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## LETTER TO THE EDITOR

### Polynomial perturbation of a hydrogen atom

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**Abstract.** We study the ground state energy of the  $s$ -wave hydrogen atom with the polynomial perturbation  $2\lambda r + 2\lambda^2 r^2$ . The usual Rayleigh-Schrödinger perturbation series in powers of  $\lambda$  for the ground state energy has been shown to fail for  $\lambda < 0$ . We construct explicitly a perturbation series in powers of  $(-\lambda)^{-1/2}$  for  $\lambda < 0$  and show that it agrees well with the results of variational and Hill determinant calculations.

The ground state of the  $s$ -wave Hamiltonian for a hydrogen atom with a polynomial perturbation

$$H = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r} + 2\lambda r + 2\lambda^2 r^2 \quad (1)$$

has been studied by Killingbeck (1978). This Hamiltonian possesses the exact ground state energy and wavefunction given respectively by

$$E^{(0)} = -\frac{1}{2} + 3\lambda \quad (2a)$$

$$\psi^{(0)} = \exp(-r - \lambda r^2). \quad (2b)$$

Killingbeck (1978) has verified by explicit calculation that the first two terms in the Rayleigh-Schrödinger (RS) perturbation series in powers of  $\lambda$  for the ground state energy ( $E^{(0)} = \sum_n \varepsilon_n \lambda^n$ ) yield exactly equation (2a) and that the coefficients  $\varepsilon_2$  and  $\varepsilon_3$  are identically zero. Killingbeck (1980) has also checked numerically that all  $\varepsilon_n$  for  $3 \leq n \leq 16$  vanish. It would thus appear that the RS series for the ground state energy for all  $\lambda$  is given by equation (2a). However, although equations (2) continue to provide a mathematical solution to the Schrödinger equation for the Hamiltonian (1) for  $\lambda < 0$ , they cannot correspond to the physical ground state of the system since the wavefunction is no longer square integrable. Thus the RS series fails to give, for no apparent reason, the ground state of the system for  $\lambda < 0$ . This is true despite the fact that the potential remains confining for both positive as well as negative values of  $\lambda$ .

In this letter we begin by pointing out why one should in fact expect the RS series for the energy in powers of  $\lambda$  to break down for  $\lambda < 0$ . We then show that a perturbation series for the ground state energy in powers of  $|\lambda|^{-1/2}$  yields not only equation (2a) for  $\lambda > 0$  but also gives for  $\lambda < 0$  an expression which is different from equation (2a) and which agrees to a considerable degree of accuracy with the results of variational calculations as well as with numerical computations based on the method of Hill determinants (Biswas *et al* 1971, 1973) for all  $\lambda < -2$ .

Although the energy spectrum of the Hamiltonian (1) is discrete and extends to  $+\infty$  for both positive and negative non-zero values of  $\lambda$ , at  $\lambda = 0$  it collapses to the spectrum of the  $s$ -wave hydrogen atom, i.e. a discrete part lying between  $-\frac{1}{2}$  and 0 and a continuum extending all the way to  $+\infty$ . Thus the spectrum of the Hamiltonian (1) changes drastically as we go from positive to negative  $\lambda$  at  $\lambda = 0$ . It is therefore unrealistic to expect the ground state energy to be representable by a single analytic function, both for positive as well as negative  $\lambda$ . In addition, scaling arguments (Datta and Mukherjee 1980, Simon 1970) show that there must exist a convergent series expansion for the energy in powers of  $\lambda^{-1/2}$  valid for large  $\lambda$ ; consequently the same power series cannot be valid both for positive as well as negative  $\lambda$ .

We begin with two remarks. Firstly, the ground state of the system for  $\lambda > 0$  can be obtained by a simple translation of the ground state of the  $s$ -wave harmonic oscillator, and therefore it is not surprising that the ground state of the present problem admits an exact solution. To see this consider the Schrödinger equation for the  $s$ -wave harmonic oscillator in its ground state

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + 2\lambda^2 r^2\right) \exp(-\lambda r^2) = 3\lambda \exp(-\lambda r^2) \quad (3)$$

and the identity

$$\frac{1}{r} \left(-\frac{1}{2\lambda} \frac{d}{dr} - a\right) \exp[-\lambda(r+a)^2] = \exp[-\lambda(r+a)^2]. \quad (4)$$

If we now use the identity (4) with  $a = 0$  in equation (3), then perform the translation  $r \rightarrow r + 1/2\lambda$  and use the identity again, we obtain immediately the result given in equation (2).

