PHYSICAL REVIEW VOLUME 79, NUMBER 1 JULY 1, 1950

On the Magnetic Shielding in He and H_2*

EGIL HYLLERAAS AND S. SKAVLEM
Institute for Theoretical Physics, University of Oslo, Oslo, Norway

(Received January 25, 1950)

The magnetic shielding constant for the He atom (i.e., the value of $(-\Delta H/H)$ at the nucleus), has been calculated to a high degree of accuracy by comparison of values obtained from a number of known first and higher approximations to the wave function. Its value is 5.9938×10^{-5}.

Next, the shielding constant for the H_2 molecule with respect to either of the nuclei has been found in the first approximation to be 2.6614×10^{-5}. The corresponding value derived from the Lamb formula is 3.1648×10^{-5}. The difference is due to the combined effect of both the center of mass and the center of the electronic charge lying outside either of the two nuclei. The numerical value 0.5034×10^{-5} of the difference fits well with the value 0.53×10^{-5} reported by N. F. Ramsay as derived from measurements of the spin-rotational interaction constant of the H_2 molecule.

However, there is also a second-order perturbation effect due to the perturbation of the ground state of the molecule by the magnetic field. By a special method its upper limit has been estimated to be 0.2864×10^{-5} and with a sign such as to weaken the magnetic field. Hence, the upper limit of the total shielding constant of H_2 should be 2.9478×10^{-5}.

I. INTRODUCTION

HIGH precision measurements of nuclear magnetic moments of light nuclei such as H and He^3 by the Rabi resonance method[1,2] have proved it necessary to take into account the faint shielding of the magnetic field in the nuclear region by the Larmor precession of the outer electronic shells. We are indebted to Dr. H. L. Anderson, for calling our attention to the importance of the problem.

As is well known,[3] the calculation of the magnetic shielding constant for an atom (with closed electronic shells) is easy in principle. If one knows the atomic wave function to some degree of accuracy, the rest of the work is to sum up the mean reciprocal values of the electronic distances from nuclei.

In the case of the He atom our interest was first concentrated on the rapidity of convergence of values obtained from the series of approximate wave functions used in our energy calculations.[4] To begin with, we were puzzled by the apparent lack of true convergence and a considerable spread among the values obtained from various kinds of wave functions. This indefiniteness, however, soon turned out to be caused by inaccurate determinations of the "flexibility" parameter, k, frequently used in energy calculations, which ensures that at the energy minimum the kinetic energy of the electrons is exactly half of the numerical value of the potential energy (virial theorem). It is not necessary that the rest of the variation parameters or expansion coefficients be very accurately chosen if only at the end the parameter k is carefully adjusted to the other given parameters so as to satisfy the virial theorem.

Following this principle, it turned out that for the He atom the shielding constant depends but very little on the accuracy of the wave function. The order of magnitude of improvement from the first to the sixth approximation is about 0.04 percent. This explains why by less accurate calculations the spread of the approximate values was more pronounced than was the real convergence of the true values. The small variations from the poor to the accurate approximation eigenfunctions make the repeated accurate calculations to some extent less important. On the other hand, we learn from this particular case of the He atom that for more complicated atomic configurations, as for instance the H_2 molecule, where accurate wave functions are not so easily obtained, we can rely rather safely even on the poorest first approximation.

II. GENERAL THEORY OF MAGNETIC SHIELDING

For a one-electron atom the diminution of a homogeneous magnetic field,

$$\mathbf{H}=\operatorname{curl}\mathbf{A},\quad \mathbf{A}=\tfrac{1}{2}\mathbf{H}\times\mathbf{r},\tag{1}$$

at the center of the atom can be obtained from the Biot-Savart law

$$\Delta\mathbf{H}=-(e/c)(\mathbf{r}\times\mathbf{v})/r^3,\tag{2}$$

expressing $\mathbf{v}$ by the aid of the equation

$$m\mathbf{v}=\mathbf{p}+(e/c)\mathbf{A}\tag{3}$$

and averaging over a stationary state of the atom, usually the ground state.

If the angular momentum $\mathbf{r}\times\mathbf{p}$ is zero, there remains from (2)

$$\begin{aligned}-\Delta\mathbf{H}&=(e^2/mc^2)(\mathbf{r}\times\mathbf{A})/r^3\\&=(e^2/2mc^2)[\mathbf{r}\times(\mathbf{H}\times\mathbf{r})]/r^3.\end{aligned}\tag{4}$$

On averaging over a spherically symmetric state the result is

$$(-\Delta H/H)=\tfrac{1}{3}\alpha^2\langle a_H/r\rangle_{\text{Av}}\tag{5}$$

where a_H is the Bohr radius and α the fine structure constant.

