PHYSICAL REVIEW VOLUME 78, NUMBER 6 JUNE 15, 1950

A Molecular Beam Resonance Method with Separated Oscillating Fields[*]

NORMAN F. RAMSEY
Harvard University, Cambridge, Massachusetts

(Received February 21, 1950)

A new molecular beam resonance method using separated oscillating fields at the incident and emergent ends of the homogeneous field region is theoretically investigated in this paper. An expression is obtained for the quantum mechanical transition probability of a system between two states when the system is subjected to such separated oscillating fields. This is numerically averaged over the molecular velocity distribution and provides the theoretical shape of the resonance curves. It is found that resonances with such a technique have a theoretical half-width only 0.6 as great as those by conventional molecular beam resonance methods. In addition to producing sharper resonance minima, the new method has its resonances much less broadened by inhomogeneities of the fixed field, it makes possible resonance experiments in regions into which an oscillating field cannot be introduced, and it is more convenient and effective with short wavelength radiation.

1. INTRODUCTION

IN all previous molecular beam resonance experiments,[1–5] the oscillating fields which induce the transitions are extended approximately uniformly throughout the regions in which the energy levels of the system are investigated. This, however, is not necessarily the most advantageous method of applying the oscillating field since more useful curves for many purposes can often be obtained if the amplitude and phase of the oscillating field are varied along the path of the beam.[6] A particular arrangement that is more advantageous in many cases is one in which the oscillating field is confined to a small region at the beginning of the space in which the energy levels are being studied and to another small region at the end, there being no oscillating field in between. This case is investigated in detail theoretically in the present paper.

It is superficially surprising that information can be obtained about the energy levels of a molecule in a region of space without the radiation field inducing the transitions being extended throughout that region. However, by considering the Fourier analysis of an oscillating field on for a time τ, off for a time T, and on again for a time τ, one can see that the method of separated oscillating fields produces transitions at frequencies corresponding to the energy levels in the intermediate region in which no oscillating field exists. Alternatively this can be seen by considering certain simple examples.

The simplest special case is that of a magnetic moment associated with such a large angular momentum that the problem can be treated classically. Consider that such a magnetic moment enters a region of a fixed strong homogeneous magnetic field at the entrance and exit ends of which a weak magnetic field perpendicular to the fixed field rotates about an axis parallel to the fixed field. The rotating magnetic field then supplies a torque perpendicular to the magnetic moment which will cause the angular momentum to be reoriented with a change in the angle ϕ between the angular momentum and the fixed field. If the rotating field is not approximately of the same magnitude and direction as the Larmor precession, the angle ϕ successively increases and decreases, resulting in little net change. On the other hand, if the two rotational frequencies are approximately the same, the effects are cumulative, resulting in an appreciable change in ϕ as in the theory of the "sleeping" top or of the normal molecular beam resonance method.[1] If the angular momentum is initially parallel to the fixed field so that ϕ is equal to zero initially, it is possible to select the magnitude of the rotating field to be such that $\phi=90°$ at the end of the first oscillating region. While in the region with no oscillating field, the magnetic moment simply precesses with the Larmor frequency appropriate to the magnetic field in that region.

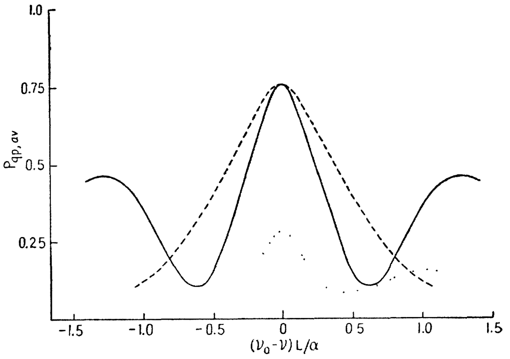

FIG. 1. Transition probability as a function of frequency near resonance. L = distance between oscillating field regions. α = most probable molecule velocity. ν = oscillator frequency. ——— New method with maximum transition probability. ····· Same with one-third the strength of oscillating field. ----- Previous method with maximum transition probability.

