Diamagnetism in relativistic theory

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A unitary transformation of the Dirac operator in a magnetic field is presented, which leads to a reformulation of the interaction of a Dirac particle with a magnetic field, in which, as in nonrelativistic theory, diamagnetic and paramagnetic contributions appear naturally, but at a four-component-spinor level. The diamagnetic contribution to the magnetic susceptibility consists of two terms, each of which is evaluated as a simple expectation value with the unperturbed relativistic wave function. One of the two terms closely resembles its nonrelativistic counterpart. The proposed formalism is analyzed in the context of the direct perturbation theory of relativistic effects. It is compared with the more traditional sum-over-states approach including negative-energy states, as well as with a Fock-space formulation. In the latter, the vacuum energy depends on the external magnetic field. The creation of a particle (electron or positron) is accompanied by a change of the vacuum energy via a kind of exclusion effect. This change can be identified with the diamagnetism of the particle. The access to diamagnetism and paramagnetism based on the Gordon decomposition of the induced current density is to some extent, but not entirely, equivalent to that which results from the unitary transformation. For a physically meaningful decomposition of the current density a combination of the Gordon approach with the unitary transformation is recommended. Neither the interpretation nor the computation of diamagnetic contributions in terms of negative-energy states is encouraged.

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I. INTRODUCTION

In *nonrelativistic* quantum mechanics, second-order magnetic properties such as susceptibilities are obtained as sums of a *diamagnetic* and a (van-Vleck) *paramagnetic* term. Although the decomposition into these terms is *gauge dependent*, one can often take care that the paramagnetic term vanishes or is very small in magnitude [1,2]. The dominating diamagnetic contribution can then easily be evaluated in terms of the unperturbed wave function only.

A similar decomposition is, at least, not obvious in relativistic theory. Some authors have attempted to recover the diamagnetic contributions by a separate summation over *negative-energy states* [3–6], or via the *Gordon decomposition* of the current density [7–9]. Neither approach is fully satisfactory, the first one for various rather fundamental reasons (see Sec. IV), the second one because it is rather complicated and indirect. The two approaches lead to different definitions of the diamagnetic part, which only agree in the nonrelativistic limit. We shall show here that a very simple and transparent way towards a decomposition of relativistic second-order properties into diamagnetic and paramagnetic contributions is possible, which is so simple that one wonders why it has not been found earlier.

It is based on a *unitary transformation* of the Dirac operator in the presence of a magnetic field. It is worth noting that in this way diamagnetism and (van-Vleck) paramagnetism appear *independently of a separation between electronic and positronic states*. Alternatively this very separation and the care for the *correct nonrelativistic limit* lead to the appearance of diamagnetic and paramagnetic terms as well, and then independently of the just-mentioned unitary transformation. These observations suggest to present a general analysis of the meaning of diamagnetism.

Actually, a magnetic field has a strong influence on the solutions of the Dirac equation. This can be rationalized either in terms of a change of the key relation $\chi = X\varphi$ between the large (φ) and the small (χ) components of the Dirac spinor $\psi = (\varphi, \chi)$ for an electronic (positive-energy) state, or in terms of a change of the *vacuum state* by the magnetic field that even survives in the nonrelativistic limit. To describe a relativistic electron in a magnetic field in terms of the states in the absence of this field is not a good choice. It is preferable to remove the coupling of φ and χ by the magnetic field at an early stage, e.g., by the unitary transformation proposed here, or by direct perturbation theory (DPT) of relativistic effects.

The Gordon decomposition of the induced current density is not strictly equivalent to the unitary transformation introduced here. The two approaches are even to some extent complementary, although they lead essentially to the same definition of the diamagnetic contribution to the magnetizability.

II. NONRELATIVISTIC THEORY

The nonrelativistic Pauli Hamiltonian for an electron in a magnetic field with vector potential $\vec{A}$, and field strength $\vec{B} = \mathrm{curl}\vec{A}$, which satisfies the Coulomb gauge $\mathrm{div}\vec{A} = 0$, is in *atomic units*

$$H = \tfrac{1}{2}(\vec{p} + b\vec{A})^2 + b\,\vec{\sigma}\cdot\vec{B} + V = H_0 + b\,H_1 + b^2 H_2\,, \tag{2.1}$$

$$H_0 = \tfrac{1}{2}p^2 + V;\quad H_1 = \vec{A}\cdot\vec{p} + \vec{\sigma}\cdot\vec{B};\quad H_2 = \tfrac{1}{2}A^2\,. \tag{2.2}$$

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The constant b depends on the chosen variant of the system of atomic units [10]. One has $b=c^{-1}$ in the original *Hartree system* [11] that was based on the *Gaussian* cgs system (with $\hbar$, m, and $|e|$ the basic units), and $b=1$ in the so-called *SI-based* system of atomic units [10,12] (with $\hbar$, m, $|e|$, and $4\pi\epsilon_0$) the basic units) In either system $\frac{1}{2}b$ can be identified with the Bohr magneton. It is convenient to keep b and to treat it as a formal perturbation parameter that measures the strength of the magnetic field.

We want to solve the Schrödinger equation (omitting the state label)

$$H\phi(b)=E(b)\phi(b) \tag{2.3}$$

in a power-series expansion with respect to the perturbation parameter b

$$E(b)=E_0+b\,E_1+b^2E_2+\cdots;$$

$$\phi(b)=\phi_0+b\quad\phi_1+b^2\phi_2+\cdots. \tag{2.4}$$

This leads for first- and second-order magnetic properties to

$$E_1=\langle\phi_0|H_1|\phi_0\rangle=\langle\phi_0|\vec{A}\cdot\vec{p}|\phi_0\rangle+\langle\phi_0|\vec{\sigma}\cdot\vec{B}|\phi_0\rangle, \tag{2.5}$$

$$E_2=E_2^d+E_2^p;\quad E_2^d=\langle\phi_0|H_2|\phi_0\rangle;\quad E_2^p=\mathrm{Re}\langle\phi_0|H_1-E_1|\phi_1\rangle \tag{2.6}$$

with ϕ_0 and ϕ_1 solutions of

$$(H_0-E_0)\phi_0=0, \tag{2.7}$$

$$(H_0-E_0)\phi_1=-(H_1-E_1)\phi_0,\quad\langle\phi_0|\phi_1\rangle=0. \tag{2.8}$$

The *diamagnetic* term E_2^d is expressible in terms of ϕ_0, while for the *paramagnetic* term E_2^p one needs ϕ_1.

For a homogeneous magnetic field the second-order energy E_2 differs (in atomic units) from the magnetizability (or susceptibility) $\chi=-d^2E/db^2$ by a factor -2. *Positive* (diamagnetic) contributions to E_2 correlate with *negative* contributions to χ. We shall here always have E_2 in mind.

When we refer to *paramagnetism* we mean in this paper exclusively a positive contribution to E_2, which is often called *van-Vleck* (or temperature-independent) paramagnetism. This is present even for nondegenerate states, for which $E_1=0$. We shall not be concerned with *ordinary* (or temperature-dependent) paramagnetism that arises for *degenerate* states, with the degeneracy split by the magnetic field, and which is determined by E_1 rather than E_2.

Our formalism holds for degenerate states, if the unperturbed wave function is chosen perturbation adapted, but we have mainly nondegenerate states in mind.

We consider explicitly only the case when the magnetic field can be characterized by a single scalar parameter (here called b). The generalization to a characterization of the field by its Cartesian components (B_x, B_y, B_z) and to the presence of more than one field as in NMR experiments is straightforward, but would complicate the formalism unnecessarily, without giving more insight.

Both E_2^d and E_2^p depend on the *gauge* of $\vec{A}$, only their sum is *gauge invariant*. Often there is a *natural gauge* and hence also a natural decomposition into E_2^d and E_2^p, e.g., for an atom in a homogeneous magnetic field with $A=\frac{1}{2}\vec{B}\times\vec{r}$ and the origin of the coordinate system at the position of the nucleus.