---

* The investigation concerning H_2 is mainly due to Hylleraas.

[1] H. L. Anderson, Phys. Rev. **76**, 1460 (1949).

[2] E. M. Purcell, Phys. Rev. **76**, 1262 (1949).

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

[4] E. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

TABLE I. Various approximations for the magnetic shielding in He.

φ	$-E/4Rh$	$(-\Delta H/H)/\frac{1}{3}\alpha^2$
$e^{-s/2}$	1.423828	$3.375\quad =4k$
$e^{-s/2}(1+c_2t^2)$ $c_2=0.01235$	1.438338	$3.37112=4k$
$e^{-s/2}\cosh c_2t/2$ $c_2=0.295$	1.437831	$3.37172=4k$
$e^{-s/2}(1+c_1u)$ $c_1=0.0988,\quad k=0.92480$	1.445560	3.377830
$\exp(-s/2+c_1u/2)$ $c_1=0.137,\quad k=0.92898$	1.444809	3.37836

TABLE II. Improved approximations for the magnetic shielding in He.

φ	$-E/4Rh$	$(-\Delta H/H)/\frac{1}{3}\alpha^2$
$e^{-s/2}(1+c_1u+c_2t^2)$ $c_1=0.0803,\quad c_2=0.0099$ $k=0.908031$	1.451216	3.37606
$\exp(-s/2+c_1u/2)\cosh[c_2(1-c_1)t/2]$ $c_1=0.11375,\quad c_2=0.237$ $k=0.911817$	1.449767	3.37657

For many-electron atoms one should rather use the Hamiltonian

$$\mathcal{H}=V+\sum_i\left\{\frac{1}{2m}\mathbf{p}_i^2+\frac{e}{mc}(\mathbf{A}_i+\mathbf{a}_i)\cdot\mathbf{p}_i+\frac{e^2}{mc^2}\mathbf{A}_i\cdot\mathbf{a}_i\right\},$$
$$\mathbf{a}_i=(\boldsymbol{\mu}\times\mathbf{r}_i)/r_i^3, \tag{6}$$

where $\mathbf{a}_i$ is the vector potential of the nuclear magnetic moment. Writing

$$\mathbf{A}_i\cdot\mathbf{p}_i=\tfrac{1}{2}\mathbf{H}\cdot(\mathbf{r}_i\times\mathbf{p}_i), \tag{7}$$

and considering states with zero total angular momentum, the sum of terms in (7) is zero as well as the sum of the mean values of $(\mathbf{a}_i\cdot\mathbf{p}_i)$. Hence, from the last sum in the Hamiltonian (6), we obtain for spherically symmetric states in conformity with (5)

$$(-\Delta H/H)=\tfrac{1}{3}\alpha^2\sum_i\langle a_H/r_i\rangle_{\text{Av}}. \tag{8}$$

A second-order perturbation energy arising from the term $\sum_i\mathbf{a}_i\cdot\mathbf{p}_i$ in (6) is quadratic in $\boldsymbol{\mu}$, and hence is insignificant in our problem.

III. APPLICATION TO THE He ATOM

Putting $\psi=\varphi(k\mathbf{r}_1,k\mathbf{r}_2)$, $s=r_1+r_2$, $t=r_2-r_1$, $u=r_{12}$, and taking $a_H/4$ for the unit of length, the result for various approximations of the He atom is given in Table I.

So far there is no indication of convergence, the dependence of the coordinate t tending to lower and that of u to raise the value of the magnetic shielding. Considering, however, both kinds of variations simultaneously, in the third-order approximation, we already get the rather definite results of Table II.

Finally, in the sixth approximation,

$$\varphi=e^{-s/2}(1+c_1u+c_2t^2+c_3s+c_4s^2+c_5u^2), \tag{9}$$

using the values of c_1 to c_5 found earlier by energy calculations,[4] and together with the corresponding best value of k, we get the figure 3.37628. As a final value we therefore choose

$$(-\Delta H/H)_{\text{He}}=\tfrac{1}{3}\alpha^2(3.3764\pm0.0002). \tag{10}$$

IV. MAGNETIC SHIELDING IN THE HYDROGEN MOLECULE

For a molecular problem a more elaborate theory is needed. There is, for instance, the difference that the total angular momentum of the whole molecule including the nuclei is no longer a constant of the motion as soon as a magnetic field is applied, even though it may be quantized and can, for instance, be taken equal to zero in the absence of the field.

