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Origin and meaning of the Fermi contact interaction*

Werner Kutzelnigg

Lehstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-4630 Bochum, Federal Republic of Germany

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The Fermi-contact interaction (FCI) can easily be derived from 1st order perturbation theory applied to the non-relativistic wave equation for a spin-(1/2) particle of Lévy-Leblond, with the nuclear spin described by the field of an "external" magnetic dipole, and it results from the fact that the "turn-over-rule" for the operator $\vec{\sigma}\vec{p}$ is only valid if the derivatives implicit in $\vec{p}$ are taken "in the distribution sense". If one avoids to apply the turn-over-rule, the FCI is obtained without the need to introduce a "δ-function". It is also shown that the formulation of a magnetic point dipole as the limit of an extended nucleus directly leads to the FCI. Traditional methods of the derivation of the FCI are analyzed in the light of this new interpretation. It is then explained why the perturbation expansions in powers of the magnetic moment of the nucleus necessarily diverges, but that the expression for the 1st order energy on which the concept of the FCI is based, can nevertheless be justified by means of the Hellmann-Feynman theorem with a correction term if singular wave functions are involved. Finally some comments on a theory beyond first order are made.

Key words: Fermi contact interaction — Lévy-Leblond equation — Hyperfine interaction — Hellmann-Feynman theorem — Perturbation theory

1. Introduction

If one wants to formulate a Hamiltonian at the two-component spinor level (Pauli Hamiltonian) for an electron in the magnetic field of the point nucleus, one is obliged to include a term which involves a δ-function, that is usually called the "Fermi-contact interaction", (FCI).

* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

In his original derivation Fermi [1, 2] has started from the Dirac equation for a one-electron atom in an s-state. Taking the non-relativistic limit at the end he arrived at an expression for the hyperfine splitting in terms of the non-relativistic wave function. Much later [3] this expression has been interpreted as the expectation value of a δ-function term, that we shall refer to here as FCI. There is no δ-function term for the same physical situation in the Dirac equation, i.e. if one describes the electron relativistically in terms of four-component spinors. Since the FCI can be "derived" from the Dirac equation via its reduction to Pauli form, it has often been interpreted as a "relativistic effect", like other terms that arise via this reduction, like spin-orbit coupling or the Darwin term.

After Fermi's discovery, other authors [4, 5] showed tht the FCI can also be understood in a purely classical framework, provided that one associates *ad hoc* an intrinsic point dipole with the electron. It thus appeared that just the magnetic moment of the electron had a relativistic origin, but that the interaction of the magnetic moment of the electron with that of the nucleus could be understood classically.

A genuinely relativistic treatment of the hyperfine interaction was given by Breit [6] (see also [7]), which in the non-relativistic reduces to that of Fermi [1].

Many textbooks (see e.g. [8, 9]) adopt the point of view that the FCI is a relativistic effect, which must be derived from the Dirac equation. A very popular derivation is that due to Blinder [10] (see also [11]). In other textbooks or review articles (see, e.g. [12–17]) it is stressed that the FCI is not a relativistic effect and that it can be understood in terms of classical electrodynamics, provided that one regards the electron as a particle with an intrinsic magnetic moment (not worrying about the origin of the gyromagnetic factor $g = 2$, that is hard to understand classically, but which is obvious in terms of the Dirac theory). In some textbooks both derivations of the FCI, the relativistic one and the non-relativistic one are presented [18].

Irrespective of whether the relativistic or the non-relativistic derivation of the FCI is chosen, the arguments found in textbooks are often to a large extent handwaving. In the non-relativistic derivation the essential point (as we shall show) is that the field of the magnetic point dipole must be described by a distribution rather than a function, and the field strength is obtained from the vector potential via a differentiation in the distribution sense. Instead of a convincing justification of why this must be done so, one finds rather miraculous ways towards the δ-function terms, e.g. by manipulating expressions such that the familiar relation $\Delta(1/r) = -4\pi\delta^3(\vec{r})$ can be used, or by intermediate use of momentum space, or by taking the electron as the source of the magnetic field that acts on the nucleus (see Sect. 4.3).

Relativistic derivations suffer from the difficulty that the Coulomb potential is so singular that the non-relativistic limit is problematic, in particular that the Pauli Hamiltonian has awkward properties and can be used safely only in the context of first-order perturbation theory. Moreover the origin of the FCI appears

to be different depending on whether one uses the method of the elimination of the small components or the Foldy-Wouthuysen transformation [9].

In order to decide whether the FCI is a relativistic or a non-relativistic effect one must first understand whether the electron-spin itself has a relativistic or a non-relativistic origin. The key to an answer to this question has been given by Lévy-Leblond [19] who has shown that the electron spin is perfectly consistent with a Galiei-invariant (i.e. non-relativistic) theory. The non-relativistic linear field equation in terms of four-component spinors derived by Lévy-Leblond [19] deserves to be better known than it actually is. Among other things it automatically accounts of the factor $g = 2$, as does the Dirac theory.

As in the Dirac theory, there is no explicit FCI if one describes the electron by the Lévy-Leblond equation. We shall show that on reducing the 4-component spinor equation to a two-component spinor equation the FCI arises naturally as a result of applying the turn-over-rule for the operator $\vec{\sigma}\vec{p}$, which is only valid "in the distribution sense" if singular functions are involved. Stated more directly, the application of the turn-over-rule implies integration by parts. When singular functions are involved, the boundary contributions cannot be neglected, and these give rise to the FCI.

The derivation of the FCI from the Lévy-Leblond equation is perfectly straightforward and free from the problems that arise in traditional derivations.

There is, however, a fundamental nontrivial problem that has usually been overlooked, namely that the FCI is only meaningful in the context of 1st order perturbation theory. The perturbation series in powers of the nuclear magnetic moment does not converge and it is not sure whether the Lévy-Leblond equation (or the Dirac equation) for an electron in the field of a nucleus with an electronic charge and a magnetic point dipole has bound state solutions. We shall show that in spite of the divergence of the perturbation series the 1st order energy is physically meaningful. This requires a generalization of the Hellmann-Feynman theorem to the case where singular wave functions are involved.

The main conclusions of this paper are:

(a) The hyperfine interaction of the electron spin with the magnetic field of the nucleus is, like the very concept of the electron spin and of the interaction of electron spin with other external magnetic fields, not a relativistic effect. It can (to the leading order) be described correctly by the Galilei-invariant four-component spinor theory of Lévy-Leblond [19]. The usual derivations from relativistic theory burden a rather simple theory with unnecessary problems.

(b) The "Fermi-contact interaction" (FCI), a δ-function-term, in the Hamiltonian is neither present in the Dirac theory nor in the Levy-Leblond theory and arises as an artifact if one wants to describe the hyperfine interaction by first order perturbation theory in terms of two-component spinors (i.e. in a Schrödinger-Pauli like formulation). It arises then naturally from a rearrangement of the exact expressions (that don't contain δ-function) via integration by parts.

(c) An alternative phrasing of the same statement is that, when singular functions are involved the "turn-over-rule" for hermitean operators only holds if the differentiations implicit in these operators are taken in the distribution sense. Not only the charge distribution and the field strength but also the vector potential must be interpreted as distributions, but it happens that the vector potential does not contain any δ-term and can hence be treated as if it were a function.

(d) The correct theory is fully consistent with the picture that the magnetic field of the point nucleus must be taken as the limit to radius zero of an extended nucleus. This limit must be taken in the "distribution sense".

(e) The perturbation theory in powers of the magnetic moment of the nucleus does not converge. The field of a magnetic point dipole is so singular that the wave function has an essential singularity at $r=0$ and an expansion of the wave function in powers of the field strength does not exist. The "naive" expression of first-order perturbation theory can nevertheless be justified via the Hellman-Feynman theorem which, however, needs a modification for singular perturbations. It is not excluded that the perturbation series of the energy is at least asymptotic, and that the series may even converge for a nucleus of finite size.

(f) The popular derivation of the FCI by Blinder [10, 11] though formally correct, possibly suggests an incorrect picture of the origin of the FCI.

On the operator level the hyperfine interaction is a one-electron effect. We only discuss this level. It is well-known that for the actual values in many-electron systems, many-body effects play a large role (see, e.g. [20]).

2. A non-relativistic spin(1/2) particle in an external magnetic field: the first order corrections to the energy

A non-relativistic electron in an electric field with potential V in the absence of a magnetic field is described by the Lévy-Leblond equation [19] (for its relation to the Dirac and Schrödinger-Pauli equations see Appendix A)

$$H_0\psi_0 = E_0 S\psi_0 \tag{2.1}$$

$$H_0 = \begin{pmatrix} V & \vec{\sigma}\vec{p} \\ \vec{\sigma}\vec{p} & -2m \end{pmatrix}; \qquad S = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \qquad \psi_0 = \begin{pmatrix} \varphi_0 \\ \tilde{\chi}_0 \end{pmatrix} \tag{2.2}$$

ψ_0 is a 4-component spinor, H_0 and S are 4×4 matrices, given in (2.2) in terms of 2×2 blocks with $\vec{\sigma}=(\sigma_x, \sigma_y, \sigma_z)$ the vector of the three Pauli matrices. The first two components of ψ_0 are the 2-component spinor φ_0, referred to as "large component", while the 2-component spinor $\tilde{\chi}_0$ is referred to as "small component". This convention is reminiscent of that current in the relativistic theory although $|\tilde{\chi}_0|$ is not significantly smaller than $|\varphi_0|$ ($\tilde{\chi}_0$ is the non-relativistic limit of the $c\chi_0$ of the Dirac theory, see Appendix A). Eq. (2.1, 2) can be rewritten as

$$\tilde{\chi}_0 = \frac{\vec{\sigma}\vec{p}}{2m}\varphi_0; \qquad (V+T)\varphi_0 = E_0\varphi_0 \tag{2.3}$$

where $V+T$ is the usual non-relativistic Hamiltonian.

We introduce an external magnetic field as a perturbation. According to the principle of minimal coupling we have to replace $\vec{p}$ in (2.2) by

$$\vec{\pi} = \vec{p} - \frac{e}{c}\vec{A} = \vec{p} - e\vec{A}' \tag{2.4}$$

where $\vec{A}$ (or $\vec{A}'$) is the vector potential of the external field (depending on the system of units used).