A change of gauge

$$A\rightarrow A'=A+\mathrm{grad}\Lambda;\quad\mathrm{div}\,\mathrm{grad}\Lambda=0 \tag{2.9}$$

is equivalent to a *gauge transformation*

$$H\rightarrow H'=\exp(-ib\Lambda)H\exp(ib\Lambda), \tag{2.10}$$

$$\Psi\rightarrow\Psi'=\exp(-ib\Lambda)\Psi. \tag{2.11}$$

III. RELATIVISTIC THEORY

The corresponding relativistic Hamiltonian is

$$D=\beta c^2+c\vec{\alpha}\cdot(\vec{p}+b\vec{A})+V=D_0+b\,D_1, \tag{3.1}$$

$$D_0=\beta c^2+c\vec{\alpha}\cdot\vec{p}+V;\quad D_1=c\vec{\alpha}\cdot\vec{A}. \tag{3.2}$$

We now want to solve (again omitting the state label)

$$D\psi(b)=W(b)\psi(b) \tag{3.3}$$

in powers of b:

$$W(b)=W_0+b\,W_1+b^2W_2+\cdots;$$

$$\psi(b)=\psi_0+b\,\psi_1+b^2\psi_2+\cdots. \tag{3.4}$$

The zeroth- and first-order wave functions are $\psi_0=(\varphi_0,\chi_0)$ and $\psi_1=(\varphi_1,\chi_1)$, respectively. For the counterparts of E_1 and E_2 we get

$$W_1=\langle\psi_0|D_1|\psi_0\rangle=2c\mathrm{Re}\langle\varphi_0|\vec{\sigma}\cdot\vec{A}|\chi_0\rangle, \tag{3.5}$$

$$W_2=\mathrm{Re}\langle\psi_0|D_1|\psi_1\rangle=c\mathrm{Re}\{\langle\varphi_0|\vec{\sigma}\cdot\vec{A}|\chi_1\rangle+\langle\varphi_1|\vec{\sigma}\cdot\vec{A}|\chi_0\rangle\} \tag{3.6}$$

with ψ_0 and ψ_1 solutions of

$$(D_0-W_0)\psi_0=0, \tag{3.7}$$

$$(D_0-W_0)\psi_1=-(D_1-W_1)\psi_0;\quad\langle\psi_0|\psi_1\rangle=0. \tag{3.8}$$

Note that W_0 contains the rest mass contribution c^2. The normalization condition contained in Eq. (3.8) is convenient, because it removes W_1 from the expression for W_2.

W_2 consists of a *single* term that formally resembles the paramagnetic contribution E_2^p to E_2 in nonrelativistic theory, while there is no counterpart of E_2^d.

A change of gauge (2.9) is now equivalent to a *gauge transformation*

$$D\rightarrow D'=\exp(-ib\Lambda)D\exp(ib\Lambda). \tag{3.9}$$

IV. SUM-OVER-STATES FORMULATION FOR W_2

For a nonrelativistic Hamiltonian of the form

$$H = H_0 + bH_1 \tag{4.1}$$

a second-order property E_2 of $O(b^2)$ corresponding to the *ground state* is always negative (energy lowering), which is easily seen from the *sum-over-states expression* for E_2. A *positive* contribution to E_2 arises in the *nonrelativistic theory* of magnetic properties, since the Hamiltonian contains an extra term $b^2H_2 \geqslant 0$. In the relativistic theory there is *a priori* no such term, but the Dirac operator D is *not bounded from below*, such that one can make the existence of *negative-energy states* responsible for positive contributions to E_2.

One can estimate the sum of the contributions of negative-energy states to W_2 for the ground state ($k=0$) in the following way (with ψ_{k0} eigenfunction of D_0 with eigenvalue W_{k0}, and $\psi_0 = \psi_{00}$, $W_0 = W_{00}$):

$$\begin{aligned} W_2^{neg} &= \sum_{k, W_{k0}<0} \frac{|\langle \psi_0 | D_1 | \psi_{k0} \rangle|^2}{W_0 - W_{k0}} \\ &\leqslant \sum_{k, W_{k0}<0} \frac{|\langle \psi_0 | D_1 | \psi_{k0} \rangle|^2}{W_0 + c^2} \leqslant \frac{\langle \psi_0 | D_1^2 | \psi_0 \rangle}{W_0 + c^2} \\ &= \frac{\langle \psi_0 | c^2 A^2 | \psi_0 \rangle}{W_0 + c^2} \\ &= \langle \psi_0 | A^2 | \psi_0 \rangle \left[1 + \frac{W_0}{c^2} \right]^{-1} \\ &= \frac{1}{2} \langle \psi_0 | A^2 | \psi_0 \rangle [1 - O(c^{-2})]. \end{aligned} \tag{4.2}$$

By this manipulation one does not get an information on whether the *mean denominator* in the sense of the Unsöld (closure) approximation is larger or smaller than $2c^2$, although plausibility arguments suggest that it is larger and approaches $2c^2$ only in the nonrelativistic limit.

A manipulation such as Eq. (4.2) is also possible for electric (diagonal) perturbations. However, for these the matrix element $\langle \psi_0 | D_1 | \psi_k \rangle$ is of $O(c^{-1})$ rather than $O(c)$ and the final result is of $O(c^{-4})$ rather than $O(c^0)$. Hence W_2^{neg} contributes even to the *nonrelativistic limit* for *magnetic* properties, but only *beyond* the leading relativistic corrections for *electric* properties.

The interpretation of diamagnetism as due to negative-energy states is—although formally plausible—unsatisfactory for various rather serious reasons.

(1) This would mean to recur to a *different mechanism* in the relativistic and the nonrelativistic context, with a discontinuity in the nonrelativistic limit. In this limit there are *no* negative-energy states.

(2) The sum-over-states formalism involving negative-energy states is tedious and inelegant if it is performed in a *brute-force* way. It is unreliable and hard to correct if one tries to *approximate this sum by a closure approximation*.

(3) The sum-over-states formalism is old fashioned anyway, and is hardly used in practice, where one rather starts from a Hylleraas-type stationarity principle, i.e., one wants to make the functional

$$F(\psi_1) = \langle \psi_1 | D_0 - W_0 | \psi_1 \rangle + 2\mathrm{Re} \langle \psi_0 | D_1 - W_1 | \psi_1 \rangle \tag{4.3}$$

stationary with respect to the variation of ψ_1. While it is appropriate to use *kinetic balance* [13–15] for the expansion of ψ_0, it is not obvious which basis should be used for ψ_1. It ought to be able to account both for positive-energy and for negative-energy states. One may be tempted to use two complementary sets. See also the following comment (4) and Sec. VIII. One can mention that Grant and Quiney [6] avoid kinetic balance and impose a certain operator identity instead, such that the above remarks do not apply to their work.

(4) Electronic states should be entirely describable in terms of a Hamiltonian for electrons only. For the theory of properties one must, of course, consider the relativistic Hamiltonian for electrons *in the presence of the perturbing field*, but one should then completely dismiss negative-energy states. We show in Sec. VIII that this is, in fact, possible.

(5) The original Dirac operator is physically meaningful only for one-electron systems. In many-electron theory one must replace it with an operator in Fock space. However the latter should also work for one-electron states. So it is interesting to look at this formulation, as it is done in Sec. IX. Now ''excitation'' to a negative-energy state is forbidden, and one must rather consider excitations accompanied by the creation of an *electron-positron pair*. This leads to a strong dependence of the *vacuum* on magnetic fields.

Fortunately it is possible, in a surprisingly simple way, to arrive at a formulation of diamagnetism in relativistic theory, to which none of the just given critical remarks apply. We come to this in the following section.

V. UNITARY TRANSFORMATION OF THE DIRAC OPERATOR

Unlike E_2 in nonrelativistic theory, the relativistic counterpart W_2 is *not* obtained as an *obvious* sum of two contributions. In order to arrive at such a decomposition, we search for a unitary transformation of D that *removes the off-diagonal operator* $c\vec{\alpha}\cdot\vec{A}$ to the leading order in b. This is somewhat in the spirit of the Foldy-Wouthuysen transformation [16]. However, we do *not* want to remove $c\vec{\alpha}\cdot\vec{p}$ at the same time. This transformation is

$$\tilde{D} = \exp\{-b\tau\} D \exp\{b\tau\} = D_0 + b\tilde{D}_1 + b^2\tilde{D}_2 + O(b^3), \tag{5.1}$$

$$\tau = -\frac{1}{2c}\beta\vec{\alpha}\cdot\vec{A} = -\tau^\dagger, \tag{5.2}$$

$$\tilde{D}_1 = D_1 + [D_0, \tau] = \tfrac{1}{2}\beta[\vec{\alpha}\cdot\vec{p}, \vec{\alpha}\cdot\vec{A}]_+ = \beta\{\vec{A}\cdot\vec{p} + \vec{\sigma}\cdot\vec{B}\} = \beta H_1, \tag{5.3}$$

$$\tilde{D}_2 = [D_1, \tau] + \tfrac{1}{2}[[D_0, \tau], \tau] = \frac{1}{2}\beta A^2 - \frac{1}{4c}[H_1, \vec{\alpha}\cdot\vec{A}]_+, \tag{5.4}$$

where we have used

$$\beta\vec{\alpha} = -\vec{\alpha}\beta;\ \ (\vec{\alpha}\cdot\vec{a})(\vec{\alpha}\cdot\vec{b}) = \vec{a}\cdot\vec{b} + i\vec{\sigma}\cdot(\vec{a}\times\vec{b});\ \ \vec{\nabla}\vec{A} = 0;$$
$$\vec{B} = \mathrm{curl}\vec{A}. \tag{5.5}$$

