raised. The observed fractional transfer into the narrow component at $\sim$15 kilogauss, namely 0.03 in polyethylene, 0.04 in Teflon (and a like figure for fused quartz), is about what one would calculate on the basis of the known values of τ_2 and the singlet-triplet energy difference for free 1-S positronium, assuming, for the sake of argument, that one-third of 0.29 of the total annihilation events are transferable.

Current experiments designed to measure the narrowness ν [defined in Sec. II (3)] as a function of magnetic field, with temperature as a parameter, are expected to yield information on positron-electron overlap and/or whether more than one-third (the $m=0$ fraction) of the supposed triplet states are available for quenching.

All that can be said about the diffusion experiments at this time has been stated in Sec. II (4).

An experiment under way is to test for narrow component enhancement in gases known to form positronium, since free and thermalized positronium should yield a rather narrow correlation in contrast to bound positronium. Here again, the field dependence of any effect should be of interest.

It would seem worthwhile to look for a Doppler-free component in the energy spectrum[22] of the annihilation photons. Plans have been made for a nuclear resonance fluorescence experiment.

IV. ACKNOWLEDGMENTS

The authors are grateful to A. J. Allen for his support, and acknowledge the assistance of O. J. Wallace and T. W. Trout in the earlier stages of the work. Also assisting, but more recently, are D. Conway, R. Gunst, A. McElroy, and C. Richardson. For fabrication of mechanical parts we are indebted to E. M. Perkins and W. L. Cook. P. Stehle is to be thanked for his interest throughout the experiment.

[22] DuMond, Lind, and Watson, Phys. Rev. **75**, 1226 (1949).

PHYSICAL REVIEW VOLUME 102, NUMBER 6 JUNE 15, 1956

Application of the Rayleigh-Schrödinger Perturbation Theory to the Hydrogen Atom

RICHARD E. TREES*
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

(Received March 6, 1956)

Wigner has calculated the ground-state energy of the hydrogen atom with second-order perturbation theory, the whole electrostatic potential being considered as the perturbation. Though his result is finite, it does not agree with the known energy for hydrogen. A fact implicit in the literature, but not usually appreciated in this connection, is pointed out—that if part of the electrostatic energy is retained in the zero-order problem, a correct result is obtained, even if the part of the energy retained is given a zero magnitude after the calculation is carried out. It is also shown that if the calculation is carried out in an Einstein hypersphere, the entire "electrostatic potential" can be regarded as the perturbation and the correct result is obtained. Perturbation theory leads to the exact energy eigenvalue in all approximations higher than the first, but the expansion of the eigenfunction converges slowly if the perturbation is made large.

I. INTRODUCTION

WIGNER[1] has recently pointed out a failure of second-order perturbation theory to give a meaningful result when applied to the hydrogen atom. Considering the whole electrostatic potential as a perturbation, he has calculated the ground-state energy and found it finite, but grossly incorrect numerically. It would be very simple to carry out perturbation calculations if the solutions of the field-free Schrödinger equation could be used as a starting point, but the results of I show that this cannot be done. The present investigation is part of an effort to find a modification that will give the correct result without introducing too much additional complication.

In the type of problem considered, the exact solution of the Schrödinger equation is assumed already known, or at least obtained to a high degree of accuracy with variational methods. In the simplest case, the Hamiltonian depends linearly on a single parameter λ which has a continuous range of values. The energy eigenvalue of the Hamiltonian $H(\lambda)$ will be some known function $E(\lambda)$. The parameter λ is then regarded as a sum of two parameters, say $\lambda=\lambda_1+\lambda_2$. The eigenfunctions and eigenvalues of $H(\lambda)$ are then obtained with perturbation theory,[2] starting from zero-order solutions of $H(\lambda_1)$. This procedure defines the energy as a series in increasing powers of λ_2. If the correct energy, $E(\lambda)=E(\lambda_1+\lambda_2)$, has an expansion in increasing powers of λ_2 that agrees with the perturbation series to a given order, then the energy calculated with the perturbation theory is considered correct to that order. Usually perturbation theory can be correct only when $\lambda_2<\lambda_1$, as

---

* On leave from the National Bureau of Standards, Washington, D. C.