We shall use the Gaussian system of units in which $\vec{A}$ appears multiplied by c^{-1}. Nevertheless one must keep in mind that the factor c^{-1} has not to be regarded as expansion parameter and does not imply that the interaction of a particle with an external field is a relativistic effect that vanishes in the non-relativistic limit (n.r.l.). In order to understand this problem one must realize that in taking the non-relativistic limit (n.r.l.) of quantum mechanics (see Appendix A) one must also take the n.r.l. of electrodynamics (which implies the incorporation of certain c^{-1} factors into the definition of electrodynamic quantities [19]).

From (2.4) we are led to the perturbing operator.

$$H' = -\frac{e}{c}\begin{pmatrix} 0 & \vec{\sigma}\vec{A} \\ \vec{\sigma}\vec{A} & 0 \end{pmatrix}. \tag{2.5}$$

We postpone a discussion on whether the application of perturbation theory is justified, to Sect. 5. The formal expression of the 1st order perturbation correction to the energy eigenvalues is

$$E_1 = \langle\psi_0|H'|\psi_0\rangle / \langle\psi_0|S|\psi_0\rangle. \tag{2.6}$$

We normalize ψ so that the denominator in (2.6) is equal to 1 and insert (2.3) and (2.5)

$$E_1 = -\frac{e}{2mc}\{\langle\vec{\sigma}\vec{p}\varphi_0|\vec{\sigma}\vec{A}\varphi_0\rangle + \langle\varphi_0|(\vec{\sigma}\vec{A})(\vec{\sigma}\vec{p})|\varphi_0\rangle\}. \tag{2.7}$$

So far the result is exact (in the framework of perturbation theory). One can use the "turnover-rule" for $\vec{\sigma}\vec{p}$ and get

$$E_1 = -\frac{e}{2mc}\langle\varphi_0|[\vec{\sigma}\vec{p}, \vec{\sigma}\vec{A}]_+|\varphi_0\rangle \tag{2.8}$$

which is straightforward if $\vec{A}$ is regular at the origin, and which is still valid for singular $\vec{A}$ if the derivative implicit in $\vec{p}$ is taken in the distribution sense (see Appendix B). Keeping this in mind (2.8) can be rewritten as

$$E_1 = -\frac{e}{2mc}\langle\varphi_0|\vec{p}\vec{A} + \vec{A}\vec{p} + i\vec{\sigma}(\vec{p}\times\vec{A}) + i\vec{\sigma}(\vec{A}\times\vec{p})|\varphi_0\rangle. \tag{2.9}$$

Introducing the magnetic field strength $\vec{B}$ and the Coulomb gauge

$$\text{rot}\,\vec{A} = \vec{B}; \qquad \text{div}\,\vec{A} = 0 \tag{2.10}$$

we get the traditional result

$$E_1 = -\frac{e}{mc}\langle\varphi_0|\vec{A}\vec{p}|\varphi_0\rangle - \frac{e\hbar}{2mc}\langle\varphi_0|\vec{\sigma}\vec{B}|\varphi_0\rangle. \tag{2.11}$$

For the special case of a homogeneous field with

$$\vec{A}_0 = \tfrac{1}{2}\vec{B}_0 \times \vec{r} \tag{2.12}$$

an alternative form of E_1 is

$$\begin{aligned} E_1 &= -\frac{e}{2mc}\langle\varphi_0|(\vec{B}_0 \times \vec{r})\cdot\vec{p}|\varphi_0\rangle - \frac{e\hbar}{2mc}\langle\varphi_0|\vec{\sigma}\vec{B}_0|\varphi_0\rangle \\ &= -\frac{e}{2mc}\langle\varphi_0|\vec{B}_0(\vec{l}+2\vec{s})|\varphi_0\rangle. \end{aligned} \tag{2.13}$$

For the field created by the spin of a nucleus with magnetic moment $\vec{\mu}$ the vector potential

$$\vec{A} = \frac{\vec{\mu}\times\vec{r}}{r^3} \tag{2.14}$$

is singular at the origin, but the integrals needed in (2.7) exist, as we shall see directly in Sect. 3.1. If we want to apply the "turn over rule" and switch to an expression like (2.9), we must take the derivative, implicit in (2.10), in the "distribution sense" (see Appendix B). This means that $\vec{B} = \mathrm{rot}\,\vec{A}$ consists now of two terms, $\vec{B}_f$ in which the derivatives are taken in the usual function sense (which is meaningful only for $r \neq 0$), and an extra term $\vec{b}$.

$$\begin{aligned} \vec{B}_f &= \mathrm{rot}_f\frac{(\vec{\mu}\times\vec{r})}{r^3} = \frac{1}{r^3}\nabla\times(\vec{\mu}\times\vec{r}) - (\vec{\mu}\times\vec{r})\times\nabla\frac{1}{r^3} \\ &= -\frac{\vec{\mu}}{r^3} + \frac{3(\vec{\mu}\vec{r})\vec{r}}{r^5} \end{aligned} \tag{2.15}$$

$$\vec{B} = \vec{B}_f + \vec{b};\ \vec{b} = -(\vec{\mu}\times\vec{r})\times\frac{\vec{r}}{r^4}\delta(r) = \vec{\mu}\frac{\delta(r)}{r^2} - \vec{r}\frac{\vec{\mu}\vec{r}}{r^4}\delta(r). \tag{2.16}$$

The extra term $\vec{b}$ gives rise to two contributions in (2.11), of which the first $\vec{\sigma}\vec{b}^{(0)}$ transforms as an irreducible tensor of rank 0 and the second one $\vec{\sigma}\vec{b}^{(2)}$ as an irreducible tensor of rank 2, i.e. $\vec{\sigma}\vec{b}^{(0)}$ is spherically symmetric, $\vec{\sigma}\vec{b}^{(2)}$ transforms like $\vec{\sigma}\vec{B}$ (see, e.g. [9])

$$\vec{b} = \vec{b}^{(0)} + \vec{b}^{(2)};\qquad \vec{b}^{(0)} = \frac{2}{3}\frac{\vec{\mu}}{r^2}\delta(r);\qquad \vec{b}^{(2)} = \frac{1}{3}\frac{\vec{\mu}}{r^2}\delta(r) - \vec{r}\frac{\vec{\mu}\vec{r}}{r^4}\delta(r). \tag{2.17}$$

One then gets

$$E_1 = -\frac{e}{mc}\left\langle\varphi_0\left|\frac{\vec{\mu}\cdot\vec{l}}{r^3}\right|\varphi_0\right\rangle - \frac{e\hbar}{2mc}\langle\varphi_0|\vec{\sigma}(\vec{B}_f + \vec{b}^{(0)} + \vec{b}^{(2)})|\varphi_0\rangle. \tag{2.18}$$

For s-states only $\vec{\sigma}\vec{b}^{(0)}$ contributes, hence

$$E_1 = -\frac{e\hbar}{3mc}\left\langle\varphi_0\left|\frac{\vec{\sigma}\vec{\mu}}{r^2}\delta(r)\right|\varphi_0\right\rangle = -\frac{4\pi e\hbar}{3mc}\langle\varphi_0|\vec{\sigma}\vec{\mu}\delta^3(\vec{r})|\varphi_0\rangle. \tag{2.19}$$

This is the Fermi-contact interaction. Of course, $\vec{b}^{(2)}$ also contains a $\delta(r)$ factor. However, $\vec{\sigma}\cdot\vec{b}^{(2)}$ only contributes if φ_0 has components with the (local) angular momentum quantum number l greater than zero, and these components vanish at $r=0$. The term $b^{(2)}$ does not contribute to E_1 and can be ignored. However, as pointed out by Moss and Watson [21] (see also [22]), this term is needed if one wants to go to higher orders in perturbation theory[1].

3. Evaluation of the first-order correction to the energy without explicit use of the Fermi-contact operator

3.1. Direct use of the Eq. (2.7)

Although the derivation given in the last section is perfectly rigorous (provided that 1st order perturbation theory is justified), one may want a derivation of the FCI, in which the concept of distributions, and hence of δ-functions is not needed at all. We do this in evaluating E_1 from the exact expression (2.7) for an atomic one-electron s-state wave functions φ_0. This derivation needs some familiarity with the handling of Pauli matrices and of the normalized eigenfunctions $\eta_\kappa^m(\vartheta,\varphi,s)$ of angular and spin variables (see, e.g. [23]) which is not necessary for the alternative derivation in Sect. 3.2. We take an atomic $s_{1/2}$ state (with the quantum number $\kappa=-1$)

$$\varphi_0 = g(r)\eta_{-1}^m(\vartheta,\varphi,s) \tag{3.1}$$

$$\vec{\sigma}\vec{p}\varphi_0 = -i\hbar\frac{\vec{\sigma}\vec{r}}{r}\frac{\partial\varphi_0}{\partial r} = -i\hbar\frac{\vec{\sigma}\vec{r}}{r}\frac{\partial g}{\partial r}\eta_{-1}^m(\vartheta,\varphi,s) = i\hbar\frac{\partial g}{\partial r}\eta_1^m(\vartheta,\varphi,s) \tag{3.2}$$

with $\eta_{-1}^m(\vartheta,\varphi,s)$ a normalized function of angular and spin coordinates for the quantum numbers $\kappa=-1$ and $m=m_s$. From (2.7) and (3.2) one gets

$$E_1 = \frac{-e\hbar}{2mc}\int_0^\infty \left[i\frac{\vec{\sigma}\vec{r}}{r}\frac{\partial g}{\partial r}, \frac{\vec{\sigma}(\vec{\mu}\times\vec{r})}{r^3}g\right]_+ r^2\,dr|\eta_{-1}^m|^2\,d\omega \tag{3.3}$$

where $d\omega$ implies integration over angular and spin variables. Since $\partial g/\partial r$ commutes with the other factors in the integral we can rearrange (3.3) to

$$\begin{aligned} E_1 &= \frac{-e\hbar}{mc}\,\mathrm{Re}\int_0^\infty \frac{i}{r^4}\frac{\partial g}{\partial r}(\vec{\sigma}\cdot\vec{r})(\vec{\sigma}\cdot[\vec{\mu}\times\vec{r}])gr^2\,dr|\eta_{-1}^m|^2\,d\omega \\ &= \frac{-e\hbar}{mc}\,\mathrm{Re}\int_0^\infty \frac{i}{r^2}\cdot\frac{\partial g}{\partial r}\{\vec{r}\cdot[\vec{\mu}\times\vec{r}]+i\vec{\sigma}\cdot[\vec{r}\times(\vec{\mu}\times\vec{r})]\}g\,dr|\eta_{-1}^m|^2\,d\omega. \end{aligned} \tag{3.4}$$

