The hydrogen atom in the presence of the Fermi-contact interaction

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It is shown that the energy associated with the Fermi-contact part of the hamiltonian of the hydrogen atom cannot be expanded as a perturbation series. A variation calculation shows that the total energy is \( E_0 \) when the Fermi-contact operation is added to \( H_0 \), and \( -\infty \) when it is subtracted. In order to do a priori variational calculations on the 'second-order' properties of this operator, such as spin–spin coupling constants, it is probably necessary to remove the singularity caused by the \( \delta \) function.

1. INTRODUCTION

The hamiltonian used to describe the magnetic interaction between a nucleus with spin \( I \) and the surrounding electrons is [1]:

\[
H' = 2\beta h I \sum_i \left( \frac{1}{r_i^3} - \frac{s_i}{r_i^3} + \frac{3r_i(s_i \cdot r_i)}{r_i^5} + \frac{8}{3} \pi s_i \delta(r_i) \right),
\]

(1)

where the symbols have their usual meaning. This operator has been used in first-order calculations to give the hyperfine splitting constants of atoms. For the hydrogen atom only the 'Fermi-contact' part of the hamiltonian:

\[
\sum_i 3 \beta h I s_i \delta(r_i),
\]

(2)

contributes to the first-order energy, and the result is very close to the observed hyperfine splitting [2]. In second order \( H' \) is used to calculate a number of molecular properties, amongst which is the indirect nuclear spin–spin coupling constant.

Both perturbation and variation methods have been used to calculate the expectation values of \( H_0 + H' \). However, the perturbation method has the disadvantage that one needs either to solve the differential equations for each order, or one needs a complete set of states which have good convergence properties for the lowest-order energies. In variational calculations the main problem is to take a suitable form for the trial wave function [3]. It is the Fermi-contact term which leads to most of the difficulties in these calculations because of its singularity at the nucleus. In order to get a better idea of what functions could be useful in a variational calculation we have examined the effect of the Fermi-contact term on the ground state energy of the hydrogen atom.

2. THE HYDROGEN ATOM WITH A \( \delta \)-FUNCTION POTENTIAL IN THE HAMILTONIAN

The second-order energy for the hydrogen atom with the Fermi-contact operator as a perturbation is \( -\infty \) [4, 5]. This result is readily shown by conventional sum-over-states perturbation theory as is done in the Appendix. The direct solution of

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the first-order perturbation equation was given by Schwartz \[4\]. As could be expected the first-order perturbed wave function contains terms which have singularities at the origin:
\[
\psi^{(1)} = N(-r^{-1} + 2 \ln r + 2r + C) \exp(-r),
\]
where \(C\) is a constant. It would be tempting to include these functions in the basis of a variational calculation of the coupling constant; however the resulting \(-\infty\) for the second-order energy must cast some doubt on the whole validity of the perturbation expansion.

We will now show that the mathematical difficulties in the calculation of the second-order properties arise not from the difficulties in finding a satisfactory basis but from the fact that the energies associated with the \(\delta\) function in the hamiltonian cannot be expanded in a perturbation series. To do this we consider the variation solution for the hydrogen atom with a potential:
\[
V = -r^{-1} + \lambda \delta(r),
\]
where \(\lambda\) is a constant and
\[
\delta(r) = \delta(r)/4\pi r^2.
\]
It should be noted that depending on the sign of \(\lambda\) in equation (2) \(\lambda\) can be positive or negative.

We consider the expectation value of the energy:
\[
E(\lambda) = \langle \psi | H_0 + \lambda \delta(r) | \psi \rangle
\]
\[
= \langle \psi | H_0 | \psi \rangle + \lambda \psi^2(0).
\]

Now
\[
\langle \psi | H_0 | \psi \rangle \geq E_0
\]

hence
\[
E(\lambda) \geq E_0 + \lambda \psi^2(0).
\]

If \(\lambda\) is positive, we deduce:
\[
E(\lambda) \geq E_0.
\]

We shall now show that there is a function for which \(E(\lambda) = E_0\). Consequently this is an exact eigenfunction of the total hamiltonian.