[1] E. P. Wigner, Phys. Rev. **94**, 77 (1954); referred to as I in this paper.

[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

for example in the case of the harmonic oscillator where $E(\lambda)$ is proportional to $\surd\lambda$.

For the hydrogen atom, the parameter λ may be taken as the atomic number Z, and with $\lambda_2=(Z-Z_1)$, the correct energy has the form

$$E(Z)=-\frac{1}{2}\frac{me^4}{\hbar^2}Z^2$$
$$=-\frac{1}{2}\frac{me^4}{\hbar^2}[(Z_1)^2+2Z_1(Z-Z_1)+(Z-Z_1)^2]. \quad (1)$$

We point out in Sec. II that the perturbation calculation with nonzero value for Z_1 is correct to second order, and gives in this case the exact energy eigenvalue no matter how much smaller Z_1 is than $(Z-Z_1)$. Unfortunately this calculation seems to have no extension that makes it applicable to the limiting case of most interest, when Z_1 is assumed zero. As long as Z_1 is nonzero both an infinite set of discrete states and a continuum are utilized in the perturbation calculation, so it is not surprising that this mixed spectrum cannot be correlated to the simpler spectrum of the field-free problem. From another viewpoint, it may be explained that though the second-order perturbation theory gives the energy correctly, even when $Z_1=0$, there is no convergent expansion of the eigenfunction in powers of $(Z-Z_1)$ unless $(Z-Z_1)$ is less than Z_1.

Since a box of radius R is used as an intermediary in the perturbation calculation of I (eventually $R\rightarrow\infty$), it is interesting to consider a Schrödinger equation which depends on an additional parameter R (as well as Z), and that has the same energy eigenvalues as the hydrogen atom when R becomes infinite. Schrödinger's equation for the hydrogen atom in an Einstein hypersphere of radius R has this form,[3] and the main point of the present paper is that a correct second-order perturbation calculation can be carried out with the solutions of the field-free equation in this case, as is shown in Sec. III. Though the perturbation calculation of Sec. III is even simpler than the calculation of I, this is because only s-electron wave functions are used in the hydrogen-atom problem, and in both calculations these wave functions are effectively the same. Calculations involving electrons with higher orbital momentum would probably be only slightly more complicated in the hypersphere than in ordinary space.

The possibility of defining a potential for the interaction between two electrons in a hypersphere, and so setting up a Schrödinger equation for the helium-type atom, has not been explored, but it must be admitted that it is questionable whether a simple perturbation calculation of the type considered is possible. One limitation may be pointed out at the start, since Hylleraas[4] has obtained a formula for the energy of helium-type atoms which is correct to fourth order:

$$E=-2Z^2+1.25Z-0.31488$$
$$+\frac{0.01980}{Z}-\frac{0.01004}{Z^2} \text{ (Rydbergs)}. \quad (2)$$

If the zero-order Hamiltonian has no dependence on e^2, while the perturbation is proportional to e^2, then the second-order perturbation must be the complete answer, since the only quantity that can be formed with the dimension of energy must be proportional to e^4. It follows that, at best, such a calculation can give only the first three terms of the expansion (2).

II. THE PERTURBATION CALCULATION WITH HYDROGENIC FUNCTIONS

The potential for the hydrogen-type atom has the form $-Ze^2/r$, and the energy of the ground state is given by the first equation of (1). A perturbation calculation can be made using zero-order solutions of the Schrödinger equation with a potential $-Z_1e^2/r$, and regarding the remainder of the potential, $-(Z-Z_1)e^2/r$, as the perturbation. It is easily seen that the zero-order energy and the first-order perturbation energy are the first and second terms, respectively, of the second equation of Eq. (1), so that only the second-order effect—corresponding to the last term—need be considered. The second-order perturbation due to discrete states is[5]

$$E_2(\text{discrete})=-\frac{e^4m}{\hbar^2}(Z-Z_1)^2 32\sum_{n=2}^{\infty}\frac{n^3(n-1)^{2n-3}}{(n+1)^{2n+3}}$$
$$=-0.169(Z-Z_1)^2\frac{e^4m}{\hbar^2}, \quad (3)$$

---

[3] E. Schrödinger, Commentationes Pontif. Acad. **2**, 321 (1938); Proc. Roy. Irish Acad. **46**, 9 (1940). See also L. Infeld and T. E. Hull, Revs. Modern Phys. **23**, 21 (1951); and A. F. Stevenson, Phys. Rev. **59**, 842 (1941).