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[1] A referee whose report arrived after revision of the manuscript has pointed out that instead of the Lévy-Leblond equation one might use the 2nd order equation on two-component spinor level

$$\{(\vec{\sigma}\vec{p})^2/(2m)+V\}\varphi = E\varphi \tag{*}$$

with, in the presence of an external magnetic field, $\vec{p}$ replaced by $\vec{\pi}$. Straightforward application of 1st order perturbation theory leads then directly to Eq. (2.8) with no "turn-over-rule" involved. This is so only at first glance. In view of the discussion in Sects. 5.2 and 5.4, taking care of the singularity of the external magnetic field and the fact that the Hamiltonian (*) is of 2nd order (unlike the LL Hamiltonian) a correction term to E_1 arises, which results from the non-validity of the turn-over-rule in deriving the Hellman-Feynman expression of E_1, and this is just the FCI. So there is no way to avoid boundary term corrections to the turn-over-rule unless one decides to define derivations in the distribution sense (which is equivalent to taking care of these boundary terms)

The first term in the parenthesis vanishes and the second one consist of an irreducible tensor of rank 0 and one of rank 2. Only the former contributes in view of (3.1) to E_1 hence

$$E_1 = \frac{2e\hbar}{3mc} \operatorname{Re} \int_0^\infty (\vec{\sigma}\vec{\mu}) \frac{\partial g}{\partial r} g \, dr \, |\eta_{-1}^m|^2 \, d\omega = \frac{-e\hbar}{3mc} [g(0)]^2 \int \vec{\sigma}\vec{\mu} |\eta_{-1}^m|^2 \, d\omega \quad (3.5)$$

in agreement with (2.19).

3.2. Use of a damping factor corresponding to a finite nucleus

An alternative derivation consists in multiplying the $\vec{A}$ of (2.14) by a damping factor which makes it regular at the origin, i.e. which describes an extended (rather than point) nucleus, e.g.

$$\tilde{\vec{A}} = \vec{A} q(r); \qquad q(r) = 1 - \exp(-br^2) \quad (3.6)$$

with $\vec{A}$ given by (2.14). One may choose $q(r)$ differently as long as $q(r) \approx 0$ for r close to 0 and $q(r) \approx 1$ otherwise.

Then

$$\tilde{\vec{B}} = \operatorname{rot} \tilde{\vec{A}} = q(r) \operatorname{rot} \vec{A} - \vec{A} \times \frac{\vec{r}}{r} \frac{dq}{dr} \quad (3.7a)$$

$$\operatorname{div} \tilde{\vec{A}} = q(r) \operatorname{div} \vec{A} - \frac{\vec{\mu} \times \vec{r}}{r^4} \cdot \vec{r} \frac{dq}{dr} = \vec{0}. \quad (3.7b)$$

We insert (3.6) into (2.7). Since $\tilde{\vec{A}}$ is regular everywhere, we can apply the turn-over-rule in the traditional sense to get (2.9) and (2.11) (with $\vec{A}$ replaced by $\tilde{\vec{A}}$ and $\vec{B}$ by $\tilde{\vec{B}}$). Using (3.7b) we obtain

$$E_1 = -\frac{e}{mc} \langle \varphi_0 | \tilde{\vec{A}} \vec{p} | \varphi_0 \rangle - \frac{e\hbar}{2mc} \langle \varphi_0 | \vec{\sigma} q(r) \operatorname{rot} \vec{A} | \varphi_0 \rangle$$
$$+ \frac{e\hbar}{2mc} \left\langle \varphi_0 \left| \vec{\sigma} [\vec{A} \times \vec{r}] \frac{1}{r} \frac{dq}{dr} \right| \varphi_0 \right\rangle. \quad (3.8)$$

In the first two terms in (3.8) $q(r)$ appears as a multiplicative factor in the integrands. Although the limit for $b \to \infty$ of $q(r)$ is equal to 1 only for $r \neq 0$, the lmits of the integrals are obtained by taking the limit $q(r) = 1$ for all r, i.e. by omitting the factor $q(r)$. The last term in (3.8) needs special consideration

$$\frac{e\hbar}{2mc} \int |\varphi_0|^2 \vec{\sigma} [\vec{A} \times \vec{r}] \frac{1}{r} \frac{dq}{dr} d\tau = \frac{e\hbar}{2mc} \int |\varphi_0|^2 \vec{\sigma} \cdot \left[\frac{\vec{\mu} \times \vec{r}}{r^3} \times \vec{r} \right] 2b \exp(-br^2) \, d\tau$$
$$= \frac{-e\hbar}{3mc} \int_0^\infty |g(r)|^2 2br \exp(-br^2) \, dr \int \vec{\sigma}\vec{\mu} |\eta_{-1}^m|^2 \, d\omega \quad (3.9)$$

where in the last line of (3.9) we have inserted (3.1) and taken the spherically symmetric part of $(\vec{\mu} \times \vec{r}) \times \vec{r}$ like in (2.16, 17).

In the radial integral in (3.9) only r-values close to zero contribute significantly if b is large. In fact the error that one makes in replacing $g(r)$ by $g(0)$ is of the order $b^{-1/2}$ [24]. This error vanishes hence in the limit $b \to \infty$ and we get

$$\lim_{b\to\infty} \int_0^\infty |g(r)|^2 2br \exp(-br^2)\, dr = |g(0)|^2 \lim_{b\to\infty} \int_0^\infty \frac{dq}{dr}\, dr$$

$$= |g(0)|^2 \{q(\infty) - q(0)\} = |g(0)|^2 \tag{3.10}$$

such that we retrieve (3.5) which is equivalent to (2.19).

This derivation uses the concept of a distribution [25] as the limit of a sequence of regular functions [24] in a most direct way and its physical interpretation is that it is justified to idealize an extended dipole by a point dipole, at least in the present context.

4. Analysis of traditional derivations

We first study Fermi's original derivation, then two popular ones of the FCI from relativistic theory and finally conventional non-relativistic approaches.

4.1. Fermi's original derivation

Fermi's original papers [1, 2] are not easy to read. Recast into a modern notation the essential steps of this derivation are the following ones. Let the 4-component spinor $\phi_0 = \begin{pmatrix} \varphi_0 \\ \chi_0 \end{pmatrix}$ satisfy the Dirac equation

$$\begin{pmatrix} V-E & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & V-E-2mc^2 \end{pmatrix} \begin{pmatrix} \varphi_0 \\ \chi_0 \end{pmatrix} = 0. \tag{4.1}$$

The perturbation due to the magnetic field is then cH' with H' given by (2.5), and the first order energy is

$$E_1 = -e\{\langle \varphi_0 | \vec{\sigma}\vec{A} | \chi_0 \rangle + \langle \chi_0 | \vec{\sigma}\vec{A} | \varphi_0 \rangle\}. \tag{4.2}$$

For an atomic s-state one inserts (3.1) for φ_0 and

$$\chi_0 = if(r)\eta_1^m(\vartheta, \varphi, s) = -if(r)\frac{\vec{\sigma}\vec{r}}{r}\eta_{-1}^m(\vartheta, \varphi, s) \tag{4.3}$$

into (4.2). One then gets (3.3) with $(\hbar/2mc)\,\partial g/\partial r$ replaced by $f(r)$. Analogous manipulations as in Sect. 3.1 lead to

$$E_1 = \frac{4e}{3} \int_0^\infty g(r)f(r)\, dr \int \vec{\sigma}\vec{\mu} |\eta_{-1}^m|^2\, d\omega. \tag{4.4}$$

Since $g(r)$ and $f(r)$ are only weakly singular, the integrals in (4.4) exist and their nonrelativistic limit (n.r.l.) is obtained in terms of the n.r.l. of $g(r)$ and $f(r)$. Noting that in this limit

$$g = \frac{\hbar}{2mc} \frac{\partial f}{\partial r} \tag{4.5}$$

one immediately arrives at (3.5).

This not only shows that Fermi's original derivation is perfectly straightforward, but also that it is easily related to a derivation from the Lévy-Leblond equation.

4.2. Elimination of the small component

Starting from the Dirac equation in the presence of a magnetic field

$$\begin{pmatrix} V-E & c\vec{\sigma}\vec{\pi} \\ c\vec{\sigma}\vec{\pi} & V-E-2mc^2 \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = 0 \tag{4.6}$$

one gets

$$\chi = \frac{1}{2mc} k(r)\vec{\sigma}\vec{\pi}\varphi;\ k(r) = \left\{1 - \frac{V(r)-E}{2mc^2}\right\}^{-1} = 1 + 0(c^{-2}) \tag{4.7}$$

$$\left\{V + \frac{1}{2m}\vec{\sigma}\vec{\pi}k(r)\vec{\sigma}\vec{\pi}\right\}\varphi = \left\{V + \frac{(\vec{\sigma}\vec{\pi})^2}{2m} + 0(c^{-2})\right\}\varphi = E\varphi. \tag{4.8}$$

If in Eq. (4.8) one neglects the term $0(c^{-2})$ and inserts (2.4) for $\vec{\pi}$, one obtains

$$\left\{H_0 - \frac{e}{2mc}(\vec{p}\vec{A} + \vec{A}\vec{p}) - \frac{ie}{2mc}\vec{\sigma}\cdot(\vec{p}\times\vec{A} + \vec{A}\times\vec{p}) + \frac{e^2}{c^2}\vec{A}^2\right\}\varphi = E\varphi \tag{4.9}$$

with H_0 the unperturbed Schrödinger operator. Note that the c^{-1} associated with $\vec{A}$ must not be regarded as expansion parameter. If one regards the terms linear in $\vec{A}$ as a perturbation, then one gets the same first order perturbation correction to the energy (2.11) as derived in Sect. 2 provided that one takes the derivatives of $\vec{A}$ implicit in (4.9) in the distribution sense.