Consider the normalized function:
\[
\psi(\xi) = N(\xi)[\exp(-r) - \exp(-\xi r)].
\]
For this function:
\[
\langle \psi(\xi) | H | \psi(\xi) \rangle = \left\{ \frac{1}{1 - \frac{16}{(1 + \xi)^3} + \frac{1}{\xi^3}} \right\}^{-1} \left\{ \frac{1}{2} + \frac{1}{\xi^3} - \frac{1}{\xi^2} + \frac{8}{(1 + \xi)^3} \right\}
\]
and
\[
[\psi^2(\xi)]_{r=0} = 0.
\]

Thus \(E(\xi)\) is independent of \(\lambda\) and
\[
\lim_{\xi \to \infty} E(\xi) = -\frac{1}{2} = E_0.
\]
Although $\psi(\xi)$ is discontinuous at $r = 0$ for $\zeta = \infty$, it is continuous for all finite values of $\zeta$, and we can always choose $\zeta$ such that $E(\xi)$ differs from $E_0$ by any specified finite small amount.

We now take $\lambda$ to be negative, and evaluating the expectation value for the normalized function:

$$\psi(\xi) = \xi^{3/2} r^{-1/2} \exp (-\xi r),$$

we have

$$E(\lambda, \zeta) = \frac{1}{8} \zeta^2 - \zeta + \lambda \xi^3 / \pi.$$  

As $\lambda$ is negative there is clearly no lower limit to the energy and

$$\lim_{\zeta \to \infty} E(\lambda, \zeta) = -\infty.$$

3. DISCUSSION

We have shown that no matter how small $\lambda$, the lower limit of the total energy for $\lambda$ positive is $E_0$, and for $\lambda$ negative is $-\infty$. Under these circumstances one clearly cannot develop the energy in a perturbation expansion in powers of $\lambda$. Therefore the solution of the first-order perturbation equation probably has no physical significance.

The nature of the solutions that we have found can be understood as follows: if $\lambda$ is positive the $\delta$ function potential tends to repel the electron from the nucleus, and the wave function is one with zero density at the nucleus. For negative $\lambda$ on the other hand the electron collapses into the nucleus. Although these results are far from the experimental energy of about $\lambda/\pi$, we can conclude that the difficulty in handling the $\delta$ function beyond first order appears not to be in the nature of its first-order wave functions, but that the potential of expression (4) is ill-behaved for a perturbation expansion.

A possible solution of these problems could be the use of an operator that allows for the finite size of the nucleus and which gives approximately the same results as the $\delta$ function in first order. The reason for the electron falling into the nucleus for negative $\lambda$ arises from the fact that the potential $\delta(r)/r^2$ is at the origin at least of order $r^{-3}$. By using the function:

$$\frac{r_0}{r^2 (r + r_0)^2},$$

which in the limit $r_0 \to 0$ reduces to the $\delta$-function potential, the behaviour at the origin is reduced to $r^{-2}$ and a finite energy can be expected for every $r_0 \neq 0$. According to the analysis of Blinder [6] this, rather than the $\delta$ function, is the form of the operator that is derived from the relativistic treatment of hyperfine interactions. In a later paper we shall investigate this function as a perturbation to the hydrogen atom, and use it as a basis for a variational calculation of the coupling constant of HD.

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APPENDIX

In this Appendix we show that a calculation of the second-order energy for the hydrogen atom with $H' = \lambda \delta(r)$ leads to $-\infty$.

$$E_0 = -\frac{1}{2}; \quad E_n = \frac{-1}{2n^2} \text{ (A.U.)}$$

For bound s states:

$$\psi_n^2(0) = \frac{1}{\pi n^2}.$$  

For continuum s waves [2]:

$$\psi_\infty^2(0) = \frac{1}{\pi} \left(1 - \exp \left[ -\frac{2}{\sqrt{2E}} \right] \right).$$

$$E^{(1)} = \psi_\infty^2(0) = \frac{1}{\pi},$$

$$E^{(2)} = - \sum_{n=2}^{\infty} \frac{\langle \delta(r) | n \rangle^2}{E_n - E_0} - \int_0^{\infty} \frac{\langle \delta(r) | E \rangle^2}{E - E_0} \frac{dE}{E - E_0}$$

$$= - \sum_{n=2}^{\infty} \frac{2}{\pi^2 n(n^2 - 1)} - \frac{1}{\pi^2} \int_0^{\infty} \left[1 - \exp \left[ -\frac{2}{\sqrt{2E}} \right] \right] \frac{dE}{E + \frac{1}{2}}.$$  

The first part can easily be summed to give $-1/2\pi^2$. The integral $I$ in the second part is divergent:

$$I > \int_0^{\infty} \frac{dE}{E + \frac{1}{2}} = \left[ \ln \left(E + \frac{1}{2} \right) \right]_0^{\infty} = \infty.$$  

Consequently

$$E^{(2)} = -\infty.$$  

One can also obtain this result using any other complete set of states, for example the discrete complete set of Löwdin–Shull orbitals [7].

REFERENCES