Denoting the electrons of H_2 by 1, 2, and the nuclei by a, b, and considering, for instance, the function

$$\psi=\psi(r_{1a},r_{1b},r_{2a},r_{2b},r_{12},r_{ab}), \tag{11}$$

which is independent of the coordinates of the center of mass, and hence corresponds to zero total linear momentum, it is easily seen that it also represents states with zero total angular momentum.

If now we let the nuclear distance r_{ab} be "frozen" (i.e., disregard the nuclear oscillations), there still remains the freedom of rotation of the nuclear axis. Since the wave function (11) is independent of the angles of the axis with respect to a fixed coordinate system, we shall have to average over all possible orientations of the molecular axis. This being accepted, we can also disregard all effects of nuclear motion to the degree of accuracy m/M, and can transform the problem into an ordinary two-electron problem depending on an additional parameter $r_{ab}=2R$.

In contrast to many-electron atomic problems this procedure of disregarding the nuclear motion does not lead to a problem in which the total angular momentum of the electrons is a constant of the motion. To see the difference we need only compare the electronic wave function $\psi(r_1,r_2,r_{12})$ of the He ground state with the function (11) in which by given r_{ab} the center of mass is now considered to be at the middle point of the internuclear axis.

For this reason, as has been pointed out to us by Dr. Fermi and Dr. Anderson of the University of Chicago, there will be a second-order effect in the magnetic shielding due to the perturbation of the ground state of the molecule by the magnetic field. In this section, however, we shall disregard this second-order effect, since there is a much more important first-order effect to be evaluated. This effect, or perhaps rather the sum of the first and second-order effects, is closely connected with the measured spin-rotational constant[5] as demonstrated by Ramsey.[6] To calculate the effect, we adopt the formal method suggested to us by Fermi and Anderson in which as in Eq. (6) the magnetic energy of the nuclei is included in the Hamiltonian of the system, since by a less rigorous method the term itself or at least its definiteness may easily be overlooked.

Denoting the magnetic moments of the nuclei by $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$, writing for the corresponding vector potentials

$$\mathbf{a}_{1a}=(\boldsymbol{\mu}_a\times\mathbf{r}_{1a})/r_{1a}^3,\quad \mathbf{a}_{1b}=(\boldsymbol{\mu}_b\times\mathbf{r}_{1b})/r_{1b}^3,\ \text{etc.,} \tag{12}$$

the Lagrangian for the whole H_2 molecule including the nuclei has been found to be

$$\begin{aligned}L=T-V-\frac{e}{c}\{&(\mathbf{v}_1+\mathbf{v}_a)\cdot\mathbf{A}_{1a}+(\mathbf{v}_2+\mathbf{v}_b)\cdot\mathbf{A}_{2b}\\&+\mathbf{v}_{1a}\cdot\mathbf{a}_{1a}+\mathbf{v}_{1b}\cdot\mathbf{a}_{1b}+\mathbf{v}_{2a}\cdot\mathbf{a}_{2a}+\mathbf{v}_{2b}\cdot\mathbf{a}_{2b}\}\end{aligned} \tag{13}$$

from which we obtain the Hamiltonian

$$\begin{aligned}\mathcal{H}=&\frac{1}{2m}(\mathbf{p}_1^2+\mathbf{p}_2^2)+\frac{1}{2M}(\mathbf{p}_a^2+\mathbf{p}_b^2)+V\\&+\frac{e}{mc}\{(\mathbf{A}_{1a}+\mathbf{a}_{1a}+\mathbf{a}_{1b})\cdot\mathbf{p}_1+(\mathbf{A}_{2b}+\mathbf{a}_{2a}+\mathbf{a}_{2b})\cdot\mathbf{p}_2\}\\&+\frac{e}{Mc}\{(\mathbf{A}_{1a}-\mathbf{a}_{1a}-\mathbf{a}_{2a})\cdot\mathbf{p}_a+(\mathbf{A}_{2b}-\mathbf{a}_{1b}-\mathbf{a}_{2b})\cdot\mathbf{p}_b\}\\&+\frac{e^2}{mc^2}\{\mathbf{A}_{1a}\cdot(\mathbf{a}_{1a}+\mathbf{a}_{1b})+\mathbf{A}_{2b}\cdot(\mathbf{a}_{2a}+\mathbf{a}_{2b})\}\\&-\frac{e^2}{Mc^2}\{\mathbf{A}_{1a}\cdot(\mathbf{a}_{1a}+\mathbf{a}_{2a})+\mathbf{A}_{2b}\cdot(\mathbf{a}_{1b}+\mathbf{a}_{2b})\}\end{aligned} \tag{14}$$

in which quadratic terms in the vector potentials are omitted.[7]

Due to the appearance of purely relative vector potentials, the total linear momentum commutes with $\mathcal{H}$ and is a constant of the motion. The total angular momentum, however, ceases to be a constant of the motion when the magnetic field is different from zero, and the wave function (11) is perturbed into a more general function of relative coordinates.

