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

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The motion of a single electron in the electrostatic field of a nucleus is treated by the Rayleigh-Schrödinger perturbation method, the whole electrostatic potential being considered as the "perturbation." The contribution of the first approximation to the energy vanishes. The second approximation gives a finite ionization energy which is, however, incorrect numerically. The first approximation also vanishes for potentials $\sim r^{-n}$ with $0<n<3$ but the second approximation is finite only for $n=1$: it vanishes for $n>1$, and is infinite for $n<1$.

THERE are several instances in which simple approximation methods yield correct results even though the conditions for the applicability of those methods are not fulfilled. The best known example is the calculation of the Rutherford scattering by Born's approximation.[1] The calculation of the interaction of a large number of particles[2] by the Rayleigh-Schrödinger method is another example. In all these cases, the wave function given by the approximation method is quite meaningless. Thus, in the case of the interaction of many particles, the wave function obtained by the Rayleigh-Schrödinger perturbation calculation's second approximation represents a state in which, at most, two particles are in excited states while, actually, the average number of particles in excited states is, if the number of particles is large, a constant fraction of the number of particles. Nevertheless, the energy given by the second approximation of the Rayleigh-Schrödinger theory appears to be meaningful. One may gain the impression, from these examples, that the second approximation is always correct if it gives a finite result and that this applies particularly to the electrostatic interaction.

It may be of some interest to note, in this connection, that the aforementioned perturbation method yields, in second approximation, a finite result if applied to the problem of an electron moving in the attractive field of a nucleus. In fact, among all the potentials cr^{-n}, this applies only in the case of $n=1$. The starting point, in every case, is a free electron moving in a very large "box." Nevertheless, the numerical result of the perturbation calculation gives a grossly inaccurate result for the Coulomb potential. The wave function is not only inaccurate but virtually meaningless, but this fact does not entail an inaccurate energy value in the cases discussed in the first paragraph.

As the starting point we choose a spherical "box" with a radius R. The unperturbed spherically symmetric wave functions are, then,

$$\psi_n=(\sin\alpha_n r)/C_n r, \tag{1}$$

with the normalization constant C_n being equal to

$$C_n^2=(2\pi/\alpha_n)(\alpha_n R-\sin\alpha_n R\cos\alpha_n R). \tag{1a}$$

The α_n are determined by the boundary condition to be used at the surface of the box. The first approximation to the energy, because of an e^2/r potential, goes to zero with increasing R because the average distance of the particle from the origin is of the order R in the state ψ_1. The second approximation becomes

$$-E=\sum_2^\infty \frac{\left(\int \psi_1(e^2/r)\psi_n 4\pi r^2 dr\right)^2}{(\hbar^2/2m)(\alpha_n^2-\alpha_1^2)}. \tag{2}$$

The denominator contains the energy difference between the states ψ_n and ψ_1. Inserting (1) into (2),

$$\begin{aligned}-E&=\sum_2^\infty \frac{32\pi^2e^4m}{C_1^2C_2^2(\alpha_n^2-\alpha_1^2)\hbar^2}\left(\int_0^R \sin\alpha_1 r\,\sin\alpha_n r dr/r\right)^2\\ &=\sum_2^\infty \frac{8\pi^2e^4m}{C_1^2C_2^2(\alpha_n^2-\alpha_1^2)\hbar^2}\left(\int_0^R [\cos(\alpha_n-\alpha_1)r\right.\\ &\qquad\left.-\cos(\alpha_n+\alpha_1)r]dr/r\right)^2.\end{aligned} \tag{2a}$$

The integrals can be transformed by substituting $x=(\alpha_n-\alpha_1)r$ and $x=(\alpha_n+\alpha_1)r$, respectively.

$$\begin{aligned}-E&=\sum_2^\infty \frac{8\pi^2e^4m}{C_1^2C_2^2(\alpha_n^2-\alpha_1^2)\hbar^2}\\ &\qquad\times\left(\int_{(\alpha_n-\alpha_1)R}^{(\alpha_n+\alpha_1)R}(\cos x-1)\frac{dx}{x}\right)^2.\end{aligned} \tag{2b}$$

In order to define the unperturbed system completely, one has to give the value of the logarithmic derivative of the unperturbed wave functions (1) for $r=R$. We set $\rho\psi'(R)=\psi(R)$, which gives

$$\cot\alpha_n R=\frac{1}{\alpha_n\rho}+\frac{1}{\alpha_n R}. \tag{3}$$

This equation determines the values of α_n. We have two cases to distinguish: ρ is either infinite or finite. In the latter case, we assume that ρ remains the same as we increase the size of the "box," i.e., increase R to

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[1] See G. Wentzel, *Geiger-Scheel's Handbuch der Physik* (Springer, Berlin, 1933), Vol. 24, Part 1, p. 703.