---

[*] This work has been partially supported by the Joint Program of the ONR and the AEC.

[1] I. I. Rabi, Phys. Rev. **51**, 652 (1937).

[2] Rabi, Millman, Kusch, and Zacharias, Phys. Rev. **55**, 526 (1939).

[3] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939).

[4] Kusch, Millman, and Rabi, Phys. Rev. **57**, 765 (1940).

[5] H. Hughes, Phys. Rev. **72**, 614 (1947).

[6] N. F. Ramsey, Phys. Rev. **76**, 996 (1949).

When the magnetic moment enters the second oscillating field region there is again a torque acting to change ϕ. If the frequency of the rotating field is exactly the same as the mean Larmor frequency in the intermediate region there is no relative phase shift between the angular momentum and the rotating field. Consequently, if the magnitude of the second rotating field and the length of time of its application are equal to those of the first region, the second rotating field has just the same effect as the first one, i.e., increases ϕ by another 90°, making $\phi=180°$, corresponding to a complete reversal of the direction of the angular momentum. On the other hand, if the field and the Larmor frequencies are slightly different so that the relative phase angle between the rotating field vector and the precessing angular momentum is changed by 180° while the system is passing through the intermediate region, the second oscillating field has just the opposite effect to the first one, with the result that ϕ is returned to zero. If the Larmor frequency and the rotating field frequency differ by just such an amount that the relative phase shift in the intermediate region is exactly an integral multiple 360°, ϕ will again be left at 180° just as at exact resonance. However, in a molecular beam resonance experiment one can easily distinguish between exact resonance and the other cases by the fact that in the former case the condition for no change in the relative phase of the rotating field and of the precessing angular momentum is independent of the molecular velocity, whereas in the other cases the condition for an integral multiple of 360° relative phase shift is velocity dependent since a slower molecule is in the intermediate region longer and so experiences a greater shift than a faster molecule. Consequently, for the molecular beam as a whole, the reorientations are incomplete in all except the resonance cases. Therefore, one would expect a resonance curve similar to that shown in Fig. 1, in which the transition probability for a particle of spin $\frac{1}{2}$ is plotted as a function of frequency.

2. TRANSITION PROBABILITIES

Consider a molecular system which at time t_1 enters a region where it is subjected to an oscillatory perturbation which induces transitions between two molecular energy eigenstates p and q, for neither of which states there can be transitions to any other state while the system is subjected to the perturbing field. Assume the perturbation V is of such a form that

$$V_{pq}=\hbar b e^{i\omega t},\quad V_{qp}=\hbar b e^{-i\omega t},\quad V_{pp}=V_{qq}=0. \tag{1}$$

Such a perturbation arises, for example, if the transitions of a system containing magnetic moments are induced by a magnetic field rotating with angular velocity ω about the axis of quantization. Then if

$$\Psi(t)=C_p(t)\psi_p+C_q(t)\psi_q. \tag{2}$$

The Schrödinger time dependent equations reduce to the forms

$$\begin{aligned} i\hbar\dot{C}_p(t)&=W_pC_p(t)+\hbar b e^{i\omega t}C_q(t),\\ i\hbar\dot{C}_q(t)&=\hbar b e^{-i\omega t}C_p(t)+W_qC_q(t). \end{aligned} \tag{3}$$

If at time t_1, C_p, and C_q had the values $C_p(t_1)$ and $C_q(t_1)$ respectively, the solution of (3) at time t_1+T subject to this initial condition is

$$\begin{aligned} C_p(t_1+T)=&\{[i\cos\theta\sin\tfrac{1}{2}aT+\cos\tfrac{1}{2}aT]C_p(t_1)\\ &-[i\sin\theta\sin\tfrac{1}{2}aT\cdot\exp(i\omega t_1)]C_q(t_1)\}\\ &\cdot\exp\{i[\tfrac{1}{2}\omega-(W_p+W_q)/2\hbar]T\},\\ C_q(t_1+T)=&\{-[i\sin\theta\sin\tfrac{1}{2}aT\cdot\exp(-i\omega t_1)]C_p(t_1)\\ &+[-i\cos\theta\sin\tfrac{1}{2}aT+\cos\tfrac{1}{2}aT]C_q(t_1)\}\\ &\cdot\exp\{i[-\tfrac{1}{2}\omega-(W_p+W_q)/2\hbar]T\}, \end{aligned} \tag{4}$$