It is now not so obvious as in Sect. 2 why one should take these derivatives in the distribution sense. However, this is seen directly if we start from perturbation theory for the Dirac equation (4.6) with (4.1) the unperturbed equation and regard the terms linear in $\vec{A}$ as the perturbation. The first order energy correction is then (4.2).

If we now insert the leading term in the $1/c$ expansion of the small component χ_0 of the unperturbed Dirac equation, namely

$$\chi_0 = \frac{1}{2mc} k(r)\vec{\sigma}\vec{p}\varphi_0 = \frac{1}{2mc}\vec{\sigma}\vec{p}\varphi_0 + 0(c^{-3}) \tag{4.10}$$

we are led immediately to Eq. (2.7) and we can follow the arguments given there.

The reasoning found in textbooks [8, 9], that goes back to Blinder [10] is, however, different. One inserts (4.10) into (4.2), keeping a finite value of c, and applies the turn-over-rule to get

$$E_1 = -\frac{e}{2mc}\{\langle\varphi_0|\vec{\sigma}\vec{p}k(r)\vec{\sigma}\vec{A}|\varphi_0\rangle + \langle\varphi_0|\vec{\sigma}\vec{p}\vec{A}k(r)\vec{\sigma}\vec{p}|\varphi_0\rangle\} \tag{4.11}$$

where φ_0 is solution of the following Schrödinger equation

$$\left\{V+\frac{1}{2m}\vec{\sigma}\vec{p}k(r)\vec{\sigma}\vec{p}\right\}\varphi_0=E_0\varphi_0. \tag{4.12}$$

Finally one performs the limit $c\to\infty$.

One can forget the physical meaning of $k(r)$ and just keep in mind that $k(r)\approx 1$ for larger and $k(r)\approx 0$ for r close to 0, very much like the damping factor $q(r)$ used in Sect. 3.2 to describe the finite extension of the nucleus. In spite of the different functional form dk/dr approaches $2\delta(r)$ in the limit $c\to\infty$, like dg/dr does in the limit $b\to\infty$. The merit of either the factor $q(r)$ (for finite b) or $k(r)$ (for finite c) is that it regularizes the integrand in (3.8) or (4.11), such that the turn-over-rule can be applied without worrying whether this must be done in the "function sense" or the "distribution sense".

If one takes the limit $c\to\infty$ before one eliminates the small component and applies the turn-over-rule, i.e. if one uses the Lévy-Leblond equation as a non-relativistic limit of the Dirac equation (see Sect. 2), one must differentiate in the distribution sense and one gets directly the FCI. The entire meaning of the factor $k(r)$ is that it enables us to obtain in an indirect way the derivatives "in the distribution sense". There is not more physics behind it.

Since the two processes "elimination of the small component" and "taking the limit $c\to\infty$" don't commute (due to the fact that the limits $r\to 0$ and $c\to\infty$ don't commute) one is somewhat lucky that in either order of the two processes one gets the same final result for the FCI. Note, however, that one obtains the conventional Schrödinger equation as non-relativistic limit of the Dirac equation only if one first let $c\to\infty$ (see Appendix A) and eliminates χ then. In the inverse order one gets (4.12), which in the limit $c\to\infty$ becomes

$$\left\{H_0+\frac{1}{2m}[\vec{\sigma}\vec{p},k(r)]\vec{\sigma}\vec{p}\right\}\varphi_0=\left\{H_0-\frac{\hbar i}{2m}\frac{\vec{\sigma}\vec{r}}{r}\frac{dk}{dr}\vec{\sigma}\vec{p}\right\}\varphi_0$$

$$=\left\{H_0-\frac{\hbar i}{m}\delta(r)\frac{\vec{\sigma}\vec{r}\vec{\sigma}\vec{p}}{r}\right\}\varphi_0=E_0\varphi_0. \tag{4.13}$$

4.3. Use of the Foldy-Wouthuysen transformation

Another popular method to arrive at the non-relativistic limit of the Dirac Hamiltonian is via the Foldy-Wouthuysen (FW) transformation. In the presence of an external electric field this transformation cannot be performed in closed form. One rather constructs it as an expansion in powers of c^{-1}, although it is known that this expansion does not converge and leads to highly singular operators. The term of $0(c^0)$ is, nevertheless, the correct Schrödinger limit, while the term $0(c^{-2})$ containing the Pauli-corrections can at least be used in the context of perturbation theory. For our example the FW-transformation is

$$W=1+\frac{\pi}{2mc}+0\left(\frac{1}{c^3}\right) \tag{4.14}$$

and the transformed Hamiltonian (that acts on two component spinors)

$$H = W^{+}DW - mc^2 = \frac{1}{2m}(\vec{\sigma}\vec{\pi})^2 + V + 0(c^{-2}) \tag{4.15}$$

agrees with (4.8). One can then follow the argument after (4.8) and arrive at (4.9) and finally at (2.11), if one accepts that derivatives have to be taken in the distribution sense, which is rather obvious (see the Appendix C), but which may cause problems to those readers who take Blinder's [10] derivation of the Fermi contact term via the $k(r)$ of the last subsection 4.2 for granted.

Therefore the following considerations may be helpful. For a free particle the FW transformation is possible in closed form with the result

$$H = \sqrt{m^2c^4 + c^2(\vec{\sigma}\vec{p})^2} - mc^2. \tag{4.16}$$

A square root of a differential operator is, a priori, not defined. The only way to give a meaning to (4.16) is in momentum space i.e. via a Fourier transformation, where $\vec{p}$ becomes a multiplicative operator. However, derivatives that are defined via a Fourier transformation, mean necessarily derivatives in the distribution sense [24, 25].

4.4. Non-relativistic derivations of the FCI

If we assume that the electron has an intrinsic magnetic moment

$$\vec{m} = \frac{\hbar e}{mc}\vec{\sigma} \tag{4.17}$$

classical electrodynamics tells us that the energy density of the interaction of $\vec{m}$ with the magnetic field created by the nuclear magnetic moment $\vec{\mu}$ is

$$\vec{m} \cdot \vec{B} = \vec{m} \cdot \mathrm{rot}\, \vec{A} \tag{4.18}$$

with $\vec{A}$ given by (2.14) and the differentiation taken in the distribution sense. On averaging (4.18) over the electron distribution for an s-state and using (2.16, 17) we immediately arrive at (2.19).

The justification of why the differentiations must be taken in the distribution sense, can be found in Appendix C. This is probably the simplest possible "non-relativistic" derivation of the FCI. Other derivations found in the literature are usually harder to understand, especially if the authors had didactic ambitions [26–28].

Since the essential point in any derivation of the FCI is to realize that the magnetic field $\vec{B}$ created by a point nucleus is a distribution (see Appendix C), the various classical derivations can be classified according to how they manage to construct $\vec{B}$ as a distribution.

The direct approach just presented has probably not been used so far. There are three main indirect ways

(a) The expression for $\vec{B}$ is manipulated so that $\Delta(r^{-1})$ appears, which can via Eq. (B.24) (Appendix B) be related to $\delta^3(\vec{r})$.

This very popular approach [14–18] goes probably back to Casimir [5]. One starts, e.g., by writing

$$\vec{A} = \mathrm{rot}\frac{\vec{\mu}}{r} \tag{4.19}$$

and gets

$$\vec{B} = \mathrm{rot}\ \mathrm{rot}\ \vec{A} = \mathrm{grad}\ \mathrm{div}\frac{\vec{\mu}}{r} - \Delta\frac{\vec{\mu}}{r} \tag{4.20}$$

One then remembers (B.24) (see Appendix B) and arrives so at a δ-function as in (2.16). One may object to this derivation that (4.19) is only correct in the function sense, not in the distribution sense (see eq. (B.17)) and that one gets the incorrect impression that (B.24) is the only relation by which one could arrive at three-dimensional δ-functions.

(b) Differentiation of $\vec{A}$ via a Fourier transformation [13]. This implies directly differentiation in the distribution sense, though without referring to the theory of distributions it is hard to see why the Fourier transformation method leads to the correct result.

(c) Description of a point nucleus as the limit for $R \to 0$ of an extended nucleus. A straightforward way would be to proceed in analogy to Sect. 3.2. One would directly get (3.8) and one could follow the arguments after (3.8). This simple approach has, to the authors' knowledge, not been used in the literature. Instead, the nucleus has been described as a sphere with homogeneous magnetic dipole density [16, 28] or as a rotating charged sphere [26]. For models of this type the argument is somewhat simplified if one inverts the role of electron and nucleus, i.e. if one studies the magnetic field created by the electron distribution and its interaction with the point nucleus. A quite simple derivation on these lines is found in Ramsey's book [26] though it is more pictorial than rigorous (see also [12]). If one divides the space into a sphere around the nucleus (with a radius R larger than the size of the nucleus, but small enough such that the electron density inside this sphere can be regarded as constant) and the rest, then for an s-electron the "rest" does not create any field inside the sphere, only the electron distribution within the sphere. This field is homogeneous and proportional to the dipole moment density, hence independent of the radius of the sphere, such that the limit $R \to 0$ can easily be taken.

5. Theory to higher order in the field strength

5.1. The formal perturbation expansion

One can think of higher orders in perturbation theory in two ways:

(a) higher orders in powers of magnetic field strength $\vec{B}$, or the nuclear magnetic moment $\vec{\mu}$;

(b) relativistic corrections, i.e. higher orders in an expansion in c^{-1}.

Since we insist in this paper on a strictly non-relativistic theory we ignore aspect (b). It is possible to "sum (b) to infinite order" at least for one-electron atoms, by starting from Dirac wave functions and performing perturbation theory in the sense (a) [6, 7].