$\tilde{D}_1$ differs from the nonrelativistic H_1 (2.2) mainly in the fact that it acts on four-component spinors. The spin-dependent contribution, to be added *ad hoc* in the Pauli Hamiltonian (2.1), is automatically there. For W_1 and W_2 we get now

$$W_1 = \langle\psi_0|\tilde{D}_1|\psi_0\rangle = \langle\varphi_0|H_1|\varphi_0\rangle - \langle\chi_0|H_1|\chi_0\rangle, \tag{5.6}$$

$$W_2 = W_2^p + W_2^{d1} + W_2^{d2}, \tag{5.7}$$

$$W_2^p = \mathrm{Re}\langle\psi_0|\tilde{D}_1 - W_1|\tilde{\psi}_1\rangle = \mathrm{Re}\{\langle\varphi_0|H_1 - W_1|\tilde{\varphi}_1\rangle - \langle\chi_0|H_1 + W_1|\tilde{\chi}_1\rangle\}, \tag{5.8}$$

$$W_2^{d1} = \tfrac{1}{2}\langle\psi_0|\beta A^2|\psi_0\rangle = \tfrac{1}{2}\langle\varphi_0|A^2|\varphi_0\rangle - \tfrac{1}{2}\langle\chi_0|A^2|\chi_0\rangle, \tag{5.9}$$

$$W_2^{d2} = -\frac{1}{2c}\mathrm{Re}\langle\varphi_0|[H_1, \vec{\sigma}\cdot\vec{A}]_+|\chi_0\rangle, \tag{5.10}$$

the first-order wave function $\tilde{\psi}_1$ is obtained from

$$(D_0 - W_0)\tilde{\psi}_1 = -(\tilde{D}_1 - W_1)\psi_0;\ \ \langle\psi_0|\tilde{\psi}_1\rangle = 0. \tag{5.11}$$

While the energy (i.e., the W_k) as well as ψ_0 are unaffected by the transformation from D to $\tilde{D}$, the relation between $\tilde{\psi}_1$ and ψ_1 is

$$\tilde{\psi}_1 = \psi_1 + \frac{1}{2c}\beta\vec{\alpha}\cdot\vec{A}\psi_0. \tag{5.12}$$

The normalization condition in Eq. (5.11) is consistent with that in Eq. (3.8), because

$$\mathrm{Re}\{\langle\psi_0|\beta\vec{\alpha}\cdot\vec{A}|\psi_0\rangle\} = 0 \tag{5.13}$$

since $\beta\vec{\alpha}\cdot\vec{A}$ is an anti-Hermitian operator.

Three *caveats* are in order.

(1) Derivatives involved in the transformation must be understood in the distribution sense [17]. E.g., if $\vec{A}$ describes the magnetic field of a nucleus, the Fermi contact interaction must be taken care of.

(2) Expressions that are equivalent in an exact theory may be different if one uses approximations, e.g., if one expands wave functions in a finite basis. Consider e.g., the expressions (5.6) and (3.5) for W_1 (note that V commutes with $\beta\vec{\alpha}\cdot\vec{A}$):

$$\begin{aligned}\langle\psi_0|\tilde{D}_1|\psi_0\rangle &= -\frac{1}{2c}\langle\psi_0|[c\vec{\alpha}\cdot\vec{p}, \beta\vec{\alpha}\cdot\vec{A}]|\psi_0\rangle \\ &= -\frac{1}{2c}\langle\psi_0|[D_0, \beta\vec{\alpha}\cdot\vec{A}]|\psi_0\rangle \\ &\quad + \frac{1}{2c}\langle\psi_0|[\beta c^2, \beta\vec{\alpha}\cdot\vec{A}]|\psi_0\rangle \\ &= -\frac{1}{2c}\langle\psi_0|D_0\beta\vec{\alpha}\cdot\vec{A} - \beta\vec{\alpha}\cdot\vec{A}D_0|\psi_0\rangle \\ &\quad + \langle\psi_0|c\vec{\alpha}\cdot\vec{A}|\psi_0\rangle.\end{aligned} \tag{5.14}$$

The two expressions (5.6) and (3.5) hence agree, if ψ_0 is an eigenfunction of D_0.

(3) The transformed operator is given as a nonterminating series in powers of b. It is hence appropriate only in the context of perturbation theory with b the perturbation parameter, and not for a treatment of an electron in a *very strong* magnetic field, where the expansion in powers of b becomes invalid. In the present context this does not matter at all, since we only care for the magnetizability, which—by definition—is the *second-order* response to the magnetic field. If one is interested in *hypersusceptibilities*, the term of $O(b^3)$ in the transformed Dirac operator must be considered explicitly.

A change of gauge (2.9) corresponds now to a more complicated *gauge transformation*

$$\tilde{D} \to \tilde{D}' = \exp\left\{-ib\Lambda - \frac{b}{2c}\beta\vec{\alpha}\cdot\mathrm{grad}\Lambda\right\} \times D \exp\left\{ib\Lambda + \frac{b}{2c}\beta\vec{\alpha}\cdot\mathrm{grad}\Lambda\right\}. \tag{5.15}$$

The expressions (5.8)–(5.10) were derived by Szmytkowski [9] in a much more tedious and indirect way, making use of the Gordon decomposition of the induced current density. Szmytkowski regarded W_2^{d2} as a *paramagnetic* term. Although this is to some extent a matter of taste (see Sec. X), the classification of W_2^{d2} as *diamagnetic* looks more natural, mainly since its evaluation only involves ψ_0, although it is not necessarily non-negative. Anyway, this is an extra term with no nonrelativistic counterpart.

It is worth noting that $\tilde{D}$ is, like D, an operator that has both electronic and positronic solutions. The definition of diamagnetic and paramagnetic contributions in analogy to the nonrelativistic limit does *not* require a decoupling of electronic from positronic states. The nonrelativistic limit of the Dirac equation itself does, however, require that one specifies whether one considers electronic or positronic states (see Sec. VI).

The factor β in front of A^2 in Eq. (5.9) is plausible, since diamagnetism should *raise* $|W|$ both for electrons and positrons.

The fact that we are still in the framework of a fully relativistic theory means that the problems related to the nonboundedness of the Dirac operator are still there. If one wants to use an expansion in a basis, one has to take care to deal with purely electronic states and avoid the *variational collapse* [18–24], even for the calculation of properties. We come back to this in Sec. VIII.

VI. THE LÉVY-LEBLOND LIMIT AND DIRECT PERTURBATION THEORY

Let us write the Dirac equation in the presence of a magnetic field in block form in terms of $\psi=(\varphi,\chi)$, with $E=W-c^2$. Again we omit the state label:

$$\begin{pmatrix} V & c\vec{\sigma}\cdot(\vec{p}+b\vec{A}) \\ c\vec{\sigma}\cdot(\vec{p}+b\vec{A}) & -2c^2+V \end{pmatrix}\begin{pmatrix}\varphi\\ \chi\end{pmatrix}=E\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}\varphi\\ \chi\end{pmatrix}. \tag{6.1}$$

We make a change of the metric [25–27] from $\psi=(\varphi,\chi)$ to $\overline{\psi}=(\varphi,\overline{\chi})=(\varphi,c\chi)$:

$$\begin{pmatrix} V & \vec{\sigma}\cdot(\vec{p}+b\vec{A}) \\ \vec{\sigma}\cdot(\vec{p}+b\vec{A}) & -2+V/c^2 \end{pmatrix}\begin{pmatrix}\varphi\\ \overline{\chi}\end{pmatrix}=E\begin{pmatrix}1 & 0\\ 0 & 1/c^2\end{pmatrix}\begin{pmatrix}\varphi\\ \overline{\chi}\end{pmatrix}. \tag{6.2}$$

If we define

$$D_{00}=\begin{pmatrix} V & \vec{\sigma}\cdot\vec{p}\\ \vec{\sigma}\cdot\vec{p} & -2\end{pmatrix};\quad D_{20}=\begin{pmatrix}0 & 0\\ 0 & V\end{pmatrix};$$

$$D_{01}=\begin{pmatrix} 0 & \vec{\sigma}\cdot\vec{A}\\ \vec{\sigma}\cdot\vec{A} & 0\end{pmatrix};\quad S_0=\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix};\quad S_2=\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}, \tag{6.3}$$

we can rewrite Eq. (6.2) as

$$(D_{00}+c^{-2}D_{20}+bD_{01}-ES_0-Ec^{-2}S_2)\overline{\psi}=0 \tag{6.4}$$

and expand $\overline{\psi}$ as well as Eq. (6.4) in powers of c^{-1} and b.

