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Remarks on the Fermi Contact Interaction

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It is shown by rigorous mathematical methods that the so-called Fermi contact interaction does not define any selfadjoint Hamiltonian, and the only possible form of contact interaction localized strictly at $\mathbf{r} = 0$ is found. However, the Fermi contact interaction retains sense when used as a bilinear form in the perturbation theory for Dirac electrons. Some results obtained earlier by other authors are confirmed and interpreted by our analysis.

Key words: Fermi contact interaction – Bilinear form – Boundary (asymptotic) conditions – Hydrogen atom.

1. Introduction

During a long time, in the quantum theory of atoms and molecules considerable interest has been paid to the so-called Fermi contact interaction (FCI) [1–6] which is a rather unusual *potential* proportional to $\delta^3(\mathbf{r})$. The same type of interaction describes the Darwin correction in the theory of hydrogen-like atoms [7, 8]. For spherically symmetric systems such a potential acts on s-states only [2–8]. Unfortunately, serious doubts about the possibility to use FCI arose on account of divergent results both in the formal perturbation theory [2, 4, 5] and variational principle estimates [6]. To remove this discrepancy, a modification of FCI has been proposed [4, 5].

The aim of the present paper is to find a mathematically correct form of *operators* acting in some sense at the point $\mathbf{r} = 0$ only. Moreover, we shall clarify the origin of the discrepancy mentioned above. To make the paper easier readable, formal mathematical considerations are strongly reduced and a proper set of references is given instead.

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2. Hamiltonians, Bilinear Forms and Boundary Conditions

First, let us consider an electron moving under the influence of a nonsingular, spherically symmetric potential $U(r)$, with the Hamiltonian (atomic units are used throughout the paper)

$$H=-\tfrac{1}{2}\Delta+U(r), \qquad \Delta=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}. \tag{1}$$

Restricting ourselves to s-states, and by means of the substitution [9]

$$F(\mathbf{r})\equiv F(r) \to f(r)=rF(r) \tag{2}$$

one can reduce the Hamiltonian (1) to the one-dimensional form

$$h=-\tfrac{1}{2}\frac{d^2}{dr^2}+U(r), \qquad 0\leq r<\infty. \tag{3}$$

When going from three- to the one-dimensional formulation, the following formula will also be useful [4–6]:

$$\delta^3(\mathbf{r}) \to (4\pi r^2)^{-1}\delta(r). \tag{4}$$

For a moment we shall consider H (or h) as differential expression acting only on such functions which are equal to zero in some neighbourhood of point $\mathbf{r}=0$ (or $r=0$). For such a type of functions, addition or even existence of a contact potential at the point $\mathbf{r}=0$ is irrelevant. Now it is easy to understand (cf. [10–12]) that the description of all interactions with support at coordinate origin is actually equivalent to finding all boundary conditions at this point, inverting the differential expression H (or h) into a selfadjoint operator. The answer is well known and the operator h(3) will be considered for simplicity [10, 13]. Namely, for any c real or $c=+\infty$, we impose the boundary conditions

$$cf(0)-f'(0)=0, \qquad c \text{ is real}, \tag{5}$$

$$f(0)=0, \qquad c=+\infty \tag{6}$$

on the functions f from the domain of an operator based on (3). By fixing c, we invert the differential expression (3), and via (2) also (1), into selfadjoint operators h_c, H_c, respectively, and all selfadjoint extensions of (1), (3) in the Hilbert space of square-integrable functions are obtained in this way. Hence, no contact interaction can be omitted in our analysis. As will be shown below (Eqs. (8) and (9)), boundary conditions determine uniquely the contact potential acting at the point $r=0$ only. In quantum theory, the case $c=+\infty$, i.e. the boundary condition (6) is used almost exclusively [9].

It is useful to consider the bilinear form (cf. Ref. [14], Chap. VI)

$$Q_c(f,g)=\int g^*(h_cf)\,dr, \tag{7}$$

associated with the operator h_c, where f fulfils (5) or (6) for chosen c. Integrating in

(7) by parts, we get ([14], Chap. VI, example 2.16)

$$Q_c(f, g) = \int [\tfrac{1}{2}g'^*f' + g^*Uf + \tfrac{1}{2}c\delta(r)g^*f]\,dr. \tag{8}$$

In (8), the expression $\infty\delta(r)$ appearing for $c = +\infty$ is a symbol, forcing the boundary condition (6). By means of the right-hand side of (8), one can extend $Q_c(f, g)$ (for finite c) also to functions not fulfilling (5). However, using the theory of bilinear forms [14] or the variational principle technique, the condition (5) will be restored again.