We first discuss the formal perturbation expansion without worrying whether the Lévy-Leblond equation in the presence of the field of a magnetic point dipole has bound state solutions and whether the perturbation expansion converges. We shall discuss these points and their consequences in Sects. 5.3 and 5.4.

The higher orders in perturbation theory with the unperturbed Hamiltonian (2.2) and the perturbation (2.5) are derived formally in a straightforward way. We concentrate our interest on the second order energy.

$$E_2 = \langle \psi_0 | H' | \psi_1 \rangle = -\frac{e}{c} \{ \langle \varphi_0 | \vec{\sigma}\vec{A} | \tilde{\chi}_1 \rangle + \langle \tilde{\chi}_0 | \vec{\sigma}\vec{A} | \varphi_1 \rangle \} \tag{5.1}$$

ψ_1 is a solution of

$$(H_0 - E_0 S)\psi_1 = -(H' - E_1 S)\psi_0 \tag{5.2}$$

or in component form

$$(V - E_0)\varphi_1 + \vec{\sigma}\vec{p}\tilde{\chi}_1 = -\frac{e}{c}\vec{\sigma}\vec{A}\tilde{\chi}_0 + E_1\varphi_0 \tag{5.3a}$$

$$\vec{\sigma}\vec{p}\varphi_1 - 2m\tilde{\chi}_1 = -\frac{e}{c}\vec{\sigma}\vec{A}\varphi_0. \tag{5.3b}$$

Elimination of the "small component" is possible which leads to

$$\chi_1 = \frac{e}{2mc}\vec{\sigma}\vec{A}\varphi_0 + \frac{1}{2m}\vec{\sigma}\vec{p}\varphi_1 \tag{5.4a}$$

$$(T + V - E_0)\varphi_1 + \frac{e}{2mc}[(\vec{\sigma}\vec{p}), (\vec{\sigma}\vec{A})]_+\varphi_0 - E_1\varphi_0 = 0 \tag{5.4b}$$

$$E_2 = -\frac{e}{2mc}\langle \varphi_0 | [(\vec{\sigma}\vec{A}), (\vec{\sigma}\vec{p})]_+ | \varphi_1 \rangle - \frac{e^2}{2mc^2}\langle \varphi_0 | (\vec{\sigma}\vec{A})^2 | \varphi_0 \rangle. \tag{5.5}$$

The usual replacement is made as in (2.9) and one notes that

$$(\vec{\sigma}\vec{A})^2 = \vec{A}^2. \tag{5.6}$$

If spin can be ignored, Eq. (5.4b) and (5.5) reduce to the well known equations of nonrelativistic theory.

Note, however, that in the 4-component spinor formulation there is only a perturbation H' linear in the field strength (while on 2-component spinor level we have a perturbation H_1 linear in the field strength and another one H_2 quadratic in it). So the "diamagnetic" and "paramagnetic" contributions are both formally expressible in terms of H' and ψ_1. On 4-component spinor level there is a "diamagnetic contribution" to the 1st order wavefunction, namely the first term

on the r.h.s. of (5.4a), which has no counterpart in the theory of the "large components only".

Practically important is double perturbation theory, e.g. with one $\vec{A}_0$ due to an external homogeneous field and another $\vec{A}$ due to a nuclear spin as in the theory of chemical shifts, or an $\vec{A}_\nu$ and an $\vec{A}_\mu$ both due to nuclear spins as in the theory of the indirect nuclear spin coupling. However our main interest is in the second-order contribution to the interaction of an electron (bound in a Coulomb field) with the field of a magnetic dipole.

It is well-known that for $\vec{A}$ created by a point dipole the second term in (5.5) diverges [29–35]. In nonrelativistic theory the integrand behaves as r^{-1} at the origin, i.e. the integral diverges as $\ln R$ (with R a cut-off parameter). In the relativistic limit, depending on how one performs it, a $\ln R$ or a R^{-1} divergence arises. With finite nuclear models finite results can be obtained, but the results appear to be rather model dependent and it is not easy to obtain physically meaningful 2nd order quantities.

There are some observables of $0(\mu^2)$ for which the divergent contributions cancel, such that finite results are obtained even for a point nucleus (like the "residual" Eq. (1) in [33]). This indicates that the perturbation series keeps some meaning in spite of it divergence, even beyond E_1.

The divergence of E_2 sheds some doubt on the validity of 1st order perturbation theory. We shall show in the following subsections that the treatment of E_1 has been allright in spite of the divergence of the series in powers of $\vec{\mu}$.

5.2. A model problem

In order to understand the structure of the non-relativistic wave functions of an atom in the presence of a magnetic point dipole we study an exactly solvable model problem that has the same kind of singularities, namely

$$H = -\frac{1}{2}\Delta - \frac{Z}{r} + \frac{\gamma^2}{2r^4} - \frac{Z\gamma}{r^2} \tag{5.7}$$

with the ground state wave function and energy

$$\varphi = \exp\{-Zr - \gamma r^{-1}\}; \qquad E = -Z^2/2. \tag{5.8}$$

In (5.7, 8) atomic (Hartree) units are used. We see that φ is equal to the eigenfunction $\exp\{-Zr\}$ for $\gamma = 0$, times a damping function

$$g(r) = \exp\{-\gamma/r\} \tag{5.9}$$

which is close to 1 for large r and equal to 0 for $r = 0$. In the limit $\gamma \to 0$ $g(r) = 1$ for $r \neq 0$ and $g(r) = 0$ for $r = 0$, very much like other damping functions considered in this paper. So $dg(r)/dr$ approaches $2\delta(r)$ for $\gamma \to 0$. Note that $g(r)$ vanishes more strongly at $r = 0$ than any r^k, i.e. that

$$\lim_{r \to 0} r^{-k} g(r) = 0, \quad \text{for all } k \tag{5.10}$$

and that $g(r)$ has an essential singularity at $r=0$ and hence no power series expansion in r. An expansion of $g(r)$ in powers of γ is formally possible

$$\frac{dg}{d\gamma} = -\frac{1}{r}\exp(-\gamma/r) = -\frac{r}{\gamma}\frac{dg}{dr} \tag{5.11a}$$

$$\frac{d^2g}{d\gamma^2} = \frac{1}{r^2}\exp(-\gamma/r) = \frac{1}{\gamma}\frac{dg}{dr} \tag{5.11b}$$

however these derivatives don't have a limit for $\gamma \to 0$, not even in the distribution sense. A perturbation expansion of the wave function is hence not possible. If one tries it nevertheless one is likely to get invalid results.

The perturbation corrections (in powers of γ) to the energy are, in view of (5.8) very simple, namely

$$E_k = 0, \quad \forall k > 0. \tag{5.12}$$

"Naive" evaluation of E_1 leads to

$$\gamma E_1 = -Z\gamma\langle\varphi_0|r^{-2}|\varphi_0\rangle/\langle\varphi_0|\varphi_0\rangle = -2\gamma Z^3 \tag{5.13}$$

which is obviously wrong. This result is surprising since one should expect from the Hellmann-Feynman theorem that the "naive" expression for E_1 agrees with $\lim_{\gamma\to 0}(\partial E/\partial\gamma)$. In the usual derivation of the Hellmann-Feynman theorem

$$\begin{aligned}\frac{\partial E}{\partial\gamma} &= \frac{\partial}{\partial\gamma}\frac{\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \frac{-\langle\varphi|H|\varphi\rangle\,\partial/\partial\gamma\,\langle\varphi|\varphi\rangle + \langle\varphi|\varphi\rangle\,\partial/\partial\gamma\,\langle\varphi|H|\varphi\rangle}{\langle\varphi|\varphi\rangle^2} \\ &= \frac{1}{\langle\varphi|\varphi\rangle^2}\left\{-\langle\varphi|H|\varphi\rangle\frac{\partial}{\partial\gamma}\langle\varphi|\varphi\rangle + \langle\varphi|\varphi\rangle \right. \\ &\quad \left. \times\left[\left\langle\frac{\partial\varphi}{\partial\gamma}\middle|H\middle|\varphi\right\rangle + \left\langle\varphi\middle|H\middle|\frac{\partial\varphi}{\partial\gamma}\right\rangle + \left\langle\varphi\middle|\frac{\partial H}{\partial\gamma}\middle|\varphi\right\rangle\right]\right\} \\ &= \left\langle\varphi\middle|\frac{\partial H}{\partial\gamma}\middle|\varphi\right\rangle\Big/\langle\varphi|\varphi\rangle\end{aligned} \tag{5.14}$$

one uses

$$H\varphi = E\varphi \tag{5.15a}$$

$$\left\langle\varphi\middle|H\middle|\frac{\partial\varphi}{\partial\gamma}\right\rangle = \left\langle H\varphi\middle|\frac{\partial\varphi}{\partial\gamma}\right\rangle \tag{5.15b}$$

and assumes that the limit of (5.14) for $\gamma\to 0$ exists. In the present example (5.15a) is certainly valid, while (5.15b), i.e. the hermiticity of H is not guaranteed, since both φ and $\partial\varphi/\partial\gamma$ are singular at $r=0$. In the limit $\gamma\to 0$ φ is regular, but $\partial\varphi/\partial\gamma$ is singular, such that the turn-over-rule for $\hat{H}$ is only justified if the differentiations implicit in H are taken "in the distribution sense" (or equivalently the boundary terms are not ignored). This means that

$$H\frac{\partial\varphi}{\partial\gamma} = -H\frac{1}{r}\varphi \tag{5.16}$$

differs from the expression obtained in the "function sense" by an extra term

$$\frac{1}{2}\left(\Delta\frac{1}{r}\right)\varphi = -2\pi\delta^3(\vec{r})\varphi = -\delta(r)r^{-2}\varphi. \tag{5.17}$$

One must hence replace (5.15b) by

$$\left\langle\varphi\left|H\right|\frac{\partial\varphi}{\partial\gamma}\right\rangle = \left\langle H\varphi\left|\frac{\partial\varphi}{\partial\gamma}\right\rangle + 2\pi\langle\varphi|\delta^3(\vec{r})|\varphi\rangle\right. \tag{5.18}$$

and consequently (5.13) by

$$\begin{aligned}\gamma E_1 &= \gamma\lim_{\gamma\to 0}\frac{\partial E}{\partial\gamma} = \gamma\left\{\left\langle\varphi_0\left|\left(\frac{\partial H}{\partial\gamma}\right)_0\right|\varphi_0\right\rangle + 2\pi\langle\varphi_0|\delta^3(\vec{r})|\varphi_0\rangle\right\}\Big/\langle\varphi_0|\varphi_0\rangle \\ &= \gamma\langle\varphi_0|-\frac{Z}{r^2}-2\pi\delta^3(\vec{r})|\varphi_0\rangle/\langle\varphi_0|\varphi_0\rangle \\ &= -2Z^3\gamma+2Z^3\gamma = 0\end{aligned} \tag{5.19}$$

which is the correct result. If we want to evaluate γE_1 as an expectation value with φ_0 we must do this with the operator

$$\gamma\tilde{H}_1 = -\frac{Z\gamma}{r^2}+\gamma 2\pi\delta^3(\vec{r}) \tag{5.20}$$

i.e. with an extra δ-function term.