$$\overline{\psi}=\sum_{k,l} c^{-k}b^l\psi_{kl}. \tag{6.5}$$

The first subscript counts orders in c^{-1}, the second subscript counts orders in b. In the nonrelativistic limit ($c^{-1}\to 0$) we get

$$(D_{00}-E_{00}S_0)\psi_{00}=0, \tag{6.6}$$

$$(D_{00}-E_{00}S_0)\psi_{01}+(D_{01}-E_{01}S_0)\psi_{00}=0. \tag{6.7}$$

The solution $\psi_{00}=(\varphi_{00},\chi_{00})$ of the *Lévy-Leblond equation* (6.6) [28,29] is obtained from

$$(H_0-E_{00})\varphi_{00}=0;\quad \chi_{00}=\tfrac{1}{2}\vec{\sigma}\cdot\vec{p}\,\varphi_{00} \tag{6.8}$$

and the first- and second-order magnetic properties are

$$E_{01}=\langle\psi_{00}|D_{01}|\psi_{00}\rangle=2\mathrm{Re}\langle\varphi_{00}|\vec{\sigma}\cdot\vec{A}|\chi_{00}\rangle, \tag{6.9}$$

$$E_{02}=\mathrm{Re}\langle\psi_{00}|D_{01}-E_{01}S_0|\psi_{01}\rangle=\mathrm{Re}\{\langle\varphi_{00}|\vec{\sigma}\cdot\vec{A}|\chi_{01}\rangle + \langle\varphi_{01}|\vec{\sigma}\cdot\vec{A}|\chi_{00}\rangle\}-E_{01}\mathrm{Re}\langle\varphi_{00}|\varphi_{01}\rangle, \tag{6.10}$$

which *formally* resemble their *relativistic* counterparts (3.5) and (3.6). However, if one inserts Eq. (6.8) and realizes that the solution of Eq. (6.7) is

$$(H_0-E_0)\varphi_{01}=-(H_1-E_{01})\varphi_0,$$

$$\chi_{01}=\tfrac{1}{2}\vec{\sigma}\cdot\vec{p}\,\varphi_{01}+\tfrac{1}{2}\vec{\sigma}\cdot\vec{A}\varphi_0,\quad \langle\varphi_0|\varphi_{01}\rangle=0, \tag{6.11}$$

remembering that

$$(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{p})=\vec{A}\cdot\vec{p}+i\vec{\sigma}\cdot(\vec{A}\times\vec{p}),$$

$$(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{A})=\vec{p}\cdot\vec{A}+\vec{\sigma}\cdot\mathrm{curl}\vec{A}-i\vec{\sigma}\cdot(\vec{A}\times\vec{p}),$$

$$\frac{1}{2}[\vec{\sigma}\cdot\vec{A},\vec{\sigma}\cdot\vec{p}]=\vec{A}\cdot\vec{p}+\vec{\sigma}\cdot\vec{B}, \tag{6.12}$$

one duplicates the *nonrelativistic* results (2.5) and (2.6), i.e., the decomposition of E_2 into a diamagnetic and a paramagnetic contribution. This decomposition is a direct consequence of the decomposition (6.11) of χ_{01}.

If we expand Eq. (6.4) both in powers of c^{-1} and b in the sense of double perturbation theory, we get the *relativistic corrections* to magnetic properties. These have been reported elsewhere [30] and we need not repeat them. As to numerical applications, see Ref. [31].

VII. THE NONRELATIVISTIC LIMIT AND DIRECT PERTURBATION THEORY OF THE TRANSFORMED DIRAC EQUATION

If we make a change of the metric analogous to Eq. (6.2) for the transformed Dirac equation, we can write this as

$$(D_{00}+c^{-2}D_{20}+b\tilde{D}_{01}+b^2\tilde{D}_{02}+c^{-2}b\tilde{D}_{21}+c^{-2}b^2\tilde{D}_{22}-ES_0 - Ec^{-2}S_2)\tilde{\psi}=0 \tag{7.1}$$

with D_{00}, D_{20}, S_0, and S_2 as in Eq. (6.3), and

$$\tilde{D}_{01}=\begin{pmatrix} H_1 & 0 \\ 0 & 0 \end{pmatrix}; \quad \tilde{D}_{02}=\begin{pmatrix} \frac{1}{2}A^2 & 0 \\ 0 & 0 \end{pmatrix};$$

$$\tilde{D}_{21}=\begin{pmatrix} 0 & 0 \\ 0 & -H_1 \end{pmatrix},$$

$$\tilde{D}_{22}=\begin{pmatrix} 0 & -\frac{1}{4}[H_1,\vec{\sigma}\cdot\vec{A}]_+ \\ -\frac{1}{4}[H_1,\vec{\sigma}\cdot\vec{A}]_+ & -\frac{1}{2}A^2 \end{pmatrix}. \quad (7.2)$$

The meaning of the subscripts is the same as in the preceding section. Let us first consider the nonrelativistic limit, i.e., keep the first subscript equal to 0, and consider the expansion in powers of b:

$$0=(D_{00}-E_0S_0)\psi_{00}, \quad (7.3)$$

$$0=(\tilde{D}_{01}-E_{01}S_0)\psi_{00}+(D_{00}-E_0S_0)\tilde{\psi}_{01}, \quad (7.4)$$

$$0=(\tilde{D}_{02}-E_{02}S_0)\psi_{00}+(\tilde{D}_{01}-E_{01}S_0)\tilde{\psi}_{01}+(D_{00}-E_0S_0)\tilde{\psi}_{02}. \quad (7.5)$$

By scalar multiplication with ψ_{00}, noting that $\langle\psi_{00}|S_0|\psi_{00}\rangle=1$ and that Eq. (7.3) holds, we get

$$E_{01}=\langle\psi_{00}|\tilde{D}_{01}|\psi_{00}\rangle=\langle\varphi_{00}|H_1|\varphi_{00}\rangle, \quad (7.6)$$

$$E_{02}=\langle\psi_{00}|\tilde{D}_{02}|\psi_{00}\rangle+\langle\psi_{00}|\tilde{D}_{01}-E_{01}S_0|\tilde{\psi}_{01}\rangle$$
$$=\langle\varphi_{00}|\tfrac{1}{2}A^2|\varphi_{00}\rangle+\mathrm{Re}\langle\varphi_{00}|H_1|\tilde{\varphi}_{01}\rangle \quad (7.7)$$

with ψ_{00} the same as in the preceding section. The solution $\tilde{\psi}_{01}$ of Eq. (7.4) is

$$(H_0-E_0)\tilde{\varphi}_{01}=-(H_1-E_{01})\varphi_{00};$$

$$\tilde{\chi}_{01}=\tfrac{1}{2}\vec{\sigma}\cdot\vec{p}\tilde{\varphi}_{01}; \quad \langle\varphi_0|\tilde{\varphi}_{01}\rangle=0. \quad (7.8)$$

Now there is—unlike in Eq. (6.11)—only a single contribution to $\tilde{\chi}_{01}$, but there is a term $\sim b^2A^2$ in the Hamiltonian, i.e., we arrive *directly* at the nonrelativistic result. Actually $\tilde{\chi}_{01}$ is *not* needed for the evaluation of E_{02}.