From (2) we see that for finite c, eigenfunctions in the three-dimensional variant (1) behave as r^{-1} for $r \to 0$. This does not violate essentially the quantum-mechanical axioms. For any volume V, $\int_V |F|^2\,d^3x$ is finite, and the flux of current of probability through any surface is due to (5) nonsingular as well. Nevertheless, let us note that the mean value of the kinetic energy operator T need not be defined in this case [6], as, by definition, $T = -\frac{1}{2}\Delta$ can only act on functions finite at $\mathbf{r} = 0$.

By means of (2) and (4) we rewrite (8) also for the three-dimensional case:

$$Q_c(F, G) = \int [\tfrac{1}{2}\nabla G^*\nabla F + G^*UF + 2\pi c\, r^2\delta^3(\mathbf{r})G^*F]\,d^3x. \tag{9}$$

One should not be surprised by the appearance of the unusual functional $r^2\delta^3(\mathbf{r})$: the latter has no (nonzero) analogy when considering continuous functions only. It can be defined due to the fact that we admit the r^{-1}-like behaviour of F, G. (Clearly, we define $\int r^2\delta^3(\mathbf{r})u(\mathbf{r})\,d^3x = \lim_{\mathbf{r}\to 0} r^2u(\mathbf{r})$.)

3. Modifications for Coulomb Interaction

For application to quantum-machanical problems [2–8] one has to include the Coulomb interaction as well, i.e. to consider the potential

$$U(r) = -r^{-1} + U_0(r) \tag{10}$$

with nonsingular $U_0(r)$. Repeating all the considerations of Sect. 2, we find that several changes have to be done. Instead of boundary conditions (5), (6), the following asymptotic conditions are found for $r \to 0+$:

$$f = \text{const}\,(1 - 2r\ln r + cr) + o(r), \qquad c \text{ is finite}, \tag{11}$$

$$f = 0(r), \qquad c = +\infty. \tag{12}$$

The asymptotes (11), (12) follow from the exact solutions (17), (18) for the hydrogen atom. The detailed derivation does not differ substantially from this for other types of singular differential operators [10–12]. Moreover, for finite c the part of integrand in (8) containing r^{-1} (and analogically in (9)) should be regularized, taking

$$\lim_{\varepsilon\to 0}\left[\int_\varepsilon g^*r^{-1}f\,dr - \ln\varepsilon\, g^*(\varepsilon)f(\varepsilon)\right]. \tag{13}$$

This result can be verified by going from (7) to (8) and taking (11) into account. The infinite regularizing term appears when integrating by parts. By means of the same method as used in [12], it can be proved that we have described all selfadjoint extensions of the differential operator (3) with the potential (10).

4. Contact Interaction

The bilinear forms (8) and (9) (or the corresponding variational principle) in the sense explained above provide a rigorous formulation of the idea of a potential acting at the coordinate origin only. We have found in Sects. 2 and 3 all the realizations of this type of interactions, and so we can state on the basis of (9) that FCI which is of the $\delta^3(\mathbf{r})$ form, defines no selfadjoint operator. Instead of this we have found another form of contact potential, $2\pi r^2\delta^3(\mathbf{r})$, which we shall call modified Fermi contact interaction (MFCI). The presence of the term r^2 in MFCI shows, roughly speaking, that FCI is infinitely large when compared with MFCI. However, MFCI is consistent, in certain sense at least, with the modified Fermi potential advocated by Blinder [4, 5, 15]. Indeed, changing MFCI slightly,

$$4\pi r^2\delta^3(\mathbf{r}) = \delta(r) \to \delta(r-r_0), \qquad r_0 > 0 \text{ but small,} \tag{14}$$

we get the modified Fermi potential of [4, 5] up to a numerical factor $2\pi r_0^2$ (proportional to surface of the sphere on which the interaction occurs), which for fixed r_0 can be absorbed into the definition of the coupling constant. However, the question about the interpretation of the coupling constant when going from FCI to MFCI remains to be clarified, see also Sect. 6. Another problem is to be mentioned. In the limit $c \to 0$, we do not return to the non-interacting model (6), (12), corresponding to $c = +\infty$ [11]. This is an example of a complication being present, perhaps, in a wider class of physical theories [16].

5. Example: The Hydrogen Atom

To get a better understanding of the conclusions made in Refs. [2, 4–6], let us consider the case of a pure Coulomb potential (10),

$$U(r) = -r^{-1}, \tag{15}$$

in more detail.

