HYPERFINE STRUCTURE AS A TEST OF A LINEAR WAVE EQUATION IN THE TWO-BODY PROBLEM

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Abstract

The proper treatment of the two-body problem is not known. Dirac's relativistic considerations, so successful in the problem of one electron, have been applied by Breit to the two-electron problem. Energy terms appear of which the physical reality is very doubtful. Here a very similar application is made to the problem of a nucleus and an electron, because of the failure of previous treatments of this problem to agree with measurements of hyperfine structure. The doubtful terms do not bring about agreement, so their reality remains improbable. The present state of the theory suggests that the proper interactions have not yet been introduced in the problem of hyperfine structure.

Introduction

DIRAC has satisfied the demands of relativity for the problem of one charged particle in a force field, obtaining spin as a consequence. Breit[1] has treated the problem of two bodies in a similar manner. He has improved the calculations of Gaunt[2] on the same subject by including the classical effects of retardation of potentials, as given by Darwin. A straightforward reduction of the linear equation, involving good approximations, leads to an equation for the largest components of the wave function. This may be compared directly with the wave equation resulting from a treatment of the atomic model with spins by the usual wave mechanical perturbation theory.[3] Breit's equation contains terms representing spin-orbit interactions (with factors in agreement with the relativistically correct results of Dirac and of Thomas and Frenkel for single electrons), terms expressing the magnetic spin-spin and orbit-orbit interactions, terms due to relativistic change of mass, terms appering in Dirac's results and having a meaning only for s-states, and in addition unexpected terms containing e^4 and no h as factors, which contradict the correspondence principle. One of these terms in e^4 Breit has tested[4] by calculating its probable effect on the He triplet. The results do not agree with experiment, whereas without this one term the agreement is quite as good as could be expected, considering the approximate nature of the wave functions involved. This contradiction means that the term making the disagreement, and perhaps all the terms in e^4, have no physical meaning. It is still barely possible that that invalidation may not be final, and even that the doubtful terms have a different meaning for a nucleus and an electron than for two

[1] G. Breit, Phys. Rev. **34**, 553 (1929).
[2] A. Gaunt, Proc. Roy. Soc. **A122**, 512 (1928); Trans. Roy. Soc. **228**, 151 (1929).
[3] W. Heisenberg, Zeits. f. Physik **49**, 499 (1926).
[4] G. Breit, Phys. Rev. **36**, 383 (1930).

electrons. The importance of the problem nurtures the hope that the following test of two of the terms in e^4 may be helpful, after the appearance of more copious data.

1. Consider an electron and a nucleus moving under one another's influence. No assumption is made regarding the spin of either. This differs from the helium problem in the absence of the field of the fixed nucleus and in the metamorphosis of one of the electrons into a nucleus. The Darwin-Hamiltonian will be,

$$H = p_{\mathrm{I}}^2/2m_{\mathrm{I}} + p_{\mathrm{II}}^2/2m_{\mathrm{II}} - p_{\mathrm{I}}^4/8c^2m_{\mathrm{I}}^3 - p_{\mathrm{II}}^4/8c^2m_{\mathrm{II}}^3 + e_{\mathrm{I}}e_{\mathrm{II}}/r - (e_{\mathrm{I}}e_{\mathrm{II}}/2c^2m_{\mathrm{I}}m_{\mathrm{II}})[(\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{p}_{\mathrm{II}})r + (\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{r})(\boldsymbol{p}_{\mathrm{II}}\cdot\boldsymbol{r})/r^3]. \quad (1)$$