where

$$\begin{aligned} &\cos\theta=(\omega_0-\omega)/a,\quad \sin\theta=2b/a,\\ &a=[(\omega_0-\omega)^2+(2b)^2]^{\frac{1}{2}},\ \omega_0=(W_q-W_p)/\hbar. \end{aligned} \tag{5}$$

That (4) is a solution of (3) can be confirmed readily by substitution. A particular case of (4) occurs when $b=0$, in which case

$$\begin{aligned} C_p(t_1+T)&=\exp(-i(W_p/\hbar)T)C_p(t_1),\\ C_q(t_1+T)&=\exp(-i(W_q/\hbar)T)C_q(t_1). \end{aligned} \tag{6}$$

Consider a molecule on which the perturbation (1) acts while the molecule goes a distance l in time τ after which it enters a region of length L and duration T in which b is zero, after which it is again acted on by the perturbation for a time τ. To achieve greater generality, corresponding to the experimental impossibility of attaining completely uniform magnetic fields, assume that the energies of the states p and q are not constant in the intermediate region where b is zero, but that the region is divided into a number of sub-regions such that in the k'th sub-region of duration Δt_k the energies are $W_{p,k}$ and $W_{q,k}$. Then if t is taken to be zero when the first perturbation begins to act, and if

$$C_p(0)=1,\quad C_q(0)=0, \tag{7}$$

successive applications of (4) and (6) yield

$$\begin{aligned} C_p(\tau)=&[i\cos\theta\sin\tfrac{1}{2}a\tau+\cos\tfrac{1}{2}a\tau]\\ &\cdot\exp\{i[\tfrac{1}{2}\omega-(W_p+W_q)/2\hbar]\tau\}, \end{aligned} \tag{8a}$$

$$\begin{aligned} C_q(\tau)=&[-i\sin\theta\sin\tfrac{1}{2}a\tau]\\ &\cdot\exp\{i[-\tfrac{1}{2}\omega-(W_p+W_q)/2\hbar]\tau\}, \end{aligned} \tag{8b}$$

$$\begin{aligned} C_p(\tau+T)&=\Pi_k[\exp(-iW_{p,k}\Delta t_k/\hbar)]\cdot C_p(\tau)\\ &=\{\exp[-(i/\hbar)\textstyle\sum_k W_{p,k}\Delta t_k]\}\cdot C_p(\tau)\\ &=[\exp(-i\bar{W}_pT/\hbar)]\cdot C_p(\tau), \end{aligned} \tag{8c}$$

$$C_q(\tau+T)=[\exp(-i\bar{W}_qT/\hbar)]\cdot C_q(\tau), \tag{8d}$$

$$\begin{aligned} C_p(2\tau+T)=&\{[i\cos\theta\sin\tfrac{1}{2}a\tau+\cos\tfrac{1}{2}a\tau]\cdot C_p(\tau+T)\\ &-[i\sin\theta\sin\tfrac{1}{2}a\tau\cdot\exp i\omega(\tau+T)]\\ &\cdot C_q(\tau+T\}\cdot\exp\{i[\tfrac{1}{2}\omega\\ &-(W_p+W_q)/2\hbar]\tau, \end{aligned} \tag{8e}$$

$$C_q(2\tau+T)=\{-[i\sin\theta\sin\tfrac{1}{2}a\tau\cdot\exp(-i\omega(\tau+T))]\cdot C_p(\tau+T)+[-i\cos\theta\sin\tfrac{1}{2}a\tau+\cos\tfrac{1}{2}a\tau]\cdot C_q(\tau+T)\}\cdot\exp\{i[-\tfrac{1}{2}\omega-(W_p+W_q)/2\hbar]\tau\}. \quad (8f)$$

Here

$$\bar{W}_p=(1/T)\textstyle\sum_k W_{p,k}\Delta t_k=(1/L)\sum_k W_{p,k}\Delta L_k = \text{space mean value of } W_p, \quad (9)$$

with a similar interpretation for $\bar{W}_q$.