Disregarding nuclear motion (except for the free orientation of nuclear axis), i.e., disregarding terms of the order of magnitude m/M, the Hamiltonian (14) simplifies to

$$\begin{aligned}\mathcal{H}=\mathcal{H}_0&+\frac{e}{mc}\{(\mathbf{A}_{1a}+\mathbf{a}_{1a}+\mathbf{a}_{1b})\cdot\mathbf{p}_1+(\mathbf{A}_{2b}+\mathbf{a}_{1b}+\mathbf{a}_{2b})\cdot\mathbf{p}_2\}\\&+\frac{e^2}{mc^2}\{\mathbf{A}_{1a}\cdot(\mathbf{a}_{1a}+\mathbf{a}_{1b})+\mathbf{A}_{2b}\cdot(\mathbf{a}_{2a}+\mathbf{a}_{2b})\}\\=\mathcal{H}_0&+\mathcal{H}_1+\mathcal{H}_2,\end{aligned} \tag{15}$$

where $\mathcal{H}_0$ is the Hamiltonian for zero magnetic field.

The mean value for the ground state of the molecule of the first perturbing term $\mathcal{H}_1$ which contains $\mathbf{p}_1$ and $\mathbf{p}_2$ in the first power is zero. From the last term, considering that $\mathbf{r}_{1b}=\mathbf{r}_{1a}-2\mathbf{R}$ and $\mathbf{r}_{2a}=\mathbf{r}_{2b}+2\mathbf{R}$, $\mathbf{A}_{1a}=\frac{1}{2}\mathbf{H}\times\mathbf{r}_{1a}$, $\mathbf{A}_{2b}=\frac{1}{2}\mathbf{H}\times\mathbf{r}_{2b}$, where $2\mathbf{R}=\mathbf{r}_{ba}$, we obtain the first-order perturbation energy with respect to the magnetic moment $\boldsymbol{\mu}_a$ of the nucleus a

$$\Delta E=\frac{e^2}{3mc^2}(\mathbf{H}\cdot\boldsymbol{\mu}_a)\left\langle\frac{1}{r_{1a}}+\frac{\mathbf{r}_{2a}^2-2\mathbf{R}\cdot\mathbf{r}_{2a}}{r_{2a}^3}\right\rangle_{\text{Av}} \tag{16}$$

corresponding to a mean diminution of the magnetic field at $\mathbf{r}_a$ of amount

$$(-\Delta H/H)_{\mathrm{H}_2}=\tfrac{1}{3}\alpha^2 a_H\cdot 2\left\langle\frac{1}{r_a}-\frac{Rz_a}{r_a^3}\right\rangle_{\text{Av}}, \tag{17}$$

r_a denoting either of the electronic distances from the nucleus a, since the wave function is symmetric in the two electrons.

V. NUMERICAL VALUES OF THE MAGNETIC SHIELDING IN HYDROGEN

Let the unit of length be $a_H/2k$ and consider a wave function

$$\psi_0=(\tfrac{1}{2})^{\frac{1}{2}}\{\psi+\bar{\psi}\}, \tag{18}$$

ψ being a normalized function and $\bar{\psi}$ being obtained from ψ by an interchange of the electronic coordinates. Then the normalization integral will be $N=1+\bar{N}$ where $\bar{N}$ is the product integral. If we take the normalization factor for ψ into the volume element $d\tau$ we may write in the first approximation

$$\psi=\exp[-\tfrac{1}{2}(r_{1a}+r_{2b})],\quad \bar{\psi}=\exp[-\tfrac{1}{2}(r_{1b}+r_{2a})]. \tag{19}$$

Squaring (18) and considering (17) we are lead to the integral

$$\begin{aligned}&I=\int\{\exp(-r_a)+2\bar{N}e^{-R\xi}+\exp(-r_b)\}\left(\frac{1}{r_a}-\frac{Rz_a}{r_a^3}\right)d\tau,\\&d\tau=\tfrac{1}{4}r_a^2\sin\vartheta_a dr_a d\vartheta_a=\tfrac{1}{4}R^3(\xi^2-\eta^2)d\xi d\eta,\\&\bar{N}=e^{-R}S(R),\quad S(R)=1+R+\tfrac{1}{3}R^2,\end{aligned} \tag{20}$$

where ξ, η are elliptic coordinates. Equation (17) is then

---

[5] Kellog, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 691 (1940).