Secondly, the ground state energy of the Hamiltonian (1) is bounded from below by

$$E^{(0)} \geq -1 \quad (5)$$

for all  $\lambda$ . This result is immediately evident provided the Hamiltonian (1) is written in the form

$$H = \left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r} - \frac{1}{2}\right) + 2(\lambda r + \frac{1}{2})^2 \quad (6)$$

and it is noticed that the second term on the RHS is non-negative for all  $\lambda$ . Equation (5) can be easily generalised to obtain lower bounds for the excited states.

We now construct the RS perturbation series for the ground state energy  $E^{(0)}$  for  $\lambda < 0$  in powers of  $(-\lambda)^{-1/2}$ . To this end, we transform to the variable  $r(-\lambda)^{-1/2}$  so that the Schrödinger equation becomes

$$(H_0 + V)\psi = -(E/\lambda)\psi \quad (7)$$

where

$$H_0 = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + 2r^2$$

$$V = -(-\lambda)^{-1/2}(1/r + 2r).$$

We write the ground state energy as

$$\frac{-E^{(0)}}{\lambda} = \sum_{n=0}^{\infty} [(-\lambda)^{-1/2}]^n E_n^{(0)} \quad (8)$$

where the unperturbed energy is  $E_0^{(0)} = 3$  and the corresponding eigenfunction is

$$|0\rangle = (2/\pi)^{3/4} \exp(-r^2).$$

It is evident that in the expression for the energy, the coefficient of the term linear in  $\lambda$  is  $-3$  which is clearly different from the corresponding term in the RS series for positive  $\lambda$ . The first-order correction to the ground state energy is immediately seen to be

$$E_1^{(0)} = 4(2/\pi)^{1/2}. \quad (9)$$

Thus there is a term proportional to  $(-\lambda)^{1/2}$  in the series for the ground state energy for  $\lambda < 0$  which was absent for  $\lambda > 0$ .

We now use the method of Dalgarno and Lewis (1955), suitably modified to take account of the fact that  $\langle 0|V|0\rangle \neq 0$ , to calculate the second-order correction. The ground state energy to this order  $E_2^{(0)}$  is given by

$$E^{(0)}(\lambda) = -3\lambda - 4(-2\lambda/\pi)^{1/2} + \frac{7}{2} - (16/\pi) \ln 2. \quad (10)$$

This perturbation result is expected to be good for  $\lambda$  large and negative. In fact, even for  $\lambda = -2$  it agrees with the numerically computed eigenvalues to an accuracy of about 2%. The series clearly breaks down for  $\lambda$  lying between  $-2$  and  $0$ .

We wish to point out that if a similar perturbative calculation is attempted for  $\lambda > 0$  using the transformation  $r \rightarrow (\lambda)^{-1/2}r$ , one recovers again the exact result  $E^{(0)} = -\frac{1}{2} + 3\lambda$ . Since in this case  $\langle 0|V|0\rangle = 0$ , it is possible to extend the method of Dalgarno and Lewis (1955) to calculate the third- and fourth-order contributions to the ground state energy and verify that these are identically zero. It is expected that higher-order contributions will also vanish identically.

An alternative approach is to use the terms  $(2\lambda r - r^{-1})$  in (1) as the formal perturbation; the energy series  $\sum \varepsilon_n$  has  $\varepsilon_0 = 3|\lambda|$  and

$$\varepsilon_1 = \left(\frac{8|\lambda|}{\pi}\right)^{1/2} \left[ \frac{\lambda}{|\lambda|} - 1 \right] \quad (11a)$$

$$\varepsilon_2 = \left(\frac{3}{2} - \frac{8}{\pi} \ln 2\right) + \frac{\lambda}{|\lambda|} \left(\frac{8}{\pi} \ln 2 - 2\right). \quad (11b)$$

The  $\varepsilon_n$  are non-analytic at  $\lambda = 0$ , but yield the correct *different*  $\lambda$  series for  $\lambda > 0$  and  $\lambda < 0$ .