[2] S. Watanabe, Z. Physik **112**, 159 (1939); **113**, 482 (1939); W. Macke, Z. Naturforsch. **A5**, 192 (1950).

infinity. If this is the case, $\alpha_n R \rightarrow n\pi$ as $R\rightarrow\infty$, no matter what the value of ρ is. In other words, the value of the expression (2b) converges to the same value as $R\rightarrow\infty$, no matter what the value of ρ is as long as ρ remains finite as $R\rightarrow\infty$. In this case, then, $C^2=2\pi R$, and

$$-E=\sum_2^\infty \frac{2e^4 m}{R^2(\alpha_n{}^2-\alpha_1{}^2)\hbar^2}\left(\int_{(n-1)\pi}^{(n+1)\pi}(1-\cos x)\frac{dx}{x}\right)^2$$

$$=\sum_2^\infty \frac{2e^4 m}{\pi^2\hbar^2(n^2-1)}(\mathrm{Ci}(n+1)\pi-\mathrm{Ci}(n-1)\pi)^2, \tag{4}$$

where Ci is the cosine integral

$$\mathrm{Ci}x=\int_0^x \frac{\cos x-1}{x}dx. \tag{4a}$$

As we anticipated, the second approximation (2) gives a finite value in this case. The sum (4) was evaluated numerically and gave

$$-E=0.1093e^4 m/\hbar^2, \tag{5}$$

as contrasted with the correct value of 0.5 $e^4 m/\hbar^2$. As a matter of fact, it is not surprising that the value (5) is so far from being correct. Although the first approximation correction to the nth characteristic value of the problem,

$$-\int_0^R \psi_n{}^2(e^2/r)4\pi r^2 dr=\frac{e^2}{R}\,\mathrm{Ci}(2n\pi), \tag{6}$$

vanishes for very large R, it vanishes only as $1/R$. Furthermore, it increases with n roughly like $\gamma+\ln 2\pi n$. The unperturbed energy differences, on the other hand, go to zero as R^{-2}. Hence, in first approximation, the energy of ψ_2 is actually lower than that of ψ_1 if R is large enough, and the same holds for a large number of other ψ_n. This reversal of the order of the first-order energy values shows again that the perturbation calculation cannot be given a direct physical interpretation in this case.

It remains to be seen whether the other boundary condition, $\psi'(R)=0$, gives more satisfactory results. In this case ψ_1 is a constant,

$$\psi_1=(3/4\pi R^3)^{\frac{1}{2}}, \tag{7}$$

while the other ψ are still given by (1). The equation defining α_n becomes

$$\alpha_n R=\tan\alpha_n R;\quad \alpha_1=0. \tag{8}$$

Denoting the solutions of this equation with $q_n=\alpha_n R=\tan q_n$, the integral

$$\int_0^R \psi_1(e^2/r)\psi_n 4\pi r^2 dr=6^{\frac{1}{2}}\frac{e^2}{R}\frac{(1+q_n{}^2)^{\frac{1}{2}}+(-)^n}{q_n{}^2} \tag{9}$$

can be expressed in closed form. For the ionization energy $-E$ one obtains

$$-E=\frac{12e^4 m}{\hbar^2}\sum_2^\infty \frac{[(1+q_n{}^2)^{\frac{1}{2}}+(-)^n]^2}{q_n{}^6}\sim 0.05\frac{e^4 m}{\hbar^2}, \tag{10}$$

i.e., a substantially smaller value than (5).

The reason it was at all possible to expect that the Rayleigh-Schrödinger perturbation method yield a correct expression for the energy is that this approximation method gives a power series expansion for the energy in terms of the perturbation parameter. A power series expansion in terms of the perturbation parameter $\lambda=e^2$ in fact does exist for the energy values of a particle in a Coulomb field: the coefficients of all powers of λ are zero, excepting that of the second power which is $m/2\hbar^2$ for the normal state. The reason that the perturbation method nevertheless gives an incorrect value in second approximation is that the energy is a function of the size R of the "box" which underlies the perturbation calculation. This function could well be of a form similar to

$$(e^4 m/2\hbar^2)[1-c\exp(-me^2R/\hbar^2)].$$

This expression gives the correct energy value for $R=\infty$ and has a convergent power series expansion in terms of e^2. However, this power series expansion does not converge term by term to the power series expansion of the energy for $R=\infty$ and, in particular, the coefficient of the e^4 term is too small by a factor $1-c$.

The fact that the Rayleigh-Schrödinger second approximation gives a definite value for the potential λ/r, but for no other potential of the form λr^{-n}, can be seen already by means of a dimensional argument. The dimension of λ is [energy][length]^n. Since the dimension of the matrix elements of the perturbation energy have the dimension of energy, they are proportional to R^{-n}. The square of the matrix element, divided by a typical difference of the unperturbed energy $\hbar^2/2mR^2$, is therefore proportional to R^{2-2n}. This gives a definite value only for $n=1$ but tends to infinity as R increases for $n<1$. It tends to zero if $n>1$.

The square integral of the first approximation to the wave function tends to infinity with increasing R for all $n<2$. In order to calculate it we have to divide the square of the matrix element with the square of a quantity of the order $\hbar^2/2mR^2$. Hence, the square integral will be proportional to R^{4-2n} and increase beyond all bounds also in the case of the Coulomb potential $n=1$. In fact, the first order wave function in our case is closely approximated by ψ_2 multiplied with a very large factor and is almost as poor an approximation to the real wave function as the unperturbed wave function ψ_1. The second approximation to the energy can be finite because it is not the expectation value of the first order wave function.