[6] N. F. Ramsay, Phys. Rev. **78**, 699 (1950).

[7] Since the Lorentz term of the applied field in L might as well have been written $(\mathbf{v}_1+\mathbf{v}_b)\cdot\mathbf{A}_{1b}+(\mathbf{v}_2+\mathbf{v}_a)\cdot\mathbf{A}_{2a}$, there is an indefiniteness in the Lagrangian corresponding to the function $\mathbf{v}_{12}\cdot\mathbf{A}_{ba}-\mathbf{v}_{ba}\cdot\mathbf{A}_{1a}$ times an aribtrary constant. As the calculation has been made such a term contributes neither to the first nor to the second-order perturbation energy. There are also two other linearly independent expressions which could be added to the Lagrangian without altering the equations of motion. The corresponding additional terms in the Hamiltonian do not, however, contribute to the resulting energy, as can easily be seen from the symmetry of the terms.

replaced by

$$-\Delta H/H=\tfrac{1}{3}\alpha^2\cdot 2kI/N. \tag{21}$$

It is found that

$$\begin{aligned}I=&\left(\frac{1}{2}+\frac{1}{2R}\right)(1-e^{-2R})+e^{-2R}(1+R)S(R)\\&-\frac{1}{4R}[1-e^{-2R}(1+R+\tfrac{1}{2}R^2)^2]\\&-6\left\{\frac{1}{2R}[e^{-2R}S^2(R)(C+\ln 2R)\right.\\&\left.-S(R)S(-R)Ei(-2R)]-e^{-2R}S(R)(1+\tfrac{1}{2}R)\right\}.\end{aligned} \tag{22}$$

On the other hand, the energy minimum is obtained from

$$E=-(L-L'-N/R)^2/NM, \tag{23}$$

where

$$M=2+2e^{-2R}S(R)(1+R-\tfrac{1}{3}R^2), \tag{23a}$$

$$L=\left(2+\frac{2}{R}\right)(1-e^{-2R})+4e^{-2R}S(R)(1+R), \tag{23b}$$

$$\begin{aligned}L'=&\frac{1}{R}[1-e^{-2R}(1+R)]-e^{-2R}(\tfrac{3}{8}+\tfrac{3}{4}R+\tfrac{1}{6}R^2)\\&+\frac{1}{5}\left\{\frac{6}{R}[e^{-2R}S^2(R)(C+\ln R)\right.\\&-2S(R)S(-R)Ei(-2R)\\&+e^{2R}S^2(-R)Ei(-4R)]\\&\left.-\left[-\frac{25}{8}+\frac{23}{4}R+3R^2+\frac{1}{3}R^3\right]e^{-2R}\right\}.\end{aligned} \tag{23c}$$

The energy minimum is found to be

$$E=-2.278387 \quad \text{for} \quad R=1.65, \quad k=1.166176. \tag{24}$$

corresponding to the dissociation energy

$$E_D=3.769\text{ ev} \quad \text{and} \quad R_0=R/k=1.415 \tag{25}$$

as the internuclear distance in units of a_H.

The last two terms with negative signs in Eq. (22) represent the deviation from the Lamb formula. For the values of R and k in (24) we get

$$2kI/N=1.78279-0.28359=1.49920. \tag{26}$$

Putting $\frac{1}{3}\alpha^2=1.7752\times10^{-5}$, Eqs. (8) and (26) lead to the shielding constants

$$\begin{aligned}(-\Delta H/H)_{\text{He}}&=3.3764\ (\tfrac{1}{3}\alpha^2)=5.9938\times10^{-5},\\(-\Delta H/H)_{\text{H}_2}&=1.49920(\tfrac{1}{3}\alpha^2)=2.6614\times10^{-5}.\end{aligned} \tag{27}$$

For these values the ratio of nuclear gyromagnetic constants $\gamma_{\text{He}^3}/\gamma_p=0.7617866$ as obtained by Anderson by direct measurement must be corrected to

$$\begin{aligned}\gamma_{\text{He}^3}/\gamma_p=&\,0.7617866\\&\times[1+(5.9931-2.6614)\times10^{-5}]=0.7618120\end{aligned} \tag{28}$$

instead of 0.7618081 by the Lamb formula.