To get the relativistic corrections to magnetic properties in the sense of *double direct perturbation theory*, we proceed as follows. Expanding in powers of c^{-1} and b, we get in addition to Eqs. (7.3)–(7.5)

$$0=(D_{20}-E_{20}S_0-E_{00}S_2)\psi_{00}+(D_{00}-E_0S_0)\psi_{20}, \quad (7.9)$$

$$0=(\tilde{D}_{21}-E_{21}S_0-E_{01}S_2)\psi_{00}+(\tilde{D}_{01}-E_{01}S_0)\psi_{20}$$
$$+(D_{20}-E_{20}S_0-E_{00}S_2)\tilde{\psi}_{01}+(D_{00}-E_0S_0)\tilde{\psi}_{21}, \quad (7.10)$$

$$0=(\tilde{D}_{22}-E_{22}S_0-E_{02}S_2)\psi_{00}+(\tilde{D}_{21}-E_{21}S_0-E_{01}S_2)\tilde{\psi}_{01}$$
$$+(D_{20}-E_{20}S_0-E_{00}S_2)\tilde{\psi}_{02}+(\tilde{D}_{02}-E_{02}S_0)\psi_{20}$$
$$+(\tilde{D}_{01}-E_{01}S_0)\tilde{\psi}_{21}+(D_{00}-E_0S_0)\tilde{\psi}_{22}. \quad (7.11)$$

By scalar multiplication with ψ_{00} we obtain

$$E_{20}=\langle\psi_{00}|D_{20}-E_{00}S_2|\psi_{00}\rangle, \quad (7.12)$$

$$E_{21}=\langle\psi_{00}|\tilde{D}_{21}-E_{01}S_2|\psi_{00}\rangle+\langle\psi_{00}|\tilde{D}_{01}-E_{01}S_0|\psi_{20}\rangle$$
$$+\langle\psi_{00}|D_{20}-E_{20}S_0-E_{00}S_2|\tilde{\psi}_{01}\rangle, \quad (7.13)$$

$$E_{22}=\langle\psi_{00}|\tilde{D}_{22}-E_{02}S_2|\psi_{00}\rangle+\langle\psi_{00}|\tilde{D}_{21}-E_{21}S_0-E_{01}S_2|\tilde{\psi}_{01}\rangle$$
$$+\langle\psi_{00}|D_{20}-E_{20}S_0-E_{00}S_2|\tilde{\psi}_{02}\rangle+\langle\psi_{00}|\tilde{D}_{02}$$
$$-E_{02}S_0|\psi_{20}\rangle+\langle\psi_{00}|\tilde{D}_{01}-E_{01}S_0|\tilde{\psi}_{21}\rangle. \quad (7.14)$$

Further reformulation is possible to

$$E_{21}=\langle\psi_{00}|\tilde{D}_{21}-E_{01}S_2|\psi_{00}\rangle+2\mathrm{Re}\langle\psi_{00}|\tilde{D}_{01}-E_{01}S_0|\psi_{20}\rangle$$
$$=\langle\psi_{00}|\tilde{D}_{21}-E_{01}S_2|\psi_{00}\rangle+2\mathrm{Re}\langle\psi_{00}|D_{20}-E_{20}S_0$$
$$-E_{00}S_2|\tilde{\psi}_{01}\rangle, \quad (7.15)$$

$$E_{22}=\langle\psi_{00}|\tilde{D}_{22}-E_{02}S_2|\psi_{00}\rangle+2\mathrm{Re}\langle\psi_{00}|\tilde{D}_{21}-E_{21}S_0$$
$$-E_{01}S_2|\tilde{\psi}_{01}\rangle+2\mathrm{Re}\langle\psi_{00}|\tilde{D}_{02}-E_{02}S_0|\psi_{20}\rangle$$
$$+2\mathrm{Re}\langle\tilde{\psi}_{01}|\tilde{D}_{01}-E_{01}S_0|\psi_{20}\rangle+\langle\tilde{\psi}_{01}|D_{20}-E_{20}S_0$$
$$-E_{00}S_2|\tilde{\psi}_{01}\rangle. \quad (7.16)$$

For E_{21}, which is a first-order relativistic correction of a first-order property, one has two alternative expressions in the sense of the Dalgarno exchange theorem [32]. One gets in component form, especially for the unitary normalization [30],

$$E_{21}=-\langle\chi_0|H_1|\chi_0\rangle+2\mathrm{Re}\langle\varphi_0|H_1|\varphi_{20}\rangle$$
$$=-\langle\chi_0|H_1|\chi_0\rangle+2\mathrm{Re}\langle\chi_0|V-E_{00}|\tilde{\chi}_{01}\rangle, \quad (7.17)$$

$$E_{22}=-\tfrac{1}{2}\langle\chi_0|A^2|\chi_0\rangle-\tfrac{1}{2}\mathrm{Re}\langle\varphi_0|[H_1,\vec{\sigma}\cdot\vec{A}]_+|\chi_0\rangle$$
$$-2\mathrm{Re}\langle\chi_0|H_1+E_{01}|\tilde{\chi}_{01}\rangle+\mathrm{Re}\langle\varphi_0|A^2|\varphi_{20}\rangle$$
$$+2\mathrm{Re}\langle\varphi_{20}|H_1-E_{01}|\tilde{\varphi}_{01}\rangle+\langle\tilde{\chi}_{01}|V-E_{00}|\tilde{\chi}_{01}\rangle$$
$$-E_{20}\langle\tilde{\varphi}_{01}|\tilde{\varphi}_{01}\rangle. \quad (7.18)$$

These expressions do, at first glance, not agree with those derived previously [30] from the expansion of the original Dirac equation. However, noting that V and $\vec{\sigma}\cdot\vec{A}$ commute, and using the following identities that hold for exact φ_{00} and φ_{01}, the equivalence of the two sets of equations can be shown as

$$(V-E_{00})\varphi_{00}=-T\varphi_{00}, \tag{7.19}$$

$$(V-E_{00})\varphi_{01}=-T\varphi_{01}-(H_1-E_{01})\varphi_{00}. \tag{7.20}$$

The big advantage with respect to the previous formulation [30] is that now *no* $\vec{\sigma}\cdot\vec{A}$ basis (as defined in the following section) is needed for the expansion of the lower (small) component, at least as long as we are only interested in the leading relativistic corrections to magnetic properties.

VIII. THE DIRAC EQUATION FOR ELECTRONS ONLY

A theory in terms of four-component spinors—as it is realized in the Dirac equation—is necessary, if one wants to describe electrons and positrons at the same time. For electrons *only*, a description in terms of two-component spinors is sufficient, in principle. Unfortunately, a simple and well-behaved theory in terms of two-component spinors for electrons is not available in explicit form. There is, however, an implicit formalism. A solution of the Dirac equation describes an *electronic state* if and only if the upper and lower components of the Dirac spinor satisfy the relation [33,34]

$$\chi=X\varphi \tag{8.1}$$

with the X solution of

$$X=\frac{1}{2c^2}(c\vec{\sigma}\cdot\vec{p}-[X,V]-cX\vec{\sigma}\cdot\vec{p}X)=\frac{1}{2c}\vec{\sigma}\cdot\vec{p}+O(c^{-3}). \tag{8.2}$$

For a positronic state the relation (8.1) has to be replaced with

$$\varphi=-X^{\dagger}\chi \tag{8.3}$$

with the same X. In the presence of a magnetic field one must, for electrons, replace Eq. (8.1) with

$$\chi=Y\varphi \tag{8.4}$$

with the Y solution of [30]

$$Y=\frac{1}{2c^2}\{c\vec{\sigma}\cdot(\vec{p}+b\vec{A})-[Y,V]-cY\vec{\sigma}\cdot(\vec{p}+b\vec{A})Y\}. \tag{8.5}$$

If we expand Y in powers of b, we get

$$Y=X+bY_1+O(b^2), \tag{8.6}$$

$$Y_1=\frac{1}{2c^2}(c\vec{\sigma}\cdot\vec{A}-[Y_1,V]-cY_1\vec{\sigma}\cdot\vec{p}X-cX\vec{\sigma}\cdot\vec{p}Y_1 - cX\vec{\sigma}\cdot\vec{A}X)=\frac{1}{2c}\vec{\sigma}\cdot\vec{A}+O(c^{-3}), \tag{8.7}$$

$$\chi_0=X\varphi_0, \tag{8.8}$$

$$\chi_1=X\varphi_1+Y_1\varphi_0. \tag{8.9}$$

If one changes V, e.g., by an *electric* (diagonal) perturbation, one also changes X. However, this change is only of $O(c^{-2})$. This means that this change of X has neither an effect on the nonrelativistic limit, nor on the leading relativistic correction, which is expressible by means of the nonrelativistic wave function. Only E_4, i.e., the second-order relativistic correction is affected, as is known for a *no-pair projection* with projectors for free particles.

A *magnetic perturbation* has a much stronger effect. The change from X to Y has even an influence on the *nonrelativistic* energy. If in the presence of a magnetic perturbation, one keeps the relation (8.1) between the upper and lower components, instead of the correct one (8.4), i.e., essentially if one imposes the *kinetic balance*, one misses an important contribution to the perturbation, namely, the entire *diamagnetic term*, even at the *nonrelativistic limit*.

In conventional relativistic four-component-spinor calculations, one uses *kinetic balance* [13–15] to avoid the *variational collapse* [18–24], i.e., one expands φ in a basis $\{\varphi_k\}$ and χ in the basis $\{\vec{\sigma}\cdot\vec{p}\varphi_k\}$ (for short $\vec{\sigma}\cdot\vec{p}$ basis). The errors that one then makes for the energy are of at most $O(c^{-4})$. In the presence of a magnetic field the natural generalization of the kinetic balance is to *offer* the basis $\{\vec{\sigma}\cdot\vec{A}\varphi_k\}$ ($\vec{\sigma}\cdot\vec{A}$ basis), in addition to the $\vec{\sigma}\cdot\vec{p}$ basis, for the expansion of χ, e.g., if one wants to determine ψ_1 by making the Hylleraas functional (4.3) stationary.