Here the numeral I refers to the nucleus, II to the electron; $e_{\mathrm{I}}=Ze$, $e_{\mathrm{II}}=-e$; and $\boldsymbol{r}$ is a vector from the nucleus to the electron. This leads one to the equivalent of Breit's Eq. (6),

$$\Big(p_0 + \sum_{k=1,2,3}(\alpha_k^{\mathrm{I}}p_k^{\mathrm{I}} + \alpha_k^{\mathrm{II}}p_k^{\mathrm{II}}) + \alpha_4^{\mathrm{I}}m_{\mathrm{I}}c + \alpha_4^{\mathrm{II}}m_{\mathrm{II}}c + (e_{\mathrm{I}}e_{\mathrm{II}}/2c)\Big\{\sum_{k=1,2,3}\alpha_k^{\mathrm{I}}\alpha_k^{\mathrm{II}}r^{-1} + (\alpha^{\mathrm{I}}\cdot\boldsymbol{r})(\alpha^{\mathrm{II}}\cdot\boldsymbol{r})r^{-3}\Big\}\Big)\psi = 0 \quad (2)$$

with

$$p_0 = -\frac{h}{2\pi i}\frac{\partial}{c\partial t} - \frac{e_{\mathrm{I}}e_{\mathrm{II}}}{cr}; \quad p_k^{\mathrm{I}} = \frac{h}{2\pi i}\frac{\partial}{\partial x_k^{\mathrm{I}}}.$$

Here we have omitted entirely the four-potential A. The reduction of this equation will be identical with the calculation of Breit, and will lead to the following modification of his Eq. (48′):

$$\{E - (m_{\mathrm{I}} + m_{\mathrm{II}})c^2 - e_{\mathrm{I}}e_{\mathrm{II}}/r - p_{\mathrm{I}}^2/2m_{\mathrm{I}} - p_{\mathrm{II}}^2/2m_{\mathrm{II}} \quad (3.0)$$

$$+ p_{\mathrm{I}}^4/8m_{\mathrm{I}}^3c^2 + p_{\mathrm{II}}^4/8m_{\mathrm{II}}^3c^2 \quad (3.1)$$

$$+ (e_{\mathrm{I}}e_{\mathrm{II}}/2m_{\mathrm{I}}m_{\mathrm{II}}c^2)[(\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{p}_{\mathrm{II}})r^{-1} + \sum_{i,j}r^{-3}(x_i^{\mathrm{II}} - x_i^{\mathrm{I}})(x_j^{\mathrm{II}} - x_j^{\mathrm{I}})p_i^{\mathrm{I}}p_j^{\mathrm{II}}] \quad (3.2)$$

$$- (e_{\mathrm{I}}e_{\mathrm{II}}hi/8\pi c^2)r^{-3}(\boldsymbol{r}\cdot[\boldsymbol{p}^{\mathrm{I}}m_{\mathrm{I}}^{-2} - \boldsymbol{p}^{\mathrm{II}}m_{\mathrm{II}}^{-2}]) \quad (3.3)$$

$$+ (e_{\mathrm{I}}e_{\mathrm{II}}h/8\pi c^2)r^{-3}(-m_{\mathrm{I}}^{-2}[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{I}}]\cdot\sigma^{\mathrm{I}} + m_{\mathrm{II}}^{-2}[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{II}}]\cdot\sigma^{\mathrm{II}} \quad (3.4)$$

$$+ (2/m_{\mathrm{I}}m_{\mathrm{II}})\{-[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{II}}]\cdot\sigma^{\mathrm{I}} + [\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{I}}]\cdot\sigma^{\mathrm{II}}\}) \quad (3.5)$$

$$- (e_{\mathrm{I}}e_{\mathrm{II}}/m_{\mathrm{I}}m_{\mathrm{II}})(h/4\pi c)^2\langle(\nabla^{\mathrm{II}}\cdot\sigma^{\mathrm{I}})(\nabla^{\mathrm{I}}\cdot\sigma^{\mathrm{II}})r^{-1}\rangle \quad (3.6)$$

$$- (e_{\mathrm{I}}^2e_{\mathrm{II}}^2/4(m_{\mathrm{I}}+m_{\mathrm{II}})c^2)[3r^{-2} - 2(\sigma^{\mathrm{I}}\cdot\sigma^{\mathrm{II}})r^{-2} + (\sigma^{\mathrm{I}}\cdot\boldsymbol{r})(\sigma^{\mathrm{II}}\cdot\boldsymbol{r})r^{-4}]\}\psi_{a,b} = 0 \quad (3.7)$$