Only the one-dimensional formulation (2), (3) for the s-states will be considered. For an energy $E < 0$,

$$E = -\frac{1}{2\nu^2}, \qquad \nu > 0, \tag{16}$$

the following set of square-integrable candidates for eigenfunctions is found (cf. [4, 5, 9]):

$$f = \rho \exp(-\rho/2)\Phi(-\nu+1, 2, \rho) = M_{\nu,1/2}(\rho),$$
$$\nu = n = 1, 2, 3, \ldots \tag{17}$$

$$f=\rho \exp(-\rho/2)\Psi(-\nu+1, 2, \rho)=W_{\nu,1/2}(\rho),$$
$$\nu \neq n, \tag{18}$$

where $\rho=2r/\nu$, Φ and Ψ are the confluent hypergeometric functions of the first and second kind, respectively, and M, W are Whittaker functions [17]. The hydrogen atom eigenfunctions ($c=+\infty$) are given by (17) [9]. To find the point spectrum for finite values of c, one has to expand (18) for small r and compare it with (11). (The continuous spectrum $E \geqq 0$ is independent of c.) For this purpose we use Eq. (13), Chap. 6.7 of Ref. [17] (see also [4]) and obtain

$$1-2r\ln r+cr=1-2r\ln r+2r\left[-2\gamma+1-\psi(1-\nu)-\ln(2/\nu)-\frac{1}{2\nu}\right], \qquad \nu>0, \tag{19}$$

which represents an equation for $\nu=\nu(c)$. In (19), γ is the Euler constant and ψ is the logarithmic derivative of the Γ-function [17]. Eq. (19) has a countable set of solutions $\nu_n(c)=n+\delta_n(c)$, $n=1, 2, 3, \ldots$, where δ_n are the so-called quantum defects [5], and are strictly increasing functions of c. Moreover, it is easy to check that $\delta_n(+\infty)=0$, $\delta_n(-\infty)=-1$. To see this, it is sufficient to consider a graphical representation of Eq. (19). We are able to find also the first term in the expansion of δ_n for $c \to \pm\infty$. For this purpose, the asymptotic formula $\psi(z)=-1/(z+n)+0(1)$, $z \to -n$ [17] is to be substituted into (19). Finally, one finds

$$\delta_n(c)=-2/c+o(1/c), \qquad c \to +\infty, \qquad n=1, 2, 3, \ldots \tag{20}$$

$$\delta_n(c)=-1-2/c+o(1/c), \qquad c \to -\infty, \qquad n=2, 3, \ldots \tag{21}$$

$$\delta_1(c)=-1-1/c+o(1/c), \qquad c \to -\infty. \tag{22}$$

Asymptotical properties of the eigenvalues follow now from (16) and (20)–(22). We see immediately that for $c \to +\infty$, we approach the hydrogen atom spectrum, whereas for $c \to -\infty$, the ground state energy diverges, $E_1 \to -\infty$. (This is, undoubtedly, an illustration of a quite general situation, cf. Refs. [12] or [14], Chap. VII, example 1.11. The last mentioned example shows that when eigenvalues are viewed as analytic functions of c, their behaviour becomes very complex when $|c| \to \infty$.) This essentially explains the results of [2, 4–6]. Indeed, the missing factor r^2 in the FCI (when compared with MFCI) makes FCI infinitely big ($|c| \to \infty$), positive for repulsive interaction ($c \to +\infty$) and negative for attractive interaction ($c \to -\infty$). (This can be easily understood, e.g. by considering the limit $r_0 \to 0$ in [4, 5] and by comparing this with MFCI.) Then, the explanation of the most important results of [2, 4–6] follows directly from the analysis of asymptotic properties of the point spectrum, as given in this section.

6. Conclusions

It has been found in Sects. 2, 3 that neither FCI nor the Darwin correction define any selfadjoint operator. On the other hand, an application of the first order formal perturbation theory to these potentials provides results in complete agreement with experiment [2–8]. Fortunately, it is possible to explain this controversy.