[4] E. A. Hylleraas, Z. Physik **65**, 209 (1930); S. Chandrasekhar, Revs. Modern Phys. **16**, 301 (1944). The first three terms of this formula are the zero-, first-, and second-order effects, respectively. Hylleraas evaluated the second-order effect with a variational method, however, so that contributions from different angular parts of the wave function were not separated. D. Layzer [Ph.D. thesis, Harvard, 1950 (unpublished)] has given a "preliminary calculation" of the second-order energy of helium using hydrogenic wave functions and has obtained the value −0.4735 as compared to the value −0.31488 given by the third term of the Hylleraas formula; in getting this result, he used a difference of first-order energies in the denominators of his second-order perturbation, so the two values do not really correspond. The amount of work involved in this calculation is naturally very great. J. M. Gerhauser and F. A. Matsen have also used hydrogenic functions and have summed "the first five terms" of the second-order perturbation to obtain a constant term −0.2514 as compared to the value −0.31488 in formula (2) [J. Chem. Phys. **23**, 1359 (1955)]. P. Kessler has tried to evaluate the entire second-order perturbation by explicitly considering only the interactions with the first six terms of the $1s\,ns\,{}^1S$ sequence; he obtains a value −0.38 for the constant term [Compt. rend. **240**, 1314 (1955)].

[5] After obtaining these expressions, it was discovered that Y. Suguira had already given them as part of a check on his perturbation calculation for the energy of excited states of helium [Z. Physik **44**, 190 (1927)].

while the contribution of the continuum is

$$E_2(\text{continuum})$$

$$= -\frac{e^4m}{\hbar^2}(Z-Z_1)^2 32 \int_0^\infty \frac{\exp(4n\tan^{-1}n)n^3dn}{(n^2+1)^3[\exp(2\pi n)-1]}$$

$$= -0.329(Z-Z_1)^2\frac{e^4m}{\hbar^2}. \tag{4}$$

The continuum contributes almost twice as much as the discrete states. The coefficients were evaluated numerically, which accounts for the sum being slightly less than $\frac{1}{2}$; it seems fairly certain that if these expressions were evaluated rigorously, their sum would be exactly the third term of the second equation of Eq. (1).

An exact expansion of the wave function would have the form

$$R_{1s}(Z) = \mathbb{S}_n c_{ns} R_{ns}(Z_1), \tag{5}$$

where the sum on the right-hand side includes an integration over the continuum. The coefficients c_{ns} are rather complicated functions of Z_1 and $(Z-Z_1)$ which we have evaluated explicitly for the discrete states only. They are, of course, proportional to $(Z-Z_1)$ (when $n\neq 1$), but they have no convergent expansion in increasing powers of $(Z-Z_1)$ unless $|(Z-Z_1)|<Z_1$. When the condition is satisfied, the series is infinite, so that the first-order wave function is not the exact wave function even though it gives the exact energy in second order. As a result of this it might not seem likely that higher order perturbations would vanish for the hydrogen atom, because one could assume $Z_1<|(Z-Z_1)|$ and the wave function would be getting worse while still giving the exact energy. However, it does not seem to be possible to either prove or rule out the vanishing of higher order perturbations by an appeal to the variational principle, since a perturbation function that gives the energy correct to a given order will also give parts of higher order effects if used in a variational calculation, and these additional parts can insure that the energy is not less than the true energy. For instance, the first-order wave function could be considered in the limit where $Z_1 \ll |(Z-Z_1)|$, so that effectively the total energy is given entirely (and exactly) by the second-order perturbation. A variational calculation with this function would introduce terms of order $(Z-Z_1)^3$, and since the sign of $(Z-Z_1)$ can be positive or negative it might seem that these third-order effects would have to vanish to avoid an energy less than the true energy. However, this conclusion does not follow since positive fourth-order terms would also appear and these would bear the ratio $|(Z-Z_1)/Z_1|$ (>1) to the third-order effects, so there seems to be no simple way of showing anything definite about the higher order perturbations.[6]