The elimination of the intermediate values of the C's from Eqs. (8a–f) yields for $C_q(2\tau+T)$,

$$C_q(2\tau+T)=2i\sin\theta[\cos\theta\sin^2\tfrac{1}{2}a\tau\sin\tfrac{1}{2}\lambda T-\tfrac{1}{2}\sin a\tau\cos\tfrac{1}{2}\lambda T]\cdot\exp\{-i[(\tfrac{1}{2}\omega+(W_p+W_q)/2\hbar)(2\tau+T)+((\bar{W}_p-W_p+\bar{W}_q-W_q)/2\hbar)T]\}, \quad (10)$$

where

$$\lambda=[(\bar{W}_q-\bar{W}_p)/\hbar]-\omega. \quad (11)$$

It follows from Eq. (10) that the probability that the system changes from state p to state q is

$$P_{p,q}=|C_q|^2=4\sin^2\theta\sin^2\tfrac{1}{2}a\tau\cdot[\cos\tfrac{1}{2}\lambda T\cos\tfrac{1}{2}a\tau-\cos\theta\sin\tfrac{1}{2}\lambda T\sin\tfrac{1}{2}a\tau]^2. \quad (12)$$

An important special case of this relation is that corresponding to a nuclear magnetic moment of spin $\frac{1}{2}$ with a gyromagnetic ratio g, in a fixed field of strength H_0, with a weak field of strength H_1 perpendicular to H_0 and rotating about H_0. In this case Eq. (12) applies with

$$\omega_0=g\mu_0H_0/\hbar,\quad \lambda=\omega_0-\omega,$$
$$2b=g\mu_0H_1/\hbar=\omega_0H_1/H_0. \quad (13)$$

These results can be extended to higher spins by the use of the Majorana formula, in the usual manner.[1, 7]

3. AVERAGE OVER MOLECULAR VELOCITY DISTRIBUTIONS

For any particular dimensions of the experimental apparatus, the transition probability (12) applies to only a single molecular velocity, since the times T and τ are inversely proportional to the velocity. Hence (12) must be averaged over the distribution of molecular velocities occurring in the molecular beam. Without loss of significant generality, this averaging can be carried out most easily by performing it in but two limiting cases. One of these is for frequencies so close to resonance that $|\omega_0-\omega|$ is much less than $|2b|$, in which case Eq. (12), when integrated over the molecular velocities with the usual molecular beam weighting factor, becomes

$$\langle P_{p,q}\rangle_{\text{Av}}=2\int_0^\infty\exp(-y^2)\cdot y^3\cdot\sin^2\left(\frac{2bl}{\alpha y}\right)\cos^2\left(\frac{\lambda L}{2\alpha y}\right)dy, \quad (14)$$

where y is the molecular velocity divided by the most probable molecular velocity $\alpha=(2kT/m)^{\frac{1}{2}}$.

The other interesting limit is that for frequencies so far from exact resonance that the quantity $\lambda L/(2\alpha y)$ is sufficiently large that in averaging over the velocities the rapidly varying factor $\sin^2(\lambda L/2\alpha y)$ can be replaced by its average value of $\frac{1}{2}$, while $\sin(\lambda L/2\alpha y)$ can be replaced by its average value of zero. In this case we have

$$\langle P_{p,q}\rangle_{\text{Av}}=4\sin^2\theta\int_0^\infty\exp(-y^2)\cdot y^3\cdot\sin^2\left(\frac{al}{2\alpha y}\right)\cdot\left[1-\sin^2\theta\sin^2\left(\frac{al}{2\alpha y}\right)\right]dy. \quad (15)$$