Again one gets errors of $O(c^{-4})$, while without the $\vec{\sigma}\cdot\vec{A}$ basis one makes errors of $O(c^0)$. The $\vec{\sigma}\cdot\vec{A}$ basis is automatically included in DPT. This basis is not necessary, at least not in the nonrelativistic limit, and with respect to the leading relativistic corrections of $O(c^{-2})$, if one uses the *transformed* operator discussed in Sec. V.

IX. FOCK-SPACE THEORY AND THE INFLUENCE OF A PERTURBATION ON THE VACUUM

Let the Dirac operator D have the positive eigenvalues W_k^+ and the negative eigenvalues W_k^-, and let the corresponding eigenfunctions be ψ_k^+ and ψ_k^-. We associate electron creation and annihilation operators $a_k^{\dagger}$ and a_k with the ψ_k^+, as well as positron creation and annihilation operators $b_k^{\dagger}$ and b_k with the ψ_k^-. The *Fock-space operator* (in normal order with respect to the vacuum of D_F)

$$D_F=\sum_k W_k^+ a_k^{\dagger}a_k-\sum_k W_k^- b_k^{\dagger}b_k \tag{9.1}$$

describes then a system of an arbitrary number of noninteracting electrons and positrons. We write formally a sum, but if there are continuum eigenstates, the sum must be replaced with an appropriate integral. All eigenvalues of D_F are positive and roughly equal to nc^2, where n is the number of particles (electrons *or* positrons). The *vacuum* $|0\rangle$ is defined as the state that contains no electron and no positron, i.e., for which

$$a_k|0\rangle=0;\quad b_k|0\rangle=0. \tag{9.2}$$

Obviously $|0\rangle$ is the *ground state* of D_F with the eigenvalue 0:

$$D_F|0\rangle = 0. \tag{9.3}$$

Let us now consider the Fock-space Dirac Hamiltonian $D_F(\lambda)$ in the presence of a perturbation, measured by the strength parameter λ. We write it in *normal order* with respect to the unperturbed Hamiltonian $D_F(0) = D_{F0}$. We need not yet specify whether the perturbation is electric or magnetic. To stress this generality, we call, in this section, the perturbation parameter λ, rather than b.

$$D_F(\lambda) = D_{F0} + \lambda D_{F1}, \tag{9.4}$$

$$D_{F0} = \sum_p W^+_{p0} a^\dagger_p a_p - \sum_k W^-_{p0} b^\dagger_p b_p, \tag{9.5}$$

$$D_{F1} = \sum_{pq} D^{++}_{pq} a^\dagger_p a_q + \sum_{pq} D^{+-}_{pq} a^\dagger_p b^\dagger_q + \sum_{pq} D^{-+}_{pq} b_p a_q - \sum_{pq} D^{--}_{qp} b^\dagger_p b_q. \tag{9.6}$$

Obviously W^+_{k0} and W^-_{k0} are the eigenvalues of D_{F0}, while D^{+-}_{pq} etc. are the matrix elements of the perturbation D_{F1} in the basis of the eigenstates of D_{F0}. Now not only the k-particle eigenstates of $D_F(\lambda)$, but even the vacuum state depends on λ.

The vacuum state $|0\rangle$ of D_F satisfies

$$D_F|0\rangle = E^v|0\rangle. \tag{9.7}$$

We expand the vacuum state and its energy in powers of the perturbation parameter λ

$$E^v = E^v_0 + \lambda E^v_1 + \cdots; \quad |0\rangle = |0_0\rangle + \lambda|0_1\rangle + \cdots. \tag{9.8}$$

Since D_{F0} is in normal order with respect to the *unperturbed vacuum* $|0_0\rangle$, we have $E^v_0 = 0$, and we get

$$D_{F0}|0_0\rangle = E^v_0|0_0\rangle = 0, \tag{9.9}$$

$$D_{F0}|0_1\rangle + (D_{F1} - E^v_1)|0_0\rangle = 0, \tag{9.10}$$

$$D_{F0}|0_2\rangle + (D_{F1} - E^v_1)|0_1\rangle - E^v_2|0_0\rangle = 0, \tag{9.11}$$

$$E^v_1 = \langle 0_0|D_{F1}|0_0\rangle = 0, \tag{9.12}$$

$$E^v_2 = \langle 0_0|D_{F1}|0_1\rangle. \tag{9.13}$$

Solutions of Eqs. (9.10) and (9.13) are

$$|0_1\rangle = \sum_{p,q} (W^-_{q0} - W^+_{p0})^{-1} D^{+-}_{pq} a^\dagger_p b^\dagger_q |0_0\rangle, \tag{9.14}$$

$$E^v_2 = \sum_{p,q} D^{-+}_{qp} (W^-_{q0} - W^+_{p0})^{-1} D^{+-}_{pq}. \tag{9.15}$$

The (unobservable) vacuum energy—which shifts the entire spectrum by a (λ-dependent) constant—starts with a contribution of $O(\lambda^2)$ and involves energy denominators that correspond to electron-positron pair creations. That E^v_2 usually diverges (unless we use a finite basis), is in the tradition of quantum field theory and is hardly worth mentioning. However, it is worth noting that—for magnetic perturbations—the matrix elements D^{+-}_{pq} are of $O(c)$ and hence E^v_2 is of $O(c^0)$ and survives in the nonrelativistic limit. For electric perturbations, the corresponding matrix elements are of $O(c^{-1})$ and hence the vacuum energy is of $O(c^{-4})$, i.e., beyond the leading relativistic order.

We next consider one-electron states

$$(D_F - E^v)|\psi_r(\lambda)\rangle = W_r(\lambda)|\psi_r(\lambda)\rangle, \tag{9.16}$$

$$|\psi_r(\lambda)\rangle = x_r(\lambda)|0\rangle. \tag{9.17}$$

Since D_F is not in normal order with respect to its own (λ-dependent) vacuum $|0\rangle$, but rather with respect to $|0_0\rangle$, the eigenvalue of D_F corresponding to $\psi_r = \psi^+_r$ is equal to the *observable* eigenvalue $W_r = W^+_r$ plus the vacuum energy E^v. One gets rid of the latter, if one uses a Liouville formulation

$$[D_F, x_r]|0\rangle = W_r|x_r 0\rangle. \tag{9.18}$$

We can treat the Liouville equation by perturbation theory and get

$$[D_{F0}, x^r_0] = W_{r0} x^r_0, \tag{9.19}$$

$$[D_{F0}, x^r_1] + [D_{F1}, x^r_0] = W_{r0} x^r_1 + W_{r1} x^r_0, \tag{9.20}$$

$$[D_{F0}, x^r_2] + [D_{F1}, x^r_1] = W_{r0} x^r_2 + W_{r1} x^r_1 + W_{r2} x^r_0 \tag{9.21}$$

with solution

$$x^r_0 = a^\dagger_r; \quad W_{r1} = D^{++}_{rr}, \tag{9.22}$$

$$x^r_1 = \sum_{p(\neq r)} D^{++}_{pr} (W^+_{r0} - W^+_{p0})^{-1} a^\dagger_p + \sum_p D^{-+}_{pr} (W^+_{r0} - W^-_{p0})^{-1} b_p, \tag{9.23}$$

$$\psi^r_1 = x^r_1|0_0\rangle + x^r_0|0_1\rangle = \sum_{p(\neq r)} D^{++}_{pr} (W^+_{r0} - W^+_{p0})^{-1} a^\dagger_p|0_0\rangle + \sum_{p,q} D^{+-}_{pq} (W^-_{q0} - W^+_{p0})^{-1} a^\dagger_r a^\dagger_p b^\dagger_q |0_0\rangle. \tag{9.24}$$

Obviously ψ^r_1 consists of two parts, one involving simple one-electron excitations, the other excitations accompanied

by *electron-positron pair* creations. For the second-order energy W_{r2} we get again two contributions

$$W_{r2}=\langle 0_0|a_r(D_{F1}-E_1)|\psi_1^r\rangle=\langle 0_0|a_r(D_{F1}-E_1)x_1^r|0_0\rangle + \langle 0_0|a_r(D_{F1}-E_1)a_r^\dagger|0_1\rangle. \tag{9.25}$$

The first term in the second line is just the *paramagnetic* contribution

$$\sum_p D_{rp}^{++}(W_{r0}^+-W_{p0}^+)^{-1}D_{pr}^{++} \tag{9.26}$$

while the second-term resembles expression (9.13) for the second-order vacuum energy E_2^v, just with $(D_{F1}-E_1)$ sandwiched by $a_r \ldots a_r^\dagger$. We can rewrite this term as

$$\begin{aligned}&\langle 0_0|a_r[D_{F1},a_r^\dagger]|0_1\rangle+\langle 0_0|a_r a_r^\dagger(D_{F1}-E_1)|0_1\rangle\\ &=\langle 0_0|a_r[D_{F1},a_r^\dagger]|0_1\rangle+E_2^v\\ &=E_2^v-\sum_p D_{rp}^{-+}(W_{p0}^--W_{r0}^+)^{-1}D_{pr}^{+-}.\end{aligned} \tag{9.27}$$

So the *diamagnetic term* arises because the creation of a particle in a state ψ_r, in the presence of a magnetic field, is accompanied by a change of the vacuum that is associated with the magnetic field. In the expression (9.13) for the vacuum, the contribution with $q=r$ is missing, if ψ_r is occupied, and hence no longer *available* for electron-positron-pair creations. This is a typical *exclusion effect*.

