MOLECULAR PHYSICS, 1970, VOL. 18, NO. 5, 693–696

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

by A. VELENIK, T. ŽIVKOVIĆ†, W. H. DE JEU and J. N. MURRELL
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

(*Received* 19 *January* 1970)

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 δ function.

1. INTRODUCTION

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

$$H' = 2\beta\hbar\gamma \mathbf{I}.\sum_i \left\{\frac{\mathbf{l}_i}{r_i^3} - \frac{\mathbf{s}_i}{r_i^3} + \frac{3\mathbf{r}_i(\mathbf{s}_i.\mathbf{r}_i)}{r_i^5} + \frac{8}{3}\pi\mathbf{s}_i\delta(\mathbf{r}_i)\right\}, \tag{1}$$

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:

$$\sum_i \tfrac{8}{3}\beta h\gamma \mathbf{I}.\mathbf{s}_i\delta(\mathbf{r}_i), \tag{2}$$

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 δ-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

† On leave from Institute ' Rudjer Bošković ', Zagreb, Yugoslavia.

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:

$$\psi^{(1)}=N(-r^{-1}+2\ln r+2r+C)\exp(-r), \tag{3}$$

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 δ 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:

$$V=-r^{-1}+\lambda\delta(\mathbf{r}), \tag{4}$$

where λ is a constant and

$$\delta(\mathbf{r})=\delta(r)/4\pi r^2.$$

It should be noted that depending on the sign of $\mathbf{I}.\mathbf{s}$ in equation (2) λ can be positive or negative.

We consider the expectation value of the energy:

$$\begin{aligned}E(\lambda)&=\langle\psi|H_0+\lambda\delta(\mathbf{r})|\psi\rangle\\&=\langle\psi|H_0|\psi\rangle+\lambda\psi^2(0).\end{aligned} \tag{5}$$

Now

$$\langle\psi|H_0|\psi\rangle\geqslant E_0$$

hence

$$E(\lambda)\geqslant E_0+\lambda\psi^2(0). \tag{6}$$

If λ is positive, we deduce:

$$E(\lambda)\geqslant E_0. \tag{7}$$

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:

$$\psi(\zeta)=N(\zeta)[\exp(-r)-\exp(-\zeta r)]. \tag{8}$$

For this function:

$$\langle\psi(\zeta)|H|\psi(\zeta)\rangle=\left\{1-\frac{16}{(1+\zeta)^3}+\frac{1}{\zeta^3}\right\}^{-1}\left\{-\frac{1}{2}+\frac{1}{2\zeta}-\frac{1}{\zeta^2}+\frac{8}{(1+\zeta)^3}\right\} \tag{9}$$

and

$$[\psi^2(\zeta)]_{r=0}=0.$$

Thus $E(\zeta)$ is independent of λ and

$$\lim_{\zeta\to\infty}E(\zeta)=-\tfrac{1}{2}=E_0.$$

Although $\psi(\zeta)$ is discontinuous at $r=0$ for $\zeta=\infty$, it is continuous for all finite values of ζ, and we can always choose ζ such that $E(\zeta)$ differs from E_0 by any specified finite small amount.

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

$$\psi(\zeta)=\zeta^{3/2}\pi^{-1/2}\exp(-\zeta r), \tag{10}$$

we have

$$E(\lambda,\zeta)=\tfrac{1}{2}\zeta^2-\zeta+\lambda\zeta^3/\pi. \tag{11}$$

As λ 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 λ, the lower limit of the total energy for λ positive is E_0, and for λ negative is $-\infty$. Under these circumstances one clearly cannot develop the energy in a perturbation expansion in powers of λ. 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 λ is positive the δ function potential tends to repel the electron from the nucleus, and the wave function is one with zero density at the nucleus. For negative λ on the other hand the electron collapses into the nucleus. Although these results are far from the experimental energy of about λ/π, we can conclude that the difficulty in handling the δ 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 δ function in first order. The reason for the electron falling into the nucleus for negative λ 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:

$$\frac{r_0}{r^2(r+r_0)^2}, \tag{12}$$

which in the limit $r_0\to 0$ reduces to the δ-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 δ 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.

W. H. J. wishes to acknowledge the award of a fellowship in the European exchange programme of the Royal Society. A. V. thanks the Institute of Biology, University of Zagreb, for financial support.

Appendix

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

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

For bound s states:

$$\psi_n^2(0) = 1/\pi n^3.$$

For continuum s waves [2]:

$$\psi_E^2(0) = \pi^{-1}\{1 - \exp[-2\pi/\sqrt{(2E)}]\}^{-1}.$$

$$E^{(1)} = \psi^2(0) = \pi^{-1},$$

$$E^{(2)} = -\sum_{n=2}^{\infty} \frac{\langle 0|\delta(\mathbf{r})|n\rangle^2}{E_n - E_0} - \int_0^{\infty} \frac{\langle 0|\delta(\mathbf{r})|E\rangle^2\, dE}{E - E_0}$$

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

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

[1] Abragam, A., 1961, *Principles of Nuclear Magnetism* (Oxford University Press), p. 172.
[2] Bethe, H. A., and Salpeter, E. E., 1957, *Quantum Mechanics of One- and Two-electron Atoms* (Berlin: Springer).
[3] Schaefer, J., and Yaris, R., 1967, *J. chem. Phys.*, **46**, 948.
[4] Schwartz, S., 1959, *Ann. Phys.*, **6**, 156.
[5] Das, T. P., and Bersohn, R., 1959, *Phys. Rev.*, **115**, 897.
[6] Blinder, S. M., 1965, *Adv. quant. Chem.*, **2**, 47.
[7] Löwdin, P. O., and Shull, H., 1956, *Phys. Rev.*, **101**, 1730.