For the sake of easy comparison, the energy equation which will be derived in §2 from this wave equation is entered here.

$$E = E_1 + E_2$$

E_1 is the same for all the states in which we are interested and consists of the unperturbed energy augmented by the contributions of (3.1), (3.2), and (3.3). E_2 splits up the doublet and is given by

$$-E_2 = (h^2e_Ie_{II}/8\pi^2c^2)\overline{r^{-3}}[m_I^{-2}(\overline{\boldsymbol{l}\cdot\mathbf{s}^I}) + m_{II}^{-2}(\boldsymbol{l}\cdot\mathbf{s}^{II}) \tag{4.4}$$

$$- (2/m_Im_{II})\{(\overline{\boldsymbol{l}\cdot\mathbf{s}^I}) + (\boldsymbol{l}\cdot\mathbf{s}^{II})\}] \tag{4.5}$$

$$- (e_Ie_{II}/m_Im_{II})(h/2\pi c)^2\overline{r^{-3}}\,[(\overline{\mathbf{s}^I\cdot\mathbf{s}^{II}}) - 3\overline{(\mathbf{s}^I\cdot\boldsymbol{r})(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}} \tag{4.6}$$

$$+ (e_I^2e_{II}^2/(m_I + m_{II})c^2)\overline{r^{-2}}\,[(\overline{\mathbf{s}^I\cdot\mathbf{s}^{II}}) - \overline{(\mathbf{s}^I\cdot\boldsymbol{r})(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}}] \tag{4.7}$$

(3.4) (and also (4.4)) represent the interaction of each spin with the field due to its own orbital motion, while (3.5) gives the interaction of the spin of each particle with the orbit of the other. (3.6) corresponds to the classical interaction energy of two dipoles. (3.7) contains the doubtful terms in e^4. If physically extant, only the last of the three terms would effect the helium triplet separation, so it alone was tested by Breit. Each of the last two terms would effect hyperfine structure, so we can test them both. The first gives only a displacement common to all the levels.

2. In the perturbation problem, (3) is the perturbed wave equation. To determine the unperturbed wave functions, we consider all the terms beyond (3.0) as perturbation terms, so that (3.0) becomes the unperturbed equation. The coordinates are taken to be those in which the center of gravity is at rest, since a transformation can always be made from more general coordinates of two particles to the coordinates of the center of gravity and the relative coordinates of the particles. The translation of the center of gravity being separated from the problem, $\boldsymbol{p}^I = -\boldsymbol{p}^{II}$. Thus we have the hydrogen wave equation, and hence use hydrogenic wave functions. The wave function in the unperturbed equation, as in (3), has two indices, each of which may have two values. The first index refers to the nuclear spin orientation, and is operated upon by σ^I; the second to the spin of the electron, and is acted upon by σ^{II}. As a function of space and spin coordinates, the unperturbed function is separable,

$$\psi_{a,b}(r, \theta, \phi) = S_a^I S_b^{II} u(r, \theta, \phi)$$

where a and b may each be either α or β of Pauli's theory, and σ^I and σ^{II} operate on S^I and S^{II}, respectively, in the usual manner. $S^{II}u$ might be replaced by the one-electron wave function stabilized for spin-orbit interaction, such as given by Bartlett,[5] e.g., and the resulting ψ would give the diagonal terms of an energy matrix from which hyperfine splitting could be had by sum rules. Since the wave function is separable in radial and angular parts, we may obtain the result of the angular integrations by considering the operators as vectors in the vector model, and averaging over the precessions. $[\boldsymbol{r}\times\boldsymbol{p}^I] = -[\boldsymbol{r}\times\boldsymbol{p}^{II}]$ is the orbital angular momentum operator. Since Breit has used in effect the negative of the Pauli matrices, σ becomes $-2\mathbf{s}$, where $|s| = \frac{1}{2}$. These substitutions in (3) give (4). In reducing it to an expression in the quantum numbers, Landé cosines are used. Goudsmit[6] has explained in detail a method for obtaining $\overline{(\mathbf{s}^I\cdot\boldsymbol{r})\,(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}}$. It consists essentially in making angular integrations in the case of a strong field, when the quantum vectors

[5] J. H. Bartlett, Jr., Phys. Rev. **35**, 230 (1930).