The numerical work of evaluation of (14) and (15) can be much simplified by first reducing the expressions to sums and differences of the single integral function

$$I(\beta)=\int_0^\infty\exp(-y^2)\cdot y^3\cdot\cos(\beta/y)dy. \quad (16)$$

With this notation Eq. (14) becomes

$$\langle P_{p,q}\rangle_{\text{Av}}=\tfrac{1}{4}-\tfrac{1}{4}I\left(\frac{\lambda L+4bl}{\alpha}\right)-\tfrac{1}{4}I\left(\frac{\lambda L-4bl}{\alpha}\right)+\tfrac{1}{2}I(\lambda L/\alpha)-\tfrac{1}{2}I(4bl/\alpha), \quad (17)$$

while Eq. (15) becomes

$$\langle P_{p,q}\rangle_{\text{Av}}=\sin^2\theta\cdot(1-\tfrac{3}{4}\sin^2\theta)-\tfrac{1}{2}\sin^2 2\theta\cdot I(al/\alpha)-\tfrac{1}{2}\sin^4\theta\cdot I(al/2\alpha). \quad (18)$$

Both (17) and (18) depend on the value assumed for the experimentally arbitrary parameter $2bl/\alpha$. One

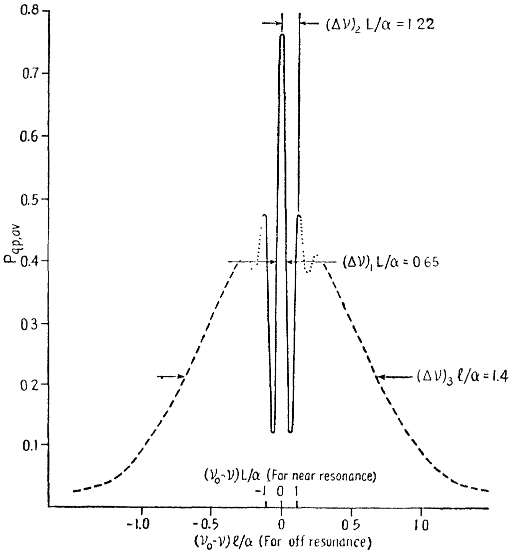

FIG. 2. Transition probability as a function of frequency. ——— Calculated near resonance. ----- Calculated off resonance. ····· Interpolated.

---

[7] E. Majorana, Nuovo Cimento **9**, 43 (1932).

TABLE I. Comparison of theoretical and experimental resonance widths.

	Theoretical value (kc)	Experimental value (kc)
$(\Delta\nu)_1$	1.16	1.2
$(\Delta\nu)_2$	2.2	2.3
$(\Delta\nu)_3$	24.0	30.0

experimental criterion that is frequently used to fix this parameter is that it is to be selected to make $\langle P_{q,p}\rangle_{\text{Av}}$ a maximum at exact resonance ($\lambda=0$). At exact resonance (14) becomes

$$\langle P_{p,q}\rangle_{\text{Av}}=2\int_0^\infty \exp(-y^2)\cdot y^3\cdot \sin^2(2bl/\alpha y)dy, \tag{19}$$

which is the same form as that to which the conventional case discussed by Torrey[8] reduces at resonance since his Eq. (7) then becomes the same as our Eq. (19) except that his β_0 is replaced by $4bl/\alpha$. Torrey shows that in his case $\langle P_{q,p}\rangle_{\text{Av}}$ is a maximum for $\beta_0=1.200\pi$. Therefore it will be a maximum in the present case for

$$2bl/\alpha=0.600\pi. \tag{20}$$

With this value the transition probability in the immediate vicinity of resonance as given in (17) has been plotted as the full line in Fig. 1 as a function of $(\nu_0-\nu)L/\alpha$, where $\nu=\omega/2\pi$. For comparative purposes, the theoretical transition probability with the conventional molecular beam resonance method as calculated by Torrey[8] is plotted with dashed lines on the same curve.