The first-order correction $0.28359(\frac{1}{3}\alpha^2)=0.5034\times10^{-5}$ to the Lamb formula is very near to the correction 0.53×10^{-5} found by Ramsey[6] on the basis of measurements[5] of the spin-rotational interaction constant. Hence, if the latter value is to be identified with the sum of first- and second-order effects, the second-order effect should be small.

VI. SECOND-ORDER CORRECTION TO THE MAGNETIC SHIELDING IN HYDROGEN

Denoting by $\mathcal{H}_1$ the second term of Eq. (15), the second-order perturbation energy can be written as

$$\Delta E=-\sum_n (\mathcal{H}_1)_{0n}{}^2/(E_n-E_0), \tag{29}$$

where E_n is the energy of the nth excited state and $(\mathcal{H}_1)_{0n}$ a matrix element of the operator $\mathcal{H}_n$, the ground state being denoted by 0. As is well known,

$$\sum_n (\mathcal{H}_1)_{0n}{}^2=\int \psi_0\mathcal{H}_1{}^2\psi_0 d\tau \tag{30}$$

for a normalized ground-state wave function. Hence, replacing all E_n in (29) by a single one, say, E_1 the series can be summed and yields an approximate value or, eventually, a lower limit to the negative perturbation energy. If we take $E_1-E_0=Rh$ as a reasonable value for the energy difference between the ground state and the bulk of higher energy states, we get the approximate perturbation energy

$$\Delta E=-\frac{1}{Rh}\int \psi_0\mathcal{H}_1{}^2\psi_0 d\tau. \tag{31}$$

This procedure of estimating a second-order perturbation energy or its lower limit is much better than the original method devised by Weinstein.[8] However, his method has been improved by Stevenson and Crawford[9, 10] and lately by Kohn[11] so as to correspond to (29) with $E_n \to E_1$ for the lower limit. A similar simplification has been made use of by van Vleck[12] in the theory of atomic and molecular diamagnetism.

---

[8] D. H. Weinstein, Proc. Nat. Acad. Sci. **20**, 529 (1934).

[9] A. F. Stevenson, Phys. Rev. **53**, 199 (1938).

[10] A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 374 (1938).

[11] W. Kohn, Phys. Rev. **71**, 902 (1947).

[12] J. H. van Vleck, and A. Frank, Proc. Nat. Acad. Sci. **15**, 539 (1929); J. H. van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

Squaring the second term $\mathcal{H}_1$ of Eq. (15) we need consider only product terms in $\mathbf{H}$ and $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$. Also product terms in $\mathbf{p}_1$ and $\mathbf{p}_2$ disappear on integration according to (30). Putting $Rh=e^2/2a_H$ and replacing $\mathbf{p}$ by $(h/2\pi i)\nabla$ and considering $a_H/2k$ as unit of length, the second-order energy affecting our problem is approximately

$$\Delta E=32\alpha^2k^3\int\psi_0\Big\{[\tfrac{1}{2}\mathbf{H}\cdot(\mathbf{r}_{1a}\times\nabla_1)]\times\Big[\boldsymbol{\mu}_a\cdot\Big(\frac{\mathbf{r}_{1a}}{r_{1a}{}^3}\times\nabla_1\Big)+\boldsymbol{\mu}_b\cdot\Big(\frac{\mathbf{r}_{1b}}{r_{1b}{}^3}\times\nabla_1\Big)\Big]+[\tfrac{1}{2}\mathbf{H}\cdot(\mathbf{r}_{2b}\times\nabla_2)]\Big[\boldsymbol{\mu}_a\cdot\Big(\frac{\mathbf{r}_{2a}}{r_{2a}{}^3}\times\nabla_2\Big)+\boldsymbol{\mu}_b\cdot\Big(\frac{\mathbf{r}_{2b}}{r_{2b}{}^3}\times\nabla_2\Big)\Big]\Big\}\psi_0 d\tau. \quad (32)$$