[6] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

are decoupled, and using the results to find the value of the interaction without field by means of energy sum rules.

From the latter term of (4.4) (the other term in $(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}})$ is negligible) we get the energy that gives rise to the doublet separation:

$$E' = -(h^2e_{\mathrm{I}}e_{\mathrm{II}}/8\pi^2c^2m_{\mathrm{II}}{}^2)\overline{r^{-3}}(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}})$$
$$= A'(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}}) = A'\tfrac{1}{2}\{j(j+1) - l(l+1) - \tfrac{3}{4}\} \quad (5)$$

It is apparent in (4) that the hyperfine structure contains the same constant A' which is determined empirically by the doublet separation. The following expressions, which give the splitting up of the two doublet levels, are derived from (4.4), (4.5), and (4.6). The order of the terms has been preserved.

$$E''_j = A_j''(\mathbf{s}^{\mathrm{I}}\cdot j) = A_j''\tfrac{1}{2}\{f(f+1) - j(j+1) - s^{\mathrm{I}}(s^{\mathrm{I}}+1)\} \quad (6)$$

$$A''_{l+\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left[\frac{2l}{l+\frac{1}{2}} - \frac{1}{l+\frac{1}{2}} + \frac{3}{(2l+3)(l+\frac{1}{2})} + \delta\frac{8\pi^2e_{\mathrm{I}}e_{\mathrm{II}}m_{\mathrm{II}}}{h^2}\frac{\overline{r^{-2}}}{\overline{r^{-3}}}\left\{\frac{1}{l+\frac{1}{2}} - \frac{2}{(2l+3)(l+\frac{1}{2})}\right\}\right] \quad (7)$$

$$A''_{l-\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left[2\frac{l+1}{l+\frac{1}{2}} + \frac{1}{l+\frac{1}{2}} + \frac{3}{2(l-\frac{1}{2})(l+\frac{1}{2})} - \delta\frac{8\pi^2e_{\mathrm{I}}e_{\mathrm{II}}m_{\mathrm{II}}}{h^2}\frac{\overline{r^{-2}}}{\overline{r^{-3}}}\left\{\frac{1}{l+\frac{1}{2}} + \frac{1}{(l-\frac{1}{2})(l+\frac{1}{2})}\right\}\right]. \quad (8)$$

The symbol δ has the value unity of the terms in e^4 are physical, otherwise it is zero.

3. To compare the terms we must have an idea of the ratio of the radial integrals. For a Coulomb field,

$$\overline{r^{-2}} = \frac{Z^2}{n^3(l+\frac{1}{2})}\frac{1}{a_0{}^2}\cdot\quad \overline{r^{-3}} = \frac{Z^3}{n^3l(l+\frac{1}{2})(l+1)}\frac{1}{a_0{}^3}\cdot\quad a_0 = \frac{h^2}{4\pi^2m_{\mathrm{II}}e^2}\cdot \quad (9)$$