Although the relation (20) will lead to the maximum transition probability at resonance, if there is plenty of beam intensity available a sharper though weaker resonance can be obtained by using an even smaller perturbation b. This corresponds physically to the fact that with the weaker perturbation the slower molecules are relatively more effective than the fast ones and the slow molecules are in the magnetic field a longer time. This result is shown by the dotted curve of Fig. 1 which shows the theoretical transition probability with the new method and with

$$2bl/\alpha=0.200. \tag{21}$$

As an indication of the general appearance of the resonance over the entire resonance region, the transition probabilities from (17) and (18) are plotted on the same graph in Fig. 2. The full line is the part of the curve calculated from (17), the dashed line is from (18), and the dotted portion of the curve is an interpolation for the intermediate region in which neither (17) nor (18) is valid.

If $(\Delta\nu)_1$ is the half-width of the central sharp maximum, $(\Delta\nu)_2$ is the separation of the central maximum from the nearest subsidiary maximum, and $(\Delta\nu)_3$ is the width of the broad background maximum, these should have the values

$$(\Delta\nu)_1=0.64\alpha/L,\quad (\Delta\nu)_2=1.23\alpha/L,$$
$$(\Delta\nu)_3=1.4\alpha/l. \tag{22}$$

4. DISCUSSION

These theoretical results can be compared with the subsequent experimental observations by Kusch[9] on potassium atoms in magnetic fields of about 1.5 gauss as shown in Fig. 3. As can be seen, there is excellent qualitative agreement between the above theory and the subsequent experimental results. The asymmetry between the position of the sharp resonances and of the broad background is presumably due to the mean field in the intermediate region of the magnet being different from the values in the vicinity of the wires carrying the oscillating current, whence λ and $\omega_0-\omega$ become zero for different values of ω. In Table I the experimental and theoretical values of the quantities in (22) are compared. The theoretical values are calculated from $L=24$ cm, $l=2.5$ cm, and $\alpha=4.3\times10^4$ cm/sec. The agreement for all except $(\Delta\nu)_3$ is excellent. The 20 percent disagreement in the latter value is probably attributable to experimental variations in the strength of the field in the vicinity of the wires carrying the oscillating current. The power of the method of separated oscillating fields is well illustrated by these experimental curves. The homogeneity of the magnetic field obtainable in this experiment was such that the width of the broad maximum approximately measures the precision that could have been obtained with the earlier molecular beam resonance methods, whereas with new method provides a maximum whose width is about twenty times less.

For many applications, the molecular beam resonance method with separated oscillating fields is superior to the conventional method in a number of ways. (1) The

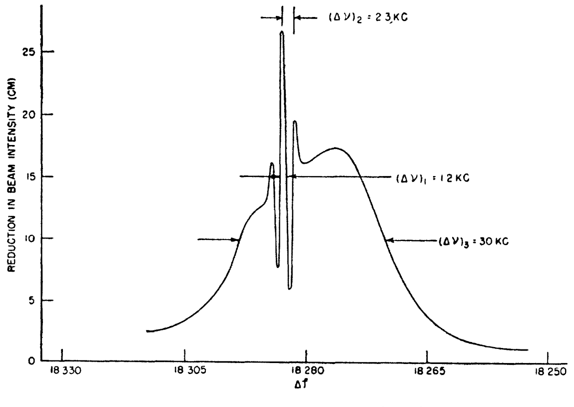

FIG. 3. Experimentally observed reduction in beam intensity as a function of frequency. Line 2,0→1,0 K^{39}; $H=1.5$ gauss; $I_{RF}\approx 8$ ma; $F=F^0-\triangle F$; $F_0=479.27$ mc; total beam intensity = 216 cm.

---

[8] H. C. Torrey, Phys. Rev. 59, 293 (1941).