To obtain a reasonably good value of this expression we use the former approximate wave function (18) and (19). To avoid an incorrect sign of the effect we must keep in mind that for first-order differential operators A and B we have

$$\int\psi_0AB\psi_0d\tau=-\int(A\psi_0)(B\psi_0)d\tau.$$

In this way we get, taking account only of the nucleus a

$$\Delta E=-(2\alpha^2k^3/N)\int\Big\{[\mathbf{H}\cdot(\mathbf{r}_{1a}\times\mathbf{r}_{1b})]\times[\boldsymbol{\mu}_a\cdot(\mathbf{r}_{1a}\times\mathbf{r}_{1b})]\frac{\bar{\psi}^2}{r_{1a}{}^3\mathbf{r}_{1b}{}^2}-[\mathbf{H}\cdot(\mathbf{r}_{2a}\times\mathbf{r}_{2b})][\boldsymbol{\mu}_a\cdot(\mathbf{r}_{2b}\times\mathbf{r}_{2a})]\frac{\psi\bar{\psi}}{r_{2a}{}^4r_{2b}}\Big\}d\tau. \quad (33)$$

In the second term we can replace 2 by 1 and carry out the integration over the coordinates of one of the electrons. Further, by rotation of the nuclear axis the vector factor transforms into $\frac{1}{3}(\mathbf{H}\boldsymbol{\mu}_a$ times the square of the vector product which is equal to $4R^2(x^2+y^2)$, x and y being electron coordinates perpendicular to the molecular axis. The net result is an energy corresponding to a diminution of the magnetic field of

$$(-\Delta H/H)_2=\tfrac{1}{3}\alpha^2\frac{8k^3}{N}\int\frac{(x^2+y^2)R^2}{r_a{}^3r_b}\times\Big\{\bar{N}\frac{\exp[-\frac{1}{2}(r_a+r_b)]}{r_a}-\frac{\exp(-r_b)}{r_b}\Big\}d\tau, \quad (34)$$

the volume element being of the same form as in (20).

The integrals are elementary except for the exponential integral. We obtain

$$(-\Delta H/H)_2=\tfrac{1}{3}\alpha^2\frac{8k^3}{N}\Big[e^{-R}(1+R+\tfrac{1}{3}R^2)\Big\{(1+\tfrac{1}{2}R)e^{-R}-\frac{1}{2R}[(1+R)e^{-R}(C+\ln 2R)-Ei(-2R)]\Big\}-\frac{1}{3}\Big\{\frac{1}{4R}[1-e^{-2R}(1+2R+2R^2)]-R^2Ei(-2R)\Big\}\Big]. \quad (35)$$

For the values of R and k in (25) the difference of the two integrals in (35) corresponding to $\psi\bar{\psi}$ and $\bar{\psi}^2$ is $0.0591139-0.0404615=0.0186524$. Multiplied with $8k^3/N$ this yields

$$(-\Delta H/H)_2=1.61343(\tfrac{1}{3}\alpha^2)=0.2864\times10^{-5}. \quad (36)$$

Hence the result of the whole calculation is

Lamb formula	3.1648×10^{-5}
First-order correction	-0.5034×10^{-5}
	2.6614×10^{-5}
Second-order correction	0.2864×10^{-5}
Total $(-\Delta H/H)_{H_2}=$	2.9478×10^{-5}.

The above figures with four decimals presented as they result from well-defined calculations must not be taken too seriously. We do not expect the two first figures to change very much by introduction of a more accurate wave function. Nevertheless, even though the difference $(3.24-3.16)\times10^{-5}$ is appreciable, it is practically not so important that on this stage we should try to decide whether the Anderson-Nordsieck value 3.24×10^{-5} from the Lamb formula is too high or not.

Much less confidence, however, must be put in the figure for the second-order correction, which is merely a rough estimation and essentially an upper limit. It may be smaller and our decision to perform the rather intricate calculation was partly based on the hope that it would turn out to be comparatively negligible. It is, however, on this stage of the calculations difficult to understand how it could be small enough as to agree with the Ramsay value 2.71×10^{-5} of the shielding constant.

The application of a more accurate ground-state wave function of H$_2$ will probably not alter the above figures very much. Since a more handy accurate wave function than that used by James and Coolidge[13] in their fundamental investigation of the H_2 molecule often is needed, the authors intend to repeat the energy calculations (eventually the magnetic shielding) for the H_2 molecule by the aid of the wave function

$$\begin{aligned}\psi_0=&\psi\{1+c_1r_{12}+c_2(r_{1a}-r_{2b})^2\}\\&+\bar{\psi}\{1+c_1r_{12}+c_2(r_{1b}-r_{2a})^2\}\end{aligned}\tag{37}$$

which should be at least as good as the corresponding third-order wave function of the He atom.