For the heavy elements some sort of approximation must be used. The electron cloud alters the radial part of the wave function by producing a non-coulomb interaction. We will content ourselves with the classical application of the charged shell model of the atom, as used by Landé for doublet separations.[7] Using (9) for outer and inner orbital segments, we get

$$\overline{r^{-2}} = \frac{2Z_0{}^2}{n_0{}^3(l+\frac{1}{2})}\frac{1}{a_0{}^2}\cdot\qquad \overline{r^{-3}} = \frac{Z_iZ_0{}^2}{n_0{}^3l(l+\frac{1}{2})(l+1)}\frac{1}{a_0{}^3}$$

of which the ratio is

$$\overline{r^{-2}}/\overline{r^{-3}} \approx 2l(l+1)a_0/Z.$$

This in (7) and (8) gives

$$A''_{l+\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left\{\frac{2l(l+1)}{(l+\frac{1}{2})(l+\frac{3}{2})} - \delta\frac{8l(l+1)}{2l+3}\right\} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left\{\frac{16}{15} - \delta\frac{16}{5}\right\}$$

[7] A. Landé, Zeits. f. Physik **25**, 46 (1924).

$$A''_{l-\frac{1}{2}} = \frac{m_{\text{II}}}{m_{\text{I}}}A'\left\{\frac{2l(l+1)}{(l-\frac{1}{2})(l+\frac{1}{2})} + \delta\frac{4l(l+1)}{l-\frac{1}{2}}\right\} = \frac{m_{\text{II}}}{m_{\text{I}}}A'\left\{\frac{16}{3} + \delta 8\right\}.$$

The last members are for the case $l=1$. The presence of other electrons also replaces $\overline{Zr^{-3}}$ by $\overline{Z_{eff}r^{-3}}$ in the expression for A', but the numerical change is small enough that it need not interest us here.[8]

The present treatment leads naturally to a nuclear spin with but two orientations possible and a Landé g-factor 2 in units $e_{\text{I}}h/4\pi m_{\text{I}}c$. For the terms that classically have a meaning it is easy to believe that we may extend the result to other cases with the vector model by assuming a larger nuclear spin vector s^{I} in (6), selecting its value and a different value of g to accord with observed intervals or intensity ratios. We postulate tentatively that a similar treatment of the terms in e^4 will give an estimate of their contribution to the energies.

A comparison is made with the few experimental data available,[9] which are for ^2P. In Tl the nuclear moment is $\frac{1}{2}$ but in Bi it is $4\frac{1}{2}$.

TABLE I.

	A' exp.	A'' exp.	A'' calc. $\delta=0$	A'' calc. $\delta=1$	A'' exp.	A'' calc. $\delta=0$	A'' calc. $\delta=1$
Tl I*	5195 cm^{-1}	0.72	0.074	0.18	~0.02	0.015	−0.03
*Bi***	10000	0.40	0.14	0.35	~0.02	0.03	−0.06

* John Wulff, appearing in Zeits. f. Physik, communicated to Professor Goudsmit.
** Indirectly derived from Bi I and II data. R. A. Fisher and S. Goudsmit, Phys. Rev., in print.

The classical values, with $\delta=0$, do not agree with experiment even when multiplied by the arbitrary factor $g(I)$ which the usual theory allows. When such an arbitrary factor is introduced, the agreement in the case $\delta=1$ is even worse. However, the present treatment of the problem, when not extended hypothetically, does not permit of such a factor. For the large separations, of which the measurements are most certain, the agreement is better with $\delta=1$ than with $\delta=0$.

In the classical terms the value of the nuclear magnetic moment is definitely determined as $Zm_{\text{II}}/m_{\text{I}}$ Bohr magnetons for the nuclear spin $\frac{1}{2}$. This is as assumed and discussed by Jackson[9] and by Fermi[8].

This paper stresses once more the fact that we have at present no satisfactory theory of spin-spin interaction.

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[8] E. Fermi, Zeits. f. Physik **60**, 332 (1930).

[9] The results for In I by Jackson (Proc. Roy. Soc. **A128**, 508, 1930) and by McLennan and Allin (Proc. Roy. Soc. **A129**, 208, 1930) disagree too radically to be of use at present. In Bi III and Tl III the second member of the P series is known, but second order effects make the values of A_j'' for our purpose uncertain. (Vide H. Casmir, Phys. Rev., in print.)