[9] P. Kusch (private communication).

resonance peaks with the new method are only 0.6 as broad as the corresponding ones with conventional method and the same length of magnetic field. (2) Unlike the earlier methods, with the new method the sharpness of the peak is not reduced by non-uniformities of the constant field since from (11) and (12) above it is only the space average value of the energies which is important. The field must still be fairly uniform along the height of the beam, but this is much more easily achieved experimentally than is uniformity along the length. This advantage of the new method is particularly important and in many cases makes possible an increase in precision of a factor of twenty or more. (3) The new method is more convenient and effective at very high frequencies where the wave-length may be comparable to the length of the region in which the energy levels are investigated. (4) The new method may be applied to study energy levels of a system in a region into which an oscillating field cannot be introduced; for example, the Larmor precession frequency of neutrons can be measured while they are inside a magnetized iron block.

PHYSICAL REVIEW VOLUME 78, NUMBER 6 JUNE 15, 1950

Magnetic Shielding of Nuclei in Molecules*

NORMAN F. RAMSEY
Harvard University, Cambridge, Massachusetts

(Received March 6, 1950)

An expression is developed for the magnetic field at a nucleus resulting from the application of an external magnetic field to a polyatomic molecule which has no resultant electron orbital or spin angular momenta in the absence of the external field. The field at the nucleus is not the same as the externally applied field because of the field arising from the motion of the electrons in the molecule. The expression for the electron contribution to the magnetic field is shown to consist of two parts. The first is a simple term that is similar to the diamagnetic correction developed by Lamb for atoms. The second is a complicated one arising from second-order paramagnetism and is analogous to the term dependent on the high frequency matrix elements in the theory of molecular diamagnetism. Under certain circumstances the second-order paramagnetic term can become quite large. Since both of these terms are altered when the same nucleus is in different molecules, they at least partially and perhaps completely explain the chemical effect that has been reported by various observers in measurements of nuclear moments. For linear molecules, the second-order paramagnetic term is shown to be directly related to the experimentally measurable spin-rotational magnetic interaction constant of the molecule. This relation is particularly valuable in the important case of molecular hydrogen where it is shown that the correction for second-order paramagnetism is -0.56×10^{-5}. When this is added to the Lamb-type term as calculated by Anderson, the total magnetic shielding constant for molecular H_2 becomes 2.68×10^{-5}.

I. INTRODUCTION

IN measurements of nuclear magnetic moments, a correction must be made for the magnetic field arising from the motions of the molecular electrons which are induced by the externally applied field. For example, the application of the external magnetic field produces a diamagnetic circulation of the electrons, which in turn produces a magnetic field at the nucleus, so that the resultant field in which the nuclear Larmor frequency is measured differs from the applied field by a small but important amount. Since this shielding field is proportional to the external field it cannot be distinguished from it merely by varying the external field. Until recently the correction has been made in accordance with a theory developed by Lamb.[1] This theory is strictly applicable only to atoms since it depends on the spherical symmetry of the electric field of the nuclear electrical potential. With the precision available in nuclear moment experiments up until recently, this method of correction has been adequate even though most of the experiments have been performed with molecules instead of atoms. This has been true because the diamagnetic correction in light molecules like hydrogen is so small as to have been negligible, while in molecules with heavy nuclei the diamagnetic correction is caused chiefly by the innermost electrons and for these the problem is approximately an atomic one. However, the atomic approximation is no longer adequate in treating present experiments. The precision of experiments with light nuclei such as hydrogen has become so great (better than one part in a million) that the diamagnetic correction (27 parts in a million in H_2) is important. Furthermore, with heavier nuclei the ratios of the resonance frequencies for the same nucleus in different molecules have been measured with high precision and discrepancies have been found by various observers[2–4] that are sometimes called the chemical effect. The change in different molecular compounds of the electronic magnetic fields described in this paper will at least be an important

---

* This work was partially supported by the joint program of the ONR and AEC.

[1] W. Lamb, Phys. Rev. **60**, 817 (1941).

[2] W. D. Knight, Phys. Rev. **76**, 1260 (1949).

[3] W. C. Dickinson, Phys. Rev. **78**, 339 (1950).

[4] F. Bloch (private communication).