Application of the Rayleigh-Schrodinger Perturbation Theory to the Hydrogen Atom*

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The ground-state energy of a hydrogen atom is treated, according to Wigner, by the Rayleigh-Schrodinger perturbation method, where unperturbed wave functions correspond to a free particle in a spherical "box" of radius R. We have calculated the perturbed energy up to fifth order in $eZ$ and as the sign of each term from the second approximation on remains negative, we may conjecture that the perturbation series is divergent for $R \to \infty$. It also appears that in this way it will be difficult to obtain a Stieltjes series in the coupling constant $e^2$. We show that it is possible, by using the Rayleigh-Schrödinger-Löwdin variational energies, to obtain good values for the ground-state energy by adjusting conveniently the value of R. The Padé approximants give bad values for $R \to \infty$.

A energia do estado fundamental de um átomo de hidrogênio é tratada, como o fêz Wigner, pelo método de perturbação de Rayleigh-Schrodinger, as funções de onda não perturbadas correspondendo a uma partícula livre em uma "caixa" esférica de raio R. A energia perturbada foi calculada até a 5.ª ordem em $e^2$ e, como o sinal de cada termo a partir da 2.ª aproximação permanece negativo, pode-se conjecturar que a série de perturbação seja divergente para $R \to \infty$. Parece assim ser difícil se obter uma série de Stieltjes na constante de acoplamento $e^2$. Mostra-se que é possível, utilizando-se as energias variacionais de Rayleigh-Schrödinger-Löwdin, se obter bons valores para a energia do estado fundamental para isso ajustando-se convenientemente o valor de R. Por outro lado, os aproximantes de Padé dão maus valores para $R \to \infty$.

1. Introduction

Under the title above, Wigner discussed the Rayleigh-Schrodinger perturbation theory of the energy values of a hydrogen atom, in s-state and in its ground state, by considering the electrostatic potential as a perturbation and the unperturbed states as those corresponding to a particle in a spherical "box" of radius R.

He also made the observation that the zeroth and first order energies go to zero as $R \to \infty$, the second order going to a finite value and the higher ones going to infinity with an increasing power of R.

The absolute value of this second order energy is about five times smaller than the correct value given by the Balmer formula.

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In this paper we determine the perturbed energy eigenvalues of the fundamental state of the hydrogen atom up to fifth order in $e^2$. By numerical computation we found that in the perturbation series for the energy the sign of each term (with the exception of the unperturbed energy) is always negative, making it in our opinion improbable that the series is convergent for $R \to \infty$ (in Wigner's paper the possibility is discussed that, although each term in the perturbation series from the third order on in $e^2$ is more and more divergent for $R \to \infty$, the whole series could converge to the actual value as $R \to \infty$).

As is known, given a perturbation series for the wave function, as well as for the energy, even if these expansions do not make sense, there are two ways of getting reasonable answers to the problem. The first one is by the use of a variational principle where we take as trial functions the perturbed wave functions; in this case, the variational energy values are expressed as a function of the different terms of the energy expansion and of scalar products of the different terms of the wave function expansion in the coupling constant. The second one is by using Padé approximants.

The fact mentioned above about the constancy of sign in the different terms of the energy expansion, makes it improbable that the energy is a Stieltjes function in the coupling constant (or even the energy minus some of the first terms of the perturbation expansion).

If we take non-diagonal Padé approximants, we obtain either the value zero or infinity for $R \to \infty$. Now, for diagonal Padé approximants and $R \to \infty$, the $[1,1]$ approximant gives a value which is 1/25 of the exact value.

Therefore, in order to obtain a meaningful energy value, there remains the variational method, if we want to obtain results with the help of the terms of the Rayleigh-Schrödinger expansion.

It is easy to see that the variational energies go to zero when $R \to \infty$. Therefore it appears that is hopeless to try to obtain any reasonable result from a power series in $e^2$ for the energy and the wave function for this kind of problem.

We will prove in this article that if we put a bound system with a central potential in s-state in a spherical "box" of radius R, its ground state energy becomes smaller as R becomes larger.
Using this fact it is then possible to choose the radius $R$ in such a way that the variational energies become the smallest ones and give a better approximation to the energy values.