---

[13] H. M. James and A. S. Coolidge, J. Chem. Phys. **12**, 825 (1933).

PHYSICAL REVIEW VOLUME 79, NUMBER 1 JULY 1, 1950

On the Energy-Momentum Tensor of the Electron

F. Villars
Institute for Advanced Study, Princeton, New Jersey

(Received March 8, 1950)

The first-order radiative correction to the energy-momentum tensor of the electron is investigated. In order to avoid the ambiguities connected with the occurrence of divergent integrals a regulization with auxiliary masses is introduced. It is shown that a procedure which is in accordance with the conservation laws necessarily has some of the features of an auxiliary field theory. The method of the present calculation corresponds to an introduction of an auxiliary neutral vector-meson field which is coupled to the electron-positron field with an imaginary coupling constant.

I. INTRODUCTION

On investigating the effects of the vacuum field fluctuations on the field source, difficulties arise due to ambiguities in the interpretation of divergent integrals. The possibility of obtaining a non-vanishing photon self-energy, in contradiction to the gauge invariance of the underlying theory, illustrates this situation.[1] Since these ambiguities occur within the framework of a covariant formalism, there is some hope that on insisting on the formal properties of the theory: covariance, gauge invariance, and the validity of conservation laws, we might find a way to get rid of these difficulties.

On the other hand, one can argue that since these ambiguities are connected with the occurrence of divergent expressions, an invariant limiting process that makes these expressions finite should resolve these ambiguities. The first point of view, supported especially by Schwinger,[2,3] furnishes a set of rules of interpretation; thus, for instance, gauge invariance implies the invariance of a certain integral in momentum space under translations of the integration variable. (For further detail we refer to a forthcoming paper by S. Borowitz and W. Kohn.)

An investigation along the lines of the second point of view[4] exhibits the remarkable fact that the postulates of gauge invariance and conservation laws strongly reduce the possible number of different regularization procedures. A common feature of all of the admissible regularization methods seems to be their "realistic" aspect; this means, more precisely, that apart from the condition of a hermitian interaction, which in general is violated,[5,6] these methods can be interpreted as auxiliary field theories in the sense of Pais' *f*-field.[7]

In the present paper the second point of view is applied to the problem of the radiative corrections to the energy-momentum tensor of the electron. A straightforward calculation may lead to results in contradiction to the conservation laws, which require that

$$\partial T_{\mu\nu}(x)/\partial x_\nu=0.$$

An equivalent expression of this fact is the result of Pais and Epstein.[8] The difficulty of this special problem was first resolved by Rohrlich.[9] His results are contained in the present calculation as a special case.

Section II will be concerned with the establishment of the expression for the first-order radiative correction to the one-particle part of $\tilde{T}_{\mu\nu}$. In Section III the regularization will be discussed, and finally in Section IV the actual form of $\tilde{T}_{\mu\nu}(p'p)$ will be determined.

II. CALCULATION OF THE FIRST-ORDER RADIATIVE CORRECTION

The symmetrized gauge-invariant energy-momentum tensor of the interacting photon and electron-positron fields can be written as

$$\begin{aligned}T_{\mu\nu}(x)=&\tfrac{1}{2}(F_{\mu\lambda}F_{\nu\lambda}+F_{\nu\lambda}F_{\mu\lambda}-\tfrac{1}{2}\delta_{\mu\nu}F_{\lambda\sigma}{}^2)\\&+\tfrac{1}{4}(\bar{\psi}\gamma^{(\mu}\partial_{\nu)}\psi-(\partial_{(\nu}{}^*\bar{\psi})\gamma^{\mu)}\psi).\end{aligned}\tag{1}$$

---

[1] G. Wentzel, Phys. Rev. **74**, 1070 (1948).

[2] J. Schwinger, Phys. Rev. **76**, 790 (1949), Appendix.

[3] Borowitz, Kohn, and Schwinger, Phys. Rev. **78**, 345 (1950).

[4] W. Pauli and F. Villars, Rev. Mod. Phys. **21**, 434 (1949).

[5] D. Feldman, Phys. Rev. **76**, 1369 (1949).

[6] W. Jost and J. Rayski, Helv. Phys. Acta **22**, 457 (1949).

[7] A. Pais, Verh. Ned. Akad. Amsterdam **XIX**, No. 1 (1947).

[8] A. Pais and S. Epstein, Rev. Mod. Phys. **21**, 445 (1949).

[9] F. Rohrlich, Phys. Rev. **77**, 357 (1950).