It is important to mention that for a (selfadjoint) Schrödinger operator H, one can define a (symmetric) bilinear form of FCI (or Darwin correction)

$$\langle F|H+\lambda\delta^3(\mathbf{r})|G\rangle. \tag{23}$$

However, no selfadjoint operator is associated with this form. Now, it is easy to solve the puzzle. The operators we consider arise from several leading terms of a transformation reducing the selfadjoint [18] Dirac Hamiltonian (DH) to a two-component Schrödinger operator, when the transformation is expanded in inverse powers of light velocity [3, 8]. Generally, the terms obtained do not represent any selfadjoint Hamiltonian. It is more rigorous to apply the same transformation to the bilinear form associated with DH, which leads to correctly defined bilinear forms (such as, e.g. (23)) instead of the corresponding badly defined "*operators*". Considering DH as perturbed Hamiltonian, and by putting in (23) $F=G=$ normalized eigenfunction of H, we find, formally at least, the linear approximation (in λ) to the respective energy eigenvalue of DH, in full agreement with earlier results [1–8]. Nevertheless, the form (23) has no simple physical interpretation as an independent quantity.

One may wonder whether FCI could be modified to lead to both, selfadjoint operator and perturbation of eigenvalues consistent with results of FCI described above. Strictly speaking, there is no simple reason supporting this idea, cf. also [15]. However, this can be achieved by a reinterpretation of MCFI. Comparing Eqs. (20)–(22) with results of FCI [1–6, 8], we find the following correspondence for the hydrogen atom:

$$\text{FCI: } \lambda\delta^3(\mathbf{r}), \qquad |\lambda|\ll 1 \rightarrow \text{MFCI: } 2\pi r^2 c\delta^3(\mathbf{r}), \qquad c=-2\pi/\lambda. \tag{24}$$

Moreover, for $\lambda>0$, the lowest energy eigenvalue $E_1(c)$ should be ignored as well as the corresponding eigenvector. It is not clear, however, whether a such defined contact interaction has actually physical sense.

To conclude, FCI has to be considered as an expression appearing in the perturbation theory for the Dirac Hamiltonian, but having no separate meaning. The question of finding a physically appropriate potential for contact interaction is open.

Recently, several abstract mathematical methods of regularization of singular Hamiltonians have been discussed [19], which are applicable also to the FCI problem. It appears, however, that they do not yield more general results when compared with classical methods (similar to the approach used in the present paper). Ref. [19] contains also an useful list of references.

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References

1. Fermi, E.: Z. Phys. **60**, 320 (1930)
2. Schwartz, C.: Ann. Phys. (N.Y.) **6**, 156 (1959)
3. Blinder, S. M.: Advan. Quantum Chem. **2**, 47 (1965)
4. Blinder, S. M.: Phys. Rev. **A18**, 853 (1978), and references cited therein
5. Blinder, S. M.: Theoret. Chim. Acta (Berl.) **53**, 159 (1979)
6. Velenik, A., Živković, T., de Jeu, W. H., Murrell, J. N.: Mol. Phys. **18**, 693 (1970)
7. Heitler, W.: The quantum theory of radiation, § 34.3. Oxford: Clarendon Press 1954
8. Beresteckii, V. B., Lifshitz, E. M., Pitaevskii, L. P.: Relativistic quantum theory, Vol. 1, § 33, 34 (in Russian, English transl. Oxford: Pergamon 1971). Moscow: Nauka 1968
9. Flügge, S.: Practical quantum mechanics, Vol. 1, problem 67. Berlin: Springer 1971
10. Naijmark, M. A.: Linear differential operators (in Russian). Moscow: Nauka 1969
11. Narnhofer, H., Klauder, J. R.: J. Math. Phys. **17**, 1201 (1976)
12. Pick, Š.: J. Math. Phys. **18**, 118 (1977)
13. Coddington, E. A., Levinson, N.: Theory of ordinary differential equations. New York: McGraw-Hill 1955
14. Kato, T.: Perturbation theory for linear operators. Berlin: Springer 1966
15. Trivedi, H. P.: Mol. Phys. **38**, 1603 (1979); Chem. Phys. Letters **70**, 159 (1980), and references cited therein
16. Klauder, J. R.: Ann. Phys. (N.Y.) **117**, 19 (1979)
17. Erdélyi, A., ed.: Higher transcendental functions, Vol. 1. New York: McGraw-Hill 1953
18. Kalf, H., Schmincke, U.-W., Walter, J., Wüst, R.: in Spectral theory and differential eqautions, Everitt, W. N., ed., pp. 182–226. Berlin: Springer 1975
19. Koshmanenko, V. D.: in Operators of mathematical physics an infinitely dimensional analysis (in Russian), Berezansky, Yu. M., ed., pp. 58–72. Kiev: Institute of Mathematics, Academy of Sciences of Ukrainian SSR 1979

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