III. THE PERTURBATION CALCULATION IN A HYPERSPHERE

The radial part of the Schrödinger wave equation for the hydrogen atom in an Einstein hypersphere of radius R has the following form[3]:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{R^2\sin^2x}\frac{d}{dx}\left(\sin^2x\frac{d\psi}{dx}\right)-\frac{l(l+1)}{R^2\sin^2x}\psi\right]$$

$$-\frac{Ze^2}{R}\cot x\psi = E\psi. \tag{6}$$

The independent variable x in this equation $(0\leqslant x\leqslant \pi)$ corresponds to the ratio r/R, where r is the radius vector of ordinary space. Replacing $\sin x$ by this ratio, and $\cos x$ by unity reduces (6) to the usual equation for the hydrogen atom. The energy eigenvalues of this equation are

$$E_n = (n^2-1)\frac{\hbar^2}{2mR^2}-\frac{Z^2}{2n^2}\frac{e^4m}{\hbar^2}. \tag{7}$$

For large R and small enough n, these energies approach the eigenvalues of the discrete states of the Schrödinger equation for the hydrogen atom in ordinary space. In contrast to the latter equation, however, the spectrum of (6) is completely discrete, even for positive energies. The eigenfunctions all remain good eigenfunctions when Z is made identically zero; there is no disappearance of an infinite set of discrete eigenfunctions for this particular value of Z, which occurs for the atom in ordinary space. The explicit form of the eigenfunctions of (6) can be determined with the factorization method.[3] They are normalized so that

$$\int_0^\pi R_{nl}^* R_{nl}\sin^2x dx = 1. \tag{8}$$

When $Z=0$, the eigenfunctions for s-states have a particularly simple form which makes them equivalent to the functions used in I.

$$R_{ns} = (2/\pi)^{\frac{1}{2}}[\sin(nx)/\sin x]. \tag{9}$$

Even when $Z=0$, however, the solutions for higher orbital angular momentum are somewhat more complicated than the solutions for a free particle in ordinary space (the form of the function depends on both n and l whereas in ordinary space the form of the solution is defined by l alone, as the spherical Bessel function of order l). However, a simplifying compensation is that they are composed of purely trigonometric functions, which can lead to more elementary integrations.

The total Coulomb potential in the hypersphere, $-(Ze^2/R)\cot x$, is regarded now as the perturbation and the energy calculated with the zero-order solu-

---

[6] An interesting possibility of summing second- and higher order perturbations rather easily is suggested by the method of A. Dalgarno and J. T. Lewis [Proc. Roy. Soc. (London) **A233**, 70 (1955)]. Unfortunately the method fails in this problem, as the function f defined by their Eq. (13) diverges too strongly at the origin.

tions (9). For the 1s ground state, (7) shows that the zero-order energy vanishes, and the ground state is a constant according to (9). From the matrix elements,

$$\int_0^\pi R_{ns}\left(-\frac{Ze^2}{R}\cot x\right)R_{1s}\sin^2 x dx=0 \qquad (n=1,3,5,\cdots) \tag{10}$$
$$=-\frac{4Ze^2n}{\pi R(n^2-1)} \qquad (n=2,4,6,\cdots),$$

it follows that the first-order energy also vanishes. The nonzero elements (10) are then squared, divided by their corresponding zero-order energy given by (7) (with $Z=0$), and summed to give the second-order energy.

$$E_2=-Z^2\frac{e^4m}{\hbar^2}\frac{32}{\pi^2}\sum_{n\text{ even}}\frac{n^2}{(n^2-1)^3}$$
$$=-\frac{Z^2}{2}\frac{e^4m}{\hbar^2}. \tag{11}$$

This is the correct energy of the ground state as given by (7), and the same as the value for the hydrogen atom in ordinary space.