We have obtained in this manner values very close to the Balmer formula. Nevertheless it is very difficult to use a similar trick for the Padé approximants. It would be necessary to know better the analytic properties of the energy as a function of the coupling constant. Even so, it would be necessary to discover some inequalities which would help us to play with the radius $R$. Up to now it is an open problem.

2. The Perturbation Series

Let us consider the normalized eigenfunctions of a free particle in a spherical "box" of radius $R$,

$$\langle n \rangle = \psi_n = \sqrt{1/2\pi R} \frac{\sin k_n r}{r}$$

with

$$k_n = n\pi/R, \quad n = 1, 2, \ldots ;$$

the boundary condition imposed is $\psi(R) = 0$. We have the following values for the matrix elements of $1/r$:

$$\langle m | 1/r | n \rangle = \left\{ Ci \left[ (m - n)\pi \right] - Ci \left[ (m + n)\pi \right] - \log (m - n) + \log (m + n) \right\}/R, \quad m > n,$$

and

$$\langle m | 1/r | m \rangle = \left[ \log (2m\pi) + \gamma - Ci (2m\pi) \right]/R,$$

where

$$Ci(z) = \gamma + \log z + \int_0^z dt (\cos t - 1)/t$$

and $\gamma = 0.57721\ldots$ is Euler's constant.

The ground-state energy of the hydrogen atom as a perturbation series in a sphere of radius $R$ is given by

$$E = e_0 + e_1 + e_2 + \ldots$$

$$= \omega_0 \pi^2/2mR^2 + \omega_1 e^2/R + \omega_2 2me^4/\pi^2$$

$$+ \omega_3 (2m/\pi^2)^2 R e^6 + \omega_4 (2m/\pi^2)^3 R^2 e^8$$

$$+ \omega_5 (2m/\pi^2)^4 R^3 e^{10} + \ldots,$$
where we have used (1)-(5) in the Rayleigh-Schrodinger expansion for the energy.

By numerical computation, we obtained
\[
\begin{align*}
\omega_0 &= 1, & \omega_1 &= -2.4377, & \omega_2 &= -0.5398, \\
\omega_3 &= -0.3028, & \omega_4 &= -0.1491, & \omega_5 &= -0.047,
\end{align*}
\]
which shows that, from the second term on in (6), all the \(\omega_i (i = 1, 2, \ldots, 5)\) have a constant negative sign.

As was mentioned in the introduction, this fact makes it somewhat implausible that the series (6) could converge to the exact value for \(R \to \infty\).


Introducing in the expression \(E = \langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle\) the perturbation series \(\xi = \phi_0 + \phi_1 + \phi_2 + \ldots, \phi_0\) being the eigenfunction of the unperturbed problem while \(\phi_1, \phi_2, \ldots\) are higher order corrections (4, proportional to \(e^2\)), we obtain the following variational energies (see Lowdin\(^2\)), according to the substitution \(\phi = \phi_0, \phi = \phi_0 + \phi_1\) and \(\phi = \phi_0 + \phi_1 + \phi_2\), respectively:

\[
\begin{align*}
\varepsilon_0^* &= \varepsilon_0 + \varepsilon_1, \\
\varepsilon_1^* &= \varepsilon_0 + \varepsilon_1 + (\varepsilon_2 + \varepsilon_3)/(1 + \langle \phi_1 | \phi_1 \rangle), \\
\varepsilon_2^* &= \varepsilon_0 + \varepsilon_1 + [\varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \varepsilon_5 + \varepsilon_2 \langle \phi_1 | \phi_2 \rangle + \\
&\quad \langle \phi_2 | \phi_1 \rangle + (\varepsilon_2 + \varepsilon_3)\langle \phi_1 | \phi_1 \rangle][1 + \langle 1 + \langle \phi_1 | \phi_1 \rangle].
\end{align*}
\]

Now it is easy to see that \(\langle \phi_1 | \phi_1 \rangle \sim R^2, \langle \phi_1 | \phi_2 \rangle \sim R^3, \langle \phi_2 | \phi_2 \rangle \sim R^4, \ldots\). Therefore, we see from (6) and (8) that the variational energies \(\varepsilon_0^*, \varepsilon_1^*, \ldots\) go to zero for \(R \to \infty\) without giving a good approximation for the exact value of the ground-state energy of the hydrogen atom.