If we add this term to the Hamiltonian (5.7) i.e. if we write

$$H = -\frac{1}{2}\Delta-\frac{Z}{r}+\frac{\gamma^2}{2r^2}-\frac{Z\gamma}{r^2}+2\pi\gamma\delta^3(\vec{r}) \tag{5.21}$$

this has no effect on the wave function and energy (5.8), since φ vanishes at $r=0$. However this δ-function term is absolutely necessary if we want to evaluate E_1 in the "naive" way, but nevertheless correctly.

One gets, of course, the same result (5.18–5.21) without worrying about distributions if one evaluates the l.h.s. of (5.18) in a pedestrian manner via two successive integrations by parts.

5.3. Behaviour of the exact wave function for small r

If one looks at the perturbation created by the magnetic field of a point dipole somewhat closely, one realizes that this is – in spite of the small effect on the eigenvalue – by no means a small perturbation. In fact for $r\to 0$ the unperturbed Hamiltonian is small compared to the perturbation. One must expect a drastic change of the wave function for small r, but almost no effect for large r, like for the model problem in Sect. 5.2.

In principle one should try to find the exact solution of the Lévy-Leblond equation

$$\begin{pmatrix} V-E & \vec{\sigma}\left(\vec{p}-\frac{e}{c}\vec{A}\right) \\ \sigma\left(\vec{p}-\frac{e}{c}\vec{A}\right) & -2m \end{pmatrix}\begin{pmatrix}\varphi\\ \tilde{\chi}\end{pmatrix}=0 \tag{5.22}$$

for $\vec{A}$ given by (2.14), or equivalently the 2nd order equation

$$\left\{H_0-E-\frac{e}{mc}\vec{A}\vec{p}+\frac{e}{mc}\vec{\sigma}\vec{B}+\frac{e^2}{2mc^2}\vec{A}^2\right\}\varphi=0. \tag{5.23}$$

Even if we are not able to find the solution of (5.22) or (5.23) in a closed non-perturbative way, we can formulate the behaviour of the exact solution in the limit $r\to 0$. In this limit all contributions $0(r^0)$ and $0(r^{-1})$ can be neglected and (5.22) reduces to

$$\begin{pmatrix} 0 & \vec{\sigma}\left(\vec{p}-\frac{e}{c}\vec{A}\right) \\ \vec{\sigma}\left(\vec{p}-\frac{e}{c}\vec{A}\right) & 0 \end{pmatrix}\begin{pmatrix}\varphi\\ \tilde{\chi}\end{pmatrix}=0. \tag{5.24}$$

Actually (5.24) is also the limit of the Dirac equation for $r\to 0$. We insert (2.14) and note that [23]

$$\vec{\sigma}(\vec{\mu}\times\vec{r})=-i(\vec{\sigma}\vec{\mu})(\vec{\sigma}\vec{r})+i\vec{\mu}\vec{r} \tag{5.25}$$

$$\vec{\sigma}\vec{p}=-i\sigma_r\left(\frac{\partial}{\partial r}+\frac{1}{r}-\frac{\beta}{r}K\right) \tag{5.26}$$

$$K=\beta(\vec{\sigma}\cdot\vec{l}+1); \qquad \sigma_r=\vec{\sigma}\vec{r}/r; \qquad \sigma_r^2=1. \tag{5.27}$$

Neglecting terms in $0(r^{-1})$ one can rewrite (5.24) as

$$-i\sigma_r\left\{\hbar\frac{\partial}{\partial r}-\frac{e}{c}\left(\frac{\vec{\sigma}\vec{\mu}}{r^2}-\sigma_r\frac{\vec{\mu}\vec{r}}{r^3}\right)\right\}\varphi=0 \tag{5.28}$$

and the same equation with φ replaced by $\tilde{\chi}$.

A formal solution of (5.28) is

$$\hat{\varphi}=\exp\left\{-\frac{\hbar e}{c}\left(\frac{\vec{\sigma}\vec{\mu}}{r}-\sigma_r\frac{\vec{\mu}\vec{r}}{r^2}\right)\right\} \tag{5.29}$$

This is not yet a wave function, since it contains the spin-operator $\vec{\sigma}$. A wave function φ is obtained if we apply $\hat{\varphi}$ to an arbitrary spin function, i.e. a constant two-component spinor. Obviously φ has an essential singularity at $r=0$. Since the factor of r^{-1} in the exponent can have either sign, φ may either vanish at $r=0$ or become infinite. The first case arises for a repulsive interaction of the electronic spin with the nuclear spin ($\vec{\sigma}$ "parallel" to $\vec{\mu}$) the latter case for an attractive interaction (spins antiparallel). We shall need the first derivative of φ

with respect to μ. Let us choose the quantization axis in the direction of $\vec{\mu}$, i.e. $\vec{\mu} = (0, 0, \mu)$. Then

$$\hat{\varphi} = \exp\left\{-\frac{\hbar e}{c}\left(\frac{\sigma_z \mu}{r} - \sigma_r \frac{\mu z}{r^2}\right)\right\} \tag{5.30a}$$

$$\frac{\partial \hat{\varphi}}{\partial \mu} = -\frac{\hbar e}{c}\left(\frac{\sigma_z}{r} - \sigma_r \frac{\cos \vartheta}{r}\right)\hat{\varphi} \tag{5.30b}$$

(with ϑ the angle between $\vec{\mu}$ and $\vec{r}$). In the limit $\mu \to 0$ φ becomes regular, while $\partial\varphi/\partial\mu$ has a singularity $\sim r^{-1}$.

With this discussion of the behaviour of the wave function for $r \to 0$ we have given a partial answer to the question of the existence of bound state solutions for atoms with a magnetic point dipole. We have also clarified that a convergent expansion of φ in powers of μ does not exist and that perturbation theory cannot converge. This holds for the Dirac equation and its non-relativistic limit, the Lévy-Leblond equation.

5.4. Justification of 1st order perturbation theory

Although the perturbation series diverges, the validity of 1st-order perturbation theory can be justified by means of the Hellmann-Feynman theorem like in Sect. 5.2. Let us first consider the 2nd order equation (5.23), which is equivalent to (5.22), such that φ has the same behaviour for $r \to 0$. Since $\partial\varphi/\partial\gamma$ is singular, we get a correction term to the Hellmann-Feynman theorem. This is derived as in Sect. 5.2, see Eq. (5.16) to (5.18). In view of (5.30b) the δ-function differs from that in (5.20) by a factor. The Hellmann-Feynman theorem is hence valid if we add the following correction term to the Hamiltonian

$$-\mu\frac{\hbar e}{2mc}(\sigma_z - \sigma_r \cos\vartheta)\left(\Delta\frac{1}{r}\right) = \mu\frac{\hbar e}{2mc}(\sigma_z - \sigma_r \cos\vartheta)\delta(r)r^{-2}$$

$$= \frac{\hbar e}{2mc}(\vec{\mu}\vec{\sigma} - \sigma_r \vec{\mu}\vec{r}/r)\delta(r)r^{-2}. \tag{5.31}$$

The isotropic part of (5.31) is exactly the Fermi-contact interaction.

It looks as if we had now still another explanation of the FCI, in addition to the two discussed previously, namely (1) point nucleus as a limit of finite nuclei, (2) limit of the relativistic case for $c \to \infty$. The new explanation (3) - correction term to the Hellmann-Feynman theorem - has with the old one (1) much in common. Both are based on the fact that the turn-over-rule for a hermitean operator, when singular functions are involved, only holds if the derivatives are taken "in the distribution sense". Alternatively one can say that the partial integrations on which the "turn-over-rule" is based, introduces "boundary terms".

We have started this paper by pointing out that there is no δ-function term if we use the Lévy-Leblond equation. We now show that for the Lévy-Leblond equation the "naive" evaluation of E_1 is justified.

We consider Eq. (5.14) but with φ replaced by the 4-component spinor ψ. The turn-over-rule holds automatically for the diagonal multiplicative operators in the Hamiltonian. So we must only show that for the differential operator the turn-over-rule is valid, i.e. that

$$\left\langle \varphi_0 \middle| \vec{\sigma}\vec{p} \middle| \left(\frac{\partial \chi}{\partial \gamma}\right)_0 \right\rangle + \left\langle \chi_0 \middle| \vec{\sigma}\vec{p} \middle| \left(\frac{\partial \varphi}{\partial \gamma}\right)_0 \right\rangle = \left\langle \vec{\sigma}\vec{p}\varphi_0 \middle| \left(\frac{\partial \chi}{\partial \gamma}\right)_0 \right\rangle + \left\langle \vec{\sigma}\vec{p}\chi_0 \middle| \left(\frac{\partial \varphi}{\partial \gamma}\right)_0 \right\rangle \tag{5.32}$$

(5.32) holds in fact for our example (with γ replaced by μ), because in view of (5.30b)

$$\left(\frac{\partial \chi}{\partial \mu}\right)_0 \sim \frac{1}{r}\chi_0; \qquad \left(\frac{\partial \varphi}{\partial \mu}\right)_0 \sim \frac{1}{r}\varphi_0 \tag{5.33}$$

and because $\vec{\sigma}\vec{p}$ is a first-order differential operator. Differention in the distribution sense introduces at most terms in $\sim\delta(r)/r$, which give no contribution to the integrals due to the factor r^2 from the volume element. (For the second-order equation (5.23) a correction term to the Hellmann-Feynman theorem arises because $-\frac{1}{2}\Delta$ is a second order differential operator).