To evaluate the eigenvalues more accurately in the region of  $\lambda$  not covered by the perturbation result, we now set up a variational scheme. We start by writing our Hamiltonian as

$$H = \tilde{H} + 4\lambda r \quad (12)$$

where

$$\tilde{H}\tilde{\psi}(r) = \left(-\frac{1}{2} - 3\lambda\right)\tilde{\psi}(r)$$

with

$$\tilde{\psi}(r) = \exp(-r + \lambda r^2) \quad \lambda < 0. \quad (13)$$

The use of  $\tilde{\psi}(r)$  as a trial function leads to an upper bound on the ground state energy given by

$$E^{(0)} \leq -\frac{1}{2} - 3\lambda - 6(-2\lambda)^{1/2} \frac{i^3 \operatorname{erfc}[(-2\lambda)^{-1/2}]}{i^2 \operatorname{erfc}[(-2\lambda)^{-1/2}]} \quad (14)$$

where the functions  $i^n \operatorname{erfc}(z)$  are repeated integrals of the error function as defined in Abramowitz and Stegun (1972). The above expression agrees with the perturbation result to order  $(-\lambda)^{1/2}$  for  $\lambda \rightarrow -\infty$ . It also tends to  $-\frac{1}{2}$ , the energy of the ground state of the hydrogen atom, as  $\lambda \rightarrow 0$ . These two features encourage us to use a set of trial functions given by

$$\psi(r) = \tilde{\psi}(r) \sum_{n=0}^{\infty} a_n r^n \quad (15)$$

in a linear variational calculation to obtain better upper bounds on the ground state energy for all negative  $\lambda$ .

In table 1 we list, for various negative values of  $\lambda$ , the results of second-order perturbation theory, variational calculations using the trial functions given in equation (15) and compare them with numerical computations of the ground state energy using the method of Hill determinants (Biswas *et al* 1971, 1973). The high degree of accuracy of the perturbation result for  $\lambda < -2$  is evident.

**Table 1.** Ground state energies for the Hamiltonian (1) for various negative values of  $\lambda$ . The Hill determinant results are converged to the last significant place, while the best available variational results have been quoted.

$\lambda$	Perturbation result <sup>†</sup>	Variational result	Hill determinant
-20 480	60 983.234 05	60 983.234 37	60 983.234 026 772
-2 560	7 518.489 34	7 518.489 27	7 518.489 264 276
-320	902.877 85	902.877 62	902.877 617 716
-40	99.784 77	99.784 077 55	99.784 077 513
-5	7.833 3	7.831 279 461 5	7.831 279 461 4
-2	1.456 3	1.452 916 838 14	1.452 916 838 11
-1	-0.221 7	-0.226 772 769 81	-0.226 772 769 86
-0.1	-0.739	-0.765 801	-0.765 826 903 96
-0.05	-0.59	-0.649 000	-0.649 106 898 05
-0.02	-0.42	-0.559 999 2	-0.559 999 998 3

$$\dagger E_0^{(0)} = 3, E_1^{(0)} = 3.191 538, E_2^{(0)} = -3.016 96 \times 10^{-2}.$$

We mention in passing that the perturbation series (10) exhibits an energy minimum at  $\lambda = -8/9\pi$  which is quite close to the minimum at  $\lambda = -0.28$  found in the Hill determinant calculations. Further, one can utilise the difference between the perturbation results and the Hill determinant results at the largest value of  $-\lambda$  to estimate  $E_3^{(0)}$  in equation (8). Such an exercise yields the value  $E_3^{(0)} \approx 0.4278 \times 10^{-2}$ . If we now use the geometric approximation (Killingbeck 1977), i.e.  $E_2^{(0)}(1 + E_3^{(0)}/\sqrt{-\lambda E_2^{(0)}})^{-1}$ , in place of  $E_2^{(0)}$  in the perturbation series, we obtain much better agreement with the energy eigenvalues. In particular, at  $\lambda = -1$  the perturbation result is now  $-0.2269$ .

We wish to conclude by remarking that similar perturbation expansions in  $|\lambda|^{-1/2}$  for the excited state energies exist and are currently being studied.

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