In order to obtain a useful approximation we shall demonstrate a simple theorem.
4. A Theorem

Let us consider the radial Schrödinger equations for s-waves in a central potential $V(r)$:

\begin{align}
    u_1'' + \left[ E - V(r) \right] u_1 &= 0, \quad (9) \\
    u_2'' + \left[ E - V(r) \right] u_2 &= 0, \quad (10)
\end{align}

where $u_1$ is the ground-state solution which corresponds to a sphere of radius $R_1$, while $u_2$ is the corresponding solution for a sphere of radius $R_2$. $E_1$ and $E_2$ are the associated energies.

Assume for definiteness that $R_1 < R_2$. We have the boundary conditions

\begin{equation}
    u_1(0) = u_2(0) = u_1(R_1) = u_2(R_2) = 0. \quad (11)
\end{equation}

Multiplying (9) by $u_2$ and (10) by $u_1$, subtracting the two resulting expressions and integrating from 0 to $R_1$, we obtain

\begin{equation}
    u_2(R_1)u_1'(R_1) = (E_2 - E_1) \int_0^{R_1} u_1(r)u_2(r) \, dr, \quad (12)
\end{equation}

where we have used the boundary condition (11).

Now as $u_1$ and $u_2$ have definite signs, which we will choose to be positive, and $u_1'(R_1) < 0$, it follows that the left hand side of (12) is negative. Therefore $E_2 < E_1$, since the integral in (12) is positive.

Thus, when we increase the radius of the sphere containing the hydrogen atom, its ground-state energy becomes smaller. Then we can write:

\begin{equation}
    E < E(R), \quad (13)
\end{equation}

where $E$ is the ground-state energy of our hydrogen atom in the whole space and $E(R)$ is the corresponding quantity in a sphere of radius $R$.

5. Use of the Variational Principle

We will see now that the variational expressions (8) for the energies, together with (13), will allow us to obtain very good approximate values for the ground-state energy of the hydrogen atom.
As \( E(R) < \varepsilon_i^*(R) \) for given \( R \), we have from (13) that

\[
E < \varepsilon_i^*(R).
\]  

(14)

This expression suggests taking for every \( i \) a value of \( R \) which makes \( \varepsilon_i^*(R) \) minimum and thus gives an approximation for \( E \). By introducing (6) and (7) into (8) we obtain the following minimum values of \( \varepsilon_i^*(R) \):

\[
\varepsilon_0^* = -0.30, \quad \varepsilon_1^* = -0.44, \quad \varepsilon_2^* = -0.48,
\]

in units of \( me^4 \). These values should be compared with the exact value \( E = -0.5 \). The corresponding values of \( R \) are 0.82, 0.85 and 0.94 in units of \( \pi^2/2me^2 \) (\( h = 1 \)).

We see that in this way the knowledge of the expansion (6) (and the corresponding one for the wave function) can give much information about the exact value of the ground-state energy of the hydrogen atom.

We wish to make the following two remarks: a) in order to obtain (14), it is not necessary to make use of the theorem discussed above since it is sufficient to take for \( r < R \) the trial function \( \phi_0 + \phi_1 + \phi_2 + \ldots \) with \( R \) as the variational parameter and zero for \( r > R \). Certainly we have the same expressions (8) and (15); b) it is interesting to notice that if we take more terms in the perturbation expansion for the trial function \( \phi \) we obtain variational energies which are improved as is seen in (15).

6. The Padé Approximants

From the expansion (6), with the values (7), and if the tendency of the \( \alpha_i \) to continue negative at higher order remains, it is improbable that the energy \( E \), as a function of the coupling constant \( e^2 \), is a Stieltjes function'.

Let us try to apply Padé approximants to \( E - E - \varepsilon_1 \). The non-diagonal approximants give either the value zero or infinity in the limit \( R \to \infty \). The \([1, 1] \) approximant gives also a bad result: its value is only 1125 of the exact one, although the sign is correct (and therefore this result is worse than the \( 2^{nd} \) order perturbation energy).

It would be interesting to extend the calculations from the sixth-order energy on, in order to see the corresponding signs.
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References