So we have finally justified the starting point of Sect. 2.

Note that the result of this subsection also applies to the Dirac equation, i.e. that 1st order perturbation theory within the Dirac theory is also justified without any additional δ-function term.

5.5. How to evaluate higher order corrections

While the question of the existence of solutions of Eq. (5.23) and of their analytic behaviour, namely for $r \to 0$ is of principal interest, the actual solution of (5.23) or the improvement of the solutions beyond first-order perturbation theory is more like an academic problem (see, however, the last but one paragraph in Sect. 5.1). In fact contributions to the hyperfine interaction of higher than first order in the nuclear magnetic moment of the nucleus are quantitatively of minor importancae [33]. Much more important are the quantum electrodynamic effects on the electronic g-factor and then the leading relativistic corrections.

Perturbation theory to higher than first order is a delicate matter, at least for a point nucleus. There may be a chance to get finite results in perturbation theory, if one starts from a different unperturbed problem. We may, e.g. choose a H_0 like in Sect. 5.2 which has an eigenfunction that goes for small r like $\exp\{-\gamma/r\}$ with $\gamma > 0$. Then all integrals that arise in perturbation theory of the type $\langle \varphi_0 | r^{-k} | \varphi_0 \rangle$ and that diverge for the conventional φ_0 will have finite values. This will still not make the perturbation series converge, but it may at least become asymptotic.

6. Concluding remarks

We have seen that the Fermi contact operator, which contains a "δ-function" is essentially an artifact due to the attempt to formulate the interaction of an electron

with the spin of a point nucleus by 1st order perturbation theory with a Pauli-like Hamiltonian. It does not arise in a non-perturbative formulation, and with the Lévy-Leblond equation not even in 1st-order perturbation theory, strictly speaking there is no δ-term in the Hamiltonian, it appears only in certain matrix elements and there due to the fact that "boundary terms" of an integration by parts don't vanish.

We have insisted on the fact that the interaction of the electron spin with the magnetic moment of the nucleus is *not* a relativistic effect. Some readers may have difficulties to appreciate this point. They may argue that the interaction between two electron spins is necessarily relativistic (to lowest order described by the Breit Hamiltonian) and that there should be no fundamental difference between the mechanisms of the interaction of various spins, even if the gyromagnetic ratio of the nuclear spin is not yet understood quantitatively. In fact, if one expresses the nuclear magnetic moment in terms of the nuclear magneton and the gyromagnetic ratio the final expression for the interaction energy contains a factor c^{-2} (or α^2) which is typical for relativistic effects.

The point is that in the theory of the interaction of two electron spins we must use a single theory, that describes both the generation of a magnetic field by one electron and the interaction of the other electron with this field. In the theory of the hyperfine splitting we have two independent theories, one (that we don't worry about here) for the origin of the magnetic moment of the nucleus, and one for interaction of the electron with an external field. We can also put it in this way: in the leading contribution of the interaction of an electron with an external magnetic field (of the nucleus) the relativistic kinematics is not involved, only the existence of the spin and its gyromagnetic ratio, which are (except for QED corrections) correctly described in a Galilei-invariant theory [19].

In a theory of the motion of electrons with fixed nuclei it is legitimate to treat the magnetic moment of the nucleus as an external source, but to make no *ad-hoc*-assumptions about the electron spin. If one does not even worry about the origin of the electron spin and the magnetic moment associated with it, then even the interaction of two electron spins can be described classically (both for the dipole and the contact part); only the factor c^{-2} in front of the spin-spin interaction suggests then that it vanishes the non-relativistic limit, and is hence a relativistic effect.

A reader may also be puzzled by our insisting on the exact (non-perturbative) non-relativistic theory and in discriminating between expansion in powers of $|\vec{\mu}|$ (non-relativistic perturbation theory) and in powers of c^{-1} (perturbation theory of relativistic effects). In a way $\vec{\mu}$ is proportional to c^{-1} and the above distinction may seem artificial. It is, however, consistent with the philosophy that the magnetic field of the nucleus is (like by the way also the electric field of the nucleus) regarded as an external field, the mechanism to which it is due does not matter. Moreover the exact non-relativistic theory is well-defined and the discussion of the analytic properties of the exact non-relativistic wave functions is interesting.

This is also important for a better understanding of the indirect coupling of two nuclear spins.

The full theory requires, of course, the inclusion of relativistic corrections as well as of QED effects, but these are well understood, at least for the H-atom, and they are outside the scope of this paper.

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Appendix A

The Lévy-Leblond equation as non-relativistic limit of the Dirac equation

We start from the Dirac equation

$$\begin{pmatrix} V-E & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & V-E-2mc^2 \end{pmatrix}\begin{pmatrix}\varphi\\ \chi\end{pmatrix}=0. \tag{A.1}$$

We limit our interest to electronic states which have a non-relativistic limit, i.e. we discard both positronic and ultrarelativistic electronic solutions. Then $|\chi|$ is smaller than $|\varphi|$ by roughly a factor c^{-1}. We replace χ by

$$\tilde{\chi}=c\chi \tag{A.2}$$

such that $\tilde{\chi}$ and φ are of comparable magnitude. Then (A.1) becomes

$$\begin{pmatrix} V-E & \vec{\sigma}\vec{p} \\ \vec{\sigma}\vec{p} & -2m+\dfrac{V-E}{c^2} \end{pmatrix}\begin{pmatrix}\varphi\\ \tilde{\chi}\end{pmatrix}=0. \tag{A.3}$$

The non-relativistic limit is then easily obtained by letting c in (A.3) go to ∞. The result is the Lévy-Leblond equation [19]

$$\begin{pmatrix} V-E & \vec{\sigma}\vec{p} \\ \vec{\sigma}\vec{p} & -2m \end{pmatrix}\begin{pmatrix}\varphi\\ \tilde{\chi}\end{pmatrix}=0 \tag{A.4}$$

that is non-relativistic, but still describes a spin-(1/2) particle, with 4-component spinor wave functions.

In the absence of a magnetic field, the "small" component $\tilde{\chi}$ (which is, strictly speaking, not small compared to φ) can easily be eliminated. Solving for $\tilde{\chi}$, i.e.

$$\tilde{\chi}=\frac{\vec{\sigma}\vec{p}}{2m}\varphi \tag{A.5}$$

and insertion of (A.5) into the first line of (A.4) yields the ordinary Schrödinger equation

$$\{V+(\vec{\sigma}\vec{p})^2/(2m)-E\}\varphi=0. \tag{A.6}$$

In the presence of a magnetic field (with $\vec{p}$ replaced by $\vec{\pi}$) its interaction with the electron spin is correctly described (including the gyromagnetic ratio 2).

The original derivation [19] of the Lévy-Leblond equation, unlike the one given here, does not start from the Dirac equation, but results from formulating a Galilei-invariant field theory for spin-(1/2) particles.

Appendix B

Distributions and the turn-over-rule

We review here what one needs to know of the theory of distributions [25] in order to understand when and why δ-terms arise. We start with a few remarks on one-dimensional distributions. The "generalized functions" of Lighthill [26], whom we follow here, are a special class of distributions, that in the general theory are referred to as "tempered distributions'. A "good functions" is, by definition, differentiable an infinite number of times and satisfies

$$\frac{\partial^n f}{\partial x^n} = f^{(n)} = 0\{|x|^{-N}\}, \forall N > 0 \quad \text{for } x \to \infty,\ n = 0, 1, 2, \ldots . \tag{B.1}$$

A "regular" sequence $f_k(x)$; $k = 0, 1, \ldots \infty$ (the index may also be continuous) of "good functions" defines a distribution f, if the limit

$$\int_{-\infty}^{\infty} f(x)F(x)\,dx \overset{\text{def}}{=} \lim_{k\to\infty} \int_{-\infty}^{\infty} f_k(x)F(x)\,dx \tag{B.2}$$

exists for all good functions $F(x)$. It is not required that the limit f_∞ of the sequence of functions exists, in particular the limit need not itself be a "good function".

The sequence

$$f_n(x) = e^{-x^2/n^2} \tag{B.3}$$

converges (for $n \to \infty$) to the function $f(x) = 1$ (which is not a good function), while the sequence

$$f_n(x) = \sqrt{\frac{n}{\pi}}\, e^{-nx^2} \tag{B.4}$$

has no limit as a function. However

$$\int_{-\infty}^{\infty} \delta(x)F(x)\,dx \overset{\text{def}}{=} \lim_{n\to\infty} \int_{-\infty}^{\infty} f_n(x)F(x)\,dx = F(0) \tag{B.5}$$

defines the δ-distribution.