In this case also, perturbation theory gives the exact energy eigenvalue in second order, but the first-order wave function is not the exact wave function. The latter has a series expansion in increasing powers of Z which is infinite, but convergent for all Z. Arguments based on the variational principle can be applied in this case to show that the third-order perturbation must vanish. Actually all the odd-order perturbations must vanish, since the Schrödinger equation (6) has the strange property of having the same eigenvalues and eigenfunctions whether the "Coulomb potential" is attractive or repulsive; i.e., if the sign of Z is changed the original equation can be recovered by introducing $(\pi-x)$ as a new independent variable. More explicitly, the third-order perturbation is

$$E_3=\sum_{n,m}{}'\frac{V_{1n}V_{nm}V_{m1}}{(E_1-E_n)(E_1-E_m)}-V_{11}\sum_n{}'\frac{V_{1n}V_{n1}}{(E_1-E_n)^2}, \tag{12}$$

where the elements V_{1n} are given by (10), and V_{mn} is a similar expression with R_{1s} replaced by R_{ms}. The V_{mn} are evidently zero if m and n are either both odd or both even, and from this it follows that E_3 vanishes, as already concluded. The form of the fourth-order perturbation is found to be[7]

$$E_4=\sum_{n,m,s}{}'\frac{V_{1n}V_{nm}V_{ms}V_{s1}}{(E_1-E_n)(E_1-E_m)(E_1-E_s)}$$
$$-V_{11}\sum_{n,s}{}'\frac{V_{1n}V_{ns}V_{s1}}{(E_1-E_n)^2(E_1-E_s)}$$
$$-V_{11}\sum_{n,s}{}'\frac{V_{1n}V_{ns}V_{s1}}{(E_1-E_n)(E_1-E_s)^2}$$
$$+(V_{11})^2\sum_n{}'\frac{V_{1n}V_{n1}}{(E_1-E_n)^3}-E_2\sum_n{}'\frac{V_{1n}V_{n1}}{(E_1-E_n)^2}. \tag{13}$$

In this case, only the first and last sums give nonzero contributions; the sums over n and s are over even integers starting with two, while m is summed over odd integers starting with three. It follows from (10) and (11) that the last sum of (13) has the value

$$\left(\frac{Z^2}{2}\frac{e^4m}{\hbar^2}\right)\left[\frac{Z^2e^4m^2R^2}{12\hbar^4}(\pi^2-6)\right]. \tag{13a}$$

The factor in square brackets is the sum of the squares of the amplitudes of the first-order perturbations of the wave function; it may be regarded as the ratio of the two contributions to the energy (7) for an effective n-value of about 1.5. If the hypersphere radius R is made large enough so that the first term is only a small percent of the second, then the zero-order wave function R_{1s} becomes a correspondingly small percent of the first-order perturbation wave function and the eigenfunction converges poorly. It is easy to evaluate the first sum in (13) if the summations over n and s are carried out before the integrals V_{nm} are evaluated by making use of the relations

$$\sin(ny)\sin(nx)=\tfrac{1}{2}[\cos n(x-y)-\cos n(x+y)],$$

and

$$\sum_{n\text{ even}}\frac{\cos(nt)}{n^2-1}=\tfrac{1}{2}-\tfrac{1}{4}\pi\sin t \quad 0<t<\pi$$
$$=\tfrac{1}{2}+\tfrac{1}{4}\pi\sin t \quad \pi<t<2\pi.$$

After making these summations and then carrying out the integrations, the first sum of (13) reduces to

$$-\frac{8Z^4e^8m^3R^2}{\hbar^6}\sum_{m\text{ odd}}{}'\frac{m^2}{(m^2-1)^3}. \tag{13b}$$

This is just the negative of (13a) and the fourth-order perturbation therefore vanishes. It seems quite likely that perturbations of all higher orders will also vanish.

ACKNOWLEDGMENTS

I would like to thank Dr. E. P. Wigner for suggesting this problem and discussing various aspects of it with me. I am also grateful to the Rockefeller Foundation for an award which made my stay at Princeton possible.

---

[7] The perturbation formulas given in *The Theory of Atomic Spectra* (reference 2) seem to give a formula for E_4 that differs from (13) by an additional factor of one-half in the last sum. Formula (13) agrees with the one given by K. A. Brueckner [Phys. Rev. **100**, 36 (1955)]; Brueckner's formulation of Rayleigh-Schrödinger perturbation theory is very convenient to use in getting explicit forms for these perturbations.