If we apply a *no-pair projection* to D_F, i.e., if we remove the part involving the b_k and $b_k^\dagger$ operators, as it has been suggested [35,36] for *n*-electron Hamiltonians, we ignore both the induced vacuum energy and the diamagnetic terms completely, also those arising in the context of the Gaunt or Breit interactions. This aspect appears to have been ignored so far.

The interpretation of diamagnetism as a change of the vacuum energy is *physically* rather suggestive, but it should be taken with great care. If we replace the original Dirac operator by the transformed one, the Fock space picture and the vacuum change completely. Then the modification of the vacuum energy due to the magnetic field is of $O(c^{-4})$, as for an electric perturbation.

In QED for bound states one defines *electrons in an external static electric field*, which leads to a different vacuum than that for *free electrons*. Probably one should treat an external magnetic field similarly.

Remember that in this paper we only consider *solutions of the Dirac equation* even if this is formulated in a Fock-space language, as just done. If one wants to include radiative corrections, positronic states will always (independently of how they are defined) be needed, e.g., in connection with the vacuum polarization, but this is beyond the scope of this paper.

X. THE GORDON DECOMPOSITION OF THE CURRENT DENSITY

Starting from the identity (for ψ eigenfunction of D)

$$\begin{aligned}0&=(D\psi)^\dagger\beta\vec{\alpha}\psi-\psi^\dagger\beta\vec{\alpha}D\psi=(\beta c^2\psi)^\dagger\beta\vec{\alpha}\psi-\psi^\dagger\beta\vec{\alpha}\beta c^2\psi\\ &+(c\vec{\alpha}\cdot\vec{p}\psi)^\dagger\beta\vec{\alpha}\psi-\psi^\dagger\beta\vec{\alpha}c\vec{\alpha}\cdot\vec{p}\psi+(bc\vec{\alpha}\cdot\vec{A}\psi)^\dagger\beta\vec{\alpha}\psi\\ &-\psi^\dagger\beta\vec{\alpha}bc\vec{\alpha}\cdot\vec{A}\psi=2c^2\psi^\dagger\vec{\alpha}\psi-(c\vec{\alpha}\cdot\vec{p}\psi)^\dagger\vec{\alpha}\beta\psi\\ &-c\psi^\dagger\beta\vec{\alpha}\vec{\alpha}\cdot\vec{p}\psi-2bc\psi^\dagger\beta\vec{A}\psi,\end{aligned} \tag{10.1}$$

one arrives at the following decomposition of the current density $\vec{j}$ [37]:

$$\begin{aligned}\vec{j}&=c\psi^\dagger\vec{\alpha}\psi=\tfrac{1}{2}(\vec{p}\psi)^\dagger\beta\psi+\tfrac{1}{2}\psi^\dagger\beta\vec{p}\psi+\tfrac{1}{2}(\vec{\nabla}\psi^\dagger)\times\vec{\sigma}\beta\psi\\ &+\tfrac{1}{2}\psi^\dagger\beta\vec{\sigma}\times(\vec{\nabla}\psi)+b\psi^\dagger\beta\vec{A}\psi=\tfrac{1}{2}\mathrm{Im}\{\psi^\dagger\vec{\nabla}\beta\psi\}\\ &+\tfrac{1}{2}\mathrm{curl}\{\psi^\dagger\vec{\sigma}\beta\psi\}+b\psi^\dagger\beta\vec{A}\psi\end{aligned} \tag{10.2}$$

that formally differs from the nonrelativistic counterpart only in the factor β. One can expand the current density $\vec{j}$, both in the original and in the Gordon form, in powers of the field strength b:

$$\vec{j}=c\psi^\dagger\vec{\alpha}\psi=\vec{j}_0+b\vec{j}_1+O(b^2). \tag{10.3}$$

In the original form we get

$$\vec{j}_0=c\psi_0^\dagger\vec{\alpha}\psi_0, \tag{10.4}$$

$$\vec{j}_1=c\psi_0^\dagger\vec{\alpha}\psi_1+c\psi_1^\dagger\vec{\alpha}\psi_0. \tag{10.5}$$

The corresponding expressions in the Gordon form are

$$\vec{j}_0=\tfrac{1}{2}\mathrm{Im}\{\psi_0^\dagger\vec{\nabla}\beta\psi_0\}+\tfrac{1}{2}\mathrm{curl}\{\psi_0^\dagger\vec{\sigma}\beta\psi_0\}, \tag{10.6}$$

$$\vec{j}_1=\vec{j}_{1p}+\vec{j}_{1d}, \tag{10.7}$$

$$\vec{j}_{1p}=\mathrm{Im}\{\psi_0^\dagger\vec{\nabla}\beta\psi_1\}+\mathrm{curl}\{\mathrm{Re}[\psi_0^\dagger\vec{\sigma}\beta\psi_1]\}, \tag{10.8}$$

$$\vec{j}_{1d}=\psi_0^\dagger\beta\vec{A}\psi_0. \tag{10.9}$$

From Eqs. (10.7)–(10.9) one can evaluate W_2 as [9]

$$W_2=\frac{1}{2}\int \vec{j}_1\cdot\vec{A}d^3r=W_{2p}+W_{2d}, \tag{10.10}$$

$$\begin{aligned}W_{2p}&=\frac{1}{2}\int \vec{j}_{1p}\cdot\vec{A}\ \ d^3r\\ &=\frac{1}{2}\mathrm{Re}\langle\psi_0|(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A})\beta|\psi_1\rangle+\mathrm{Re}\langle\psi_0|\vec{\sigma}\cdot\mathrm{curl}\vec{A}\beta|\psi_1\rangle\\ &=\mathrm{Re}\langle\psi_0|\tilde{D}_1|\psi_1\rangle,\end{aligned} \tag{10.11}$$

$$W_{2d}=\frac{1}{2}\int \vec{j}_{1d}\cdot\vec{A}d^3r=\frac{1}{2}\langle\psi_0|\beta A^2|\psi_0\rangle \tag{10.12}$$

with $\tilde{D}_1$ defined by Eq. (5.3)

We have written W_{2p} and W_{2d} to make clear that these expressions differ from similar ones W_2^p, W_2^{d1}, and W_2^{d2} derived previously Eqs. (5.8)–(5.10). The expression for W_{2p} is *asymmetric*. It involves the perturbation operator $\tilde{D}_1$, but ψ_1 is the response to the perturbation D_1. This causes problems with the interpretation of W_{2p} and W_{2d}.