In view of the properties of good functions, partial integration is always possible, without a boundary contribution

$$\begin{aligned}\int_{-\infty}^{\infty} f_n'(x)F(x)\,dx &= f_n(x)F(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f_n(x)F'(x)\,dx \\ &= -\int_{-\infty}^{\infty} f_n(x)F'(x)\,dx.\end{aligned} \tag{B.6}$$

One can therefore define the derivative of a distribution without a need for studying the sequence which defines it, namely via

$$\int f'(x)F(x)\,dx = -\int f(x)F'(x)\,dx \tag{B.7}$$

e.g. one can define $\delta'(x)$ via

$$\int \delta'(x)F(x)\,dx = -F'(0). \tag{B.8}$$

In view of (B.6) the operator $-i(d/dx)$ (with differentiation understood in the distribution sense) is hermitean for f a distribution and F a good function.

$$\left\langle f(x)\left| -i\frac{d}{dx}\right| F(x)\right\rangle = \left\langle F(x)\left| -i\frac{d}{dx}\right| f(x)\right\rangle^{*}. \tag{B.9}$$

If the sequence $f_n(x)$ of "good functions" that defines a distribution $f(x)$ has a continuous limit $f_\infty(x)$ in the function sense, we say that the distribution $f(x)$ is equal to the function $f_\infty(x)$. If furthermore $f_\infty(x)$ is differentiable everywhere and has a continuous first derivative, then the first derivative of $f(x)$ in the distribution sense agrees with its counterpart in the traditional sense. It may, however, happen that $f(x) = f_\infty(x)$, but that $f_\infty(x)$ is discontinuous for some x, e.g. $x = 0$, or that $f_\infty(x)$ has a discontinuous first derivative. An example for the first case is the sign function

$$\operatorname{sgn}(x) = \begin{cases} +1 & \text{for } x > 0 \\ 0 & \text{for } x = 0 \\ -1 & \text{for } x < 0. \end{cases} \tag{B.10}$$

From (B.6) we easily get

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d}{dx}(\operatorname{sgn} x)F(x)\,dx &= -\int_{-\infty}^{\infty} \operatorname{sgn} x F'(x)\,dx \\ &= \int_{-\infty}^{0} F'(x)\,dx - \int_{0}^{\infty} F'(x)\,dx = 2F(0). \end{aligned} \tag{B.11}$$

Hence

$$\frac{d}{dx}(\operatorname{sgn} x) = 2\delta(x). \tag{B.12}$$

We are especially interested in distributions in three dimensions, in particular those that correspond to the functions r^{-k} and their gradients (see also [21]).

Let us first construct ∇r^{-k} by the three-dimensional generalization of (B.7). We hence evaluate

$$I = \int (\nabla r^{-k})F(\vec{r})\,d\tau = -\int r^{-k}[\nabla F(\vec{r})]\,d\tau. \tag{B.13}$$

It is appropriate to choose the good function $F(\vec{r})$ vector valued and to interpret the product in (B.13) as a dot product such that I becomes a scalar. A convenient choice of $F(\vec{r})$ is then

$$F(\vec{r}) = \vec{r}\tilde{F}(r) \tag{B.14}$$

with $\tilde{F}(r)$ a scalar good function. Then, noting that

$$\int_0^\infty F(r)\delta(r)\,dr = \frac{1}{2}\int_{-\infty}^{\infty} F(|r|)\delta(r)\,dr = \frac{1}{2}F(0) \tag{B.15}$$

we get

$$\begin{aligned} I &= -\int r^{-k}\nabla[\vec{r}\tilde{F}(r)]\,d\tau = -3\int r^{-k}\tilde{F}(r)\,d\tau - \int r^{-k+1}\tilde{F}'(r)\,d\tau \\ &= -12\pi\int_0^\infty r^{-k+2}\tilde{F}(r)\,dr - 4\pi\int_0^\infty r^{-k+3}\tilde{F}'(r)\,dr \\ &= -12\pi\int_0^\infty r^{-k+2}\tilde{F}(r)\,dr - 4\pi r^{-k+3}\tilde{F}(r)\Big|_0^\infty + 4\pi(-k+3)\int_0^\infty r^{-k+2}\tilde{F}(r)\,dr \\ &= -4\pi k\int_0^\infty r^{-k+2}\tilde{F}(r)\,dr - 8\pi\int_0^\infty r^{-k+3}\tilde{F}(r)\delta(r)\,dr \end{aligned} \tag{B.16}$$

and we conclude that

$$\nabla r^{-k} = -k\vec{r}r^{-k-2} + 2\vec{r}r^{-k-1}\delta(r) \tag{B.17}$$

since insertion of the r.h.s. of (B.17) into (B.13) yields (B.16).

The δ-term in (B.17) results from the boundary term of an integration by parts. This clearly indicates that the operator $i\nabla$ is, if singular functions are involved, in view of (B.13) only hermitean if the derivatives are taken in the distribution sense.

There is an alternative way to arrive at (B.17), namely by considering the sequence $f_n(r)$ which defines the distribution r^{-k}

$$f_n(r) = r^{-k}g_n(r);\ g_n(r) = 1 - \exp(-nr^m) \tag{B.18}$$

with $m \geq k-1$. Then

$$\nabla f_n(r) = -k\vec{r}r^{-k-2}g_n(r) + \vec{r}r^{-k-1}\frac{dg(r)}{dr} \tag{B.19}$$

noting that for $n \to \infty$, g_n approaches 1 (except at $r=0$, where $g(r)=0$), and $dg_n(r)/dr$ approaches the δ-distribution, (B.19) leads to (B.17). To see that $dg_n(r)/dr$ defines the δ-functions we note (B.15) and that

$$\begin{aligned} \lim_{n\to\infty}\int_0^\infty \frac{dg_n(r)}{dr}F(r)\,dr &= F(0)\lim_{n\to\infty}\int_0^\infty \frac{dg_n(r)}{dr}\,dr = F(0) \\ &= 2\int_0^\infty \delta(r)F(r)\,dr. \end{aligned} \tag{B.20}$$

(The factor 2 arise because we integrate from 0 to ∞, rather than from $-\infty$ to ∞).

For $k=1$, the δ-term, though present in (B.19) does not contribute to the integral (B.16), since it vanishes. It becomes important mainly for $k=3$ (see Appendix C).

Note finally that taking the divergence of (B.17) yields

$$\nabla \cdot \nabla r^{-k} = k(k-1)r^{-k-2} - 4(k-1)r^{-k-1}\delta(r) + 2r^{-k}\delta'(r) \tag{B.21}$$

especially for $k=1$

$$\Delta r^{-1} = 2r^{-1}\delta'(r) \tag{B.22}$$

In view of

$$\begin{aligned}\int_0^\infty 2r^{-1}\delta'(r)\tilde{F}(r)\,d\tau &= 8\pi\int_0^\infty \delta'(r)r\tilde{F}(r)\,dr \\ &= -8\pi\int_0^\infty \delta(r)\{\tilde{F}'(r)r+\tilde{F}(r)\}\,dr = -4\pi\tilde{F}(0) \\ &= -\int \tilde{F}(r)\delta^3(\vec{r})\,d\tau\end{aligned} \tag{B.23}$$

we can rewrite (B.21) as

$$\Delta r^{-1} = -4\pi\delta^3(\vec{r}); \qquad \delta^3(\vec{r}) = \delta(x)\delta(y)\delta(z) \tag{B.24}$$

with $\delta^3(\vec{r})$ the three-dimensional δ-function. (B.24) is probably the best known relation that involves $\delta^3(\vec{r})$.

Let us finally note another property of tempered distributions as defined in this section. Their Fourier transform (in the distribution sense) always exists and is invertible. This allows one e.g. to evaluate $\nabla f(r)$ in the distribution sense by first constructing the three dimensional Fourier transformation $g(p)$, then multiplying $g(p)$ by ip (or by $2\pi ip$ depending on how one defines the Fourier transformation) and transforming back $ipg(p)$.

Appendix C

The field strengths of an electric monopole and a magnetic dipole

The potential $\phi(\vec{r})$ created by a charge distribution $\varrho(\vec{r})$ satisfies the Poisson equation

$$\Delta\phi = -4\pi\varrho. \tag{C.1}$$

If one chooses a sequence ϱ_n of charge distributions that define (see appendix B) the distribution $\delta^3(\vec{r})$, then in the limit $n\to\infty$ ϕ approaches the distribution $1/r$ which is equal to the function $1/r$. Although $1/r$ is singular at $r=0$ this does not matter for its expectation values, since it only appears in integrals multiplied by r^2 from the volume element.

The electric field strength corresponding to a point charge is according to (B.17)

$$E = -\text{grad}\frac{1}{r} = \frac{\vec{r}}{r^3} - 2\frac{\vec{r}}{r^2}\delta(r) \tag{C.2}$$

However the 2nd term in (C.2) can usually be ignored since its expectation value vanishes in view of $\vec{r}\delta(r) = \vec{0}$.

Multiplication of $1/r$ by a damping factor $g(r)$ like (B.18) amounts to "spreading out" the point charge

$$\Delta\left\{\frac{1}{r}g(r)\right\} = \frac{1}{r}\frac{d^2g}{dr^2} = -4\pi\varrho(r) \tag{C.3}$$

The vector potential created by a magnetic point dipole satisfies the Poisson equation

$$\Delta\vec{A} = \frac{4\pi}{c}\vec{j} = \frac{4\pi}{c}\vec{\mu}\times\nabla\delta(\vec{r}) \tag{C.4}$$

Since $\vec{j}$ is a distribution, $\vec{A}$ must be a distribution as well, although, like ϕ, it is equal to a function

$$\vec{A} = \frac{\vec{\mu}\times\vec{r}}{r^3}. \tag{C.5}$$

According to the rule of appendix B we get

$$\vec{B} = \mathrm{rot}\,\frac{\vec{\mu}\times\vec{r}}{r^3} = \frac{\vec{r}}{r^3} - \frac{3(\vec{\mu}\vec{r})\vec{r}}{r^5} + \vec{\mu}\frac{\delta(r)}{r^2} - \vec{r}\frac{\vec{\mu}\vec{r}}{r^4}\delta(r) \tag{C.6}$$

$$4\pi\vec{j} = \mathrm{div}\,\vec{B} = -\frac{\vec{\mu}\vec{r}}{r^4}\delta(r) \tag{C.7}$$

which agrees with (C.4), if we note that

$$2\pi\delta^3(\vec{r}) = \frac{\delta(r)}{r^2} = -\frac{\delta'(r)}{r}. \tag{C.8}$$

That all quantities in this appendix ϱ, ϕ, $\vec{E}$, $\vec{j}$, $\vec{A}$ and $\vec{B}$ must be interpreted in the distribution sense is obvious, if one realizes that in reality there are no point charges or point dipoles and the point limit of extended charge contributions is only taken under integral signs and is meaningless otherwise. It turns out, however that for ϕ and $\vec{A}$ (not $\vec{E}$ and $\vec{B}$) the limits exist even in the function sense, i.e. that if one uses ϕ and $\vec{A}$ only, one need not introduce distributions, unless one has to differentiate ϕ or $\vec{A}$.

One should mention that the wave functions of quantum mechanics are not "good functions" in the strict sense, since they may have discontinuous first derivations for $r = 0$. However that has hardly an effect on the applicability of the theory of distributions.

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