary.

Energy eigenfunctions must be continuous and have continuous first derivatives. Approximate eigenfunctions may have discontinuous first derivatives or even be discontinuous themselves, *if* suitable formulas are used for kinetic-energy matrix elements.[1-4] This paper is to clarify some confusion concerning the justification of these "suitable formulas."

When ψ is continuous but has jump discontinuities in its first derivatives, the kinetic-energy expectation value is correctly given by[1]

$$\langle\psi|-\tfrac{1}{2}\nabla^2|\psi\rangle=\tfrac{1}{2}\int(\nabla\psi)^*\cdot(\nabla\psi)\,dV\ . \tag{1}$$

It is not always appreciated that

$$\langle\psi|-\tfrac{1}{2}\nabla^2|\psi\rangle=-\tfrac{1}{2}\int\psi^*\nabla^2\psi\,dV \tag{2}$$

is also correct if $\nabla^2\psi$ *is evaluated correctly.*

Consider for simplicity one dimension. Let the first derivative of $\psi=\psi(x)$ have a jump discontinuity $[\psi'(x_0+0)-\psi'(x_0-0]$ at x_0, where $\psi'(x)$ denotes $(d/dx)\psi(x)$. Let $\hat{\psi}''(x_0)=0$ and $\hat{\psi}''(x)=(d/dx)^2\psi(x)$ when $x\neq x_0$; then the *correct* formula for $(d/dx)^2\times\psi(x)$ involves a Dirac δ function[5]:

$$\left(\frac{d}{dx}\right)^2\psi(x)=\hat{\psi}''(x)+[\psi'(x_0+0)-\psi'(x_0-0)]\,\delta(x-x_0)\ . \tag{3}$$

Thus we have

$$-\tfrac{1}{2}\int_{-\infty}^{\infty}\psi^*\left(\frac{d}{dx}\right)^2\psi\,dx$$

$$=-\tfrac{1}{2}\left(\int_{-\infty}^{x_0-0}+\int_{x_0+0}^{\infty}\right)\psi^*\left(\frac{d}{dx}\right)^2\psi\,dx$$

$$-\tfrac{1}{2}\psi^*(x_0)[\psi'(x_0+0)-\psi'(x_0-0)]\ . \tag{4}$$

The three-dimensional version is[2]

$$-\tfrac{1}{2}\int\psi^*\nabla^2\psi\,dV=-\tfrac{1}{2}\int_{V_i+V_o}\psi^*\nabla^2\psi\,dV$$

$$-\tfrac{1}{2}\int_S\psi^*(\nabla\psi_o-\nabla\psi_i)\cdot d\vec{S}\ , \tag{5}$$

where $\int_{V_i+V_o}dV$ denotes the integral over the volume excluding the surface of discontinuity S, and $(\nabla\psi_o-\nabla\psi_i)$ denotes the discontinuity in the gradient across the surface and represents the "strength" of the δ function obtained by differentiating the discontinuous function $\nabla\psi$ across the surface. By integration by parts (Green's theorem), the right-hand side of Eq. (5) is $-\frac{1}{2}\int(\nabla\psi)^*\cdot(\nabla\psi)\,dV$. Hence Eqs. (1) and (2) are equivalent when Eq. (5) is used to evaluate the right-hand side of Eq. (2). Q.E.D.

By way of example, the augmented-plane-wave method of Slater[1,6,7] uses continuous wave functions with discontinuous first derivatives. Slater[1] clearly understood the content of Eqs. (2)–(5), which he stated[1] more or less in words (also see Ref. 2). (Indeed, the rigorous mathematical theory of δ functions came several years later.[5])

If ψ itself is discontinuous, the kinetic-energy expectation value is infinite, but the infinity is easily identified and removed. The essence of this exorcism is revealed by the following heuristic (but decidedly nonrigorous) considerations. (The