The most elegant way to arrive at *symmetric* and hence physically interpretable results is to *combine* the Gordon decomposition with the unitary transformation. Let us, in Eqs. (10.8) and (10.11) eliminate ψ_1, by means of Eq. (5.12) in favor of $\tilde{\psi}_1$:

$$\vec{j}_{1p} = \vec{j}_1^{\,p} + \vec{j}_1^{\,d2}, \tag{10.13}$$

$$\vec{j}_1^{\,p} = \mathrm{Im}\{\psi_0^\dagger \vec{\nabla} \beta \tilde{\psi}_1\} + \mathrm{curl}\{\mathrm{Re}[\psi_0^\dagger \vec{\sigma} \beta \tilde{\psi}_1]\}, \tag{10.14}$$

$$\vec{j}_1^{\,d2} = -\frac{1}{2c}\mathrm{Im}\{\psi_0^\dagger \vec{\nabla} \alpha \cdot \vec{A} \psi_0\} - \frac{1}{2c}\mathrm{curl}\{\mathrm{Re}[\psi_0^\dagger \vec{\sigma} \alpha \cdot \vec{A} \psi_0]\}, \tag{10.15}$$

$$W_{2p} = W_2^p + W_2^{d2}, \tag{10.16}$$

$$W_2^p = \frac{1}{2}\int \vec{j}_1^{\,p} \cdot \vec{A} d^3r = \mathrm{Re}\langle \psi_0 | \tilde{D}_1 | \tilde{\psi}_1 \rangle, \tag{10.17}$$

$$W_2^{d2} = \frac{1}{2}\int \vec{j}_1^{\,d2} \cdot \vec{A} d^3r = -\frac{1}{2c}\mathrm{Re}\langle \psi_0 | \tilde{D}_1 \beta \vec{\alpha} \cdot \vec{A} | \psi_0 \rangle. \tag{10.18}$$

Now the quantities W_2^p, W_2^{d2}, and $W_2^{d1} = W_{2p}$ are the same as those derived previously (5.8)–(5.10). The decomposition of the susceptibility W_2 into the contributions W_2^p, W_2^{d1}, and W_2^{d2} is completely parallel to the respective contributions $\vec{j}_1^{\,p}$, $\vec{j}_1^{\,d1}$ and $\vec{j}_1^{\,d2} = \vec{j}_{1d}$ to the current density $\vec{j}_1$.

One understands to some extent, why, coming from the Gordon decomposition of the current density [9], one is tempted to regard W_2^{d2} as belonging to the paramagnetic contribution, because in the Gordon decomposition $\vec{j}_1^{\,d2}$ is contained in $\vec{j}_{1p}$.

Let us finally have a look at what one obtains, if one decomposes the current density by means of the unitary transformation, without using the Gordon decomposition. Inserting Eq. (5.12) into Eq. (10.5) one gets

$$\vec{j}_1' = \vec{j}_{1p}' + \vec{j}_{1d}', \tag{10.19}$$

$$\vec{j}_{1p}' = c\psi_0^\dagger \vec{\alpha} \tilde{\psi}_1 + c\tilde{\psi}_1^\dagger \vec{\alpha} \psi_0, \tag{10.20}$$

$$\vec{j}_{1d}' = -\frac{1}{2}\psi_0^\dagger \vec{\alpha} \beta \vec{\alpha} \cdot \vec{A} \psi_0 - \frac{1}{2}\psi_0^\dagger \vec{\alpha} \cdot \vec{A} \beta \vec{\alpha} \psi_0 = \psi_0^\dagger \beta \vec{A} \psi_0, \tag{10.21}$$

$$W_2 = \frac{1}{2}\int \vec{j}_1 \cdot \vec{A} d^3r = W_{2p}' + W_{2d}', \tag{10.22}$$

$$W_{2p}' = \frac{1}{2}\int \vec{j}_{1p} \cdot \vec{A} d^3r = \mathrm{Re}\langle \psi_0 | c\vec{\alpha} \cdot \vec{A} | \tilde{\psi}_1 \rangle = \mathrm{Re}\langle \psi_0 | D_1 | \tilde{\psi}_1 \rangle,$$

$$W_{2d}' = \frac{1}{2}\int \vec{j}_{1d} \cdot \vec{A} \;\; d^3r = \frac{1}{2}\langle \psi_0 | \beta A^2 | \psi_0 \rangle. \tag{10.23}$$

Since j_{1d}' is the same as j_{1d} in Eq. (10.9), j_{1p}' as given by Eq. (10.20), must be identical with j_{1p}' defined by Eq. (10.8). Obviously we also get

$$W_{2p}' = W_{2p}; \;\; W_{2d}' = W_{2d}. \tag{10.24}$$

W_{2p}' looks asymmetric in a way complementary to W_{2p}. The tilde is now on ψ_1 rather than on D_1. Using just the unitary transformation we get essentially the same decomposition of $\vec{j}_1$ as from the Gordon decomposition, but for a slightly different reason. (The two procedures disagree to higher orders in b). Only the combination of the Gordon decomposition and the unitary transformation leads to a physically satisfactory breakdown of the current density, namely, into three parts $\vec{j}_1^{\,p}$, $\vec{j}_1^{\,d1}$, and $\vec{j}_1^{\,d2}$.

XI. CONCLUSIONS

(1) An external magnetic field strongly affects the coupling between upper (large) and lower (small) components, φ and χ, respectively, of the Dirac spinor of an electron. This effect can be rationalized as (a) a change of the fundamental relation $\chi = X\varphi$ between φ and χ, (b) a strong mixing in of negative-energy states of the unperturbed Dirac operator, (c) a change of the vacuum energy due to the magnetic field by the presence of an electron.

(2) In the traditional formulation of the relativistic perturbation theory of magnetic effects, one first decouples electronic states from positronic states in the absence of the magnetic field, and makes afterwards an additional decoupling in the presence of the magnetic field. The approach suggested here consists in removing the coupling due to the magnetic field, to the leading order, already in the Dirac Hamiltonian (by means of a unitary transformation) before one decouples electronic states from positronic states. So there is no more need for an additional decoupling *at the end*. This need arises only in higher orders in c^{-2}, such as for electric perturbations.

(3) In the transformed operator diamagnetic and paramagnetic contributions arise explicitly, *without a need to separate electronic states from positronic states at the same time*. Actually there are *two* distinct diamagnetic contributions, one of which has no nonrelativistic counterpart. The transformed operator appears to simplify the evaluation of magnetic properties, since the diamagnetic contributions are obtained as expectation values of the wave function in the absence of the magnetic field.

(4) If one treats the relativistic corrections to magnetic properties by means of direct perturbation theory (DPT), which means that one considers *electronic states* only, the nonrelativistic limit (including the separation into diamagnetic and paramagnetic contributions) is automatically ob-

tained, and no serious problems arise with the relativistic corrections. In this context the use of the *transformed* Dirac operator does not lead to dramatic changes, but it is likely to allow some simplifications.

(5) The explanation as well as the evaluation of the diamagnetic contributions to magnetic properties as *due to negative-energy states* in a *sum-over-states* formulation must be regarded as obsolete, because the diamagnetic contributions can be more easily evaluated without the need to sum over contributions of negative-energy states. An expectation value is usually preferable to a sum-over-states formulation.

(6) The diamagnetic contributions obtained on the two main ways discussed here do not agree exactly, except in the nonrelativistic limit. There is, of course, formal agreement between the expressions based on the sum-over-states formulation of the Dirac operator and the Fock-space approach. The full W_2 is, anyway, independent of how one decomposes it into a diamagnetic and a paramagnetic part.

(7) Use of the Gordon decomposition of the current density leads to the same results for the magnetic susceptibility as the unitary transformation of the Dirac operator, but in a much more indirect way. The two approaches are not entirely equivalent, and are even to some extent complementary. To arrive at a physically meaningful decomposition of the induced current density, one must combine the two approaches. The Gordon decomposition by itself leads to a somewhat counterintuitive definition of diamagnetic and paramagnetic contributions to the susceptibility.

(8) If one does not want to choose the transformed Dirac operator, one should, for the evaluation of magnetic properties, use at least the *augmented kinetic balance*, i.e., expand the small component χ in a combined $\vec{\sigma}\cdot\vec{p}$ and $\vec{\sigma}\cdot\vec{A}$ basis.

(9) One may finally wonder whether one should care for the appropriate definition of the diamagnetic part of the magnetizability in relativistic theory, since a change of gauge affects its decomposition into a diamagnetic and a paramagnetic part. The answer is twofold: (a) The problem of the appropriate definition arises for any chosen gauge, it is, so-to-say *gauge independent*. (b) As mentioned already in the Introduction, there is often a *natural gauge*, e.g., for an atom the *natural gauge origin* is at the position of the nucleus. For this choice the paramagnetic contribution vanishes in the nonrelativistic limit. For molecules the best gauge is that with *distributed gauge origins*, such as in the ansatz with London orbitals (LO) [38], also called *gauge including atomic orbitals* GIAOs, or the *individual gauge for localized orbitals* IGLO method [39]. The latter can be rationalized in terms of a *nonlocal* gauge transformation [40]. With these *distributed gauge origins* one achieves, as for atoms in their natural gauge, that the (positive) diamagnetic part of E_2 is minimized, and that there is as little compensation as possible of spurious terms due to an inappropriate choice of the gauge. The approach presented here allows us to generalize this paradigm to the relativistic regime. Our conclusions are not affected by the fact that distributed gauge origins can also be used in combination with the evaluation of diamatic contributions in terms of negative-energy states [6].

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