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Polynomial perturbation of a hydrogen-like atom

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Abstract. The ground state energy of a hydrogenic atom of nuclear charge Z , perturbed by a polynomial perturbation $2\lambda Zr + 2\lambda^2 r^2$, is calculated by means of a variational modification of Rayleigh–Schrödinger perturbation theory, which is effective for all negative λ .

1. Introduction

In a recent letter, Saxena and Varma (1982) used the method of Dalgarno and Lewis (1955) in a study of the ground state of a hydrogen atom in the field of a polynomial perturbation. Here, we treat a slightly generalised version of the same problem, with Hamiltonian in the usual atomic units (au)

$$H(Z, \lambda) = -\frac{1}{2}\nabla^2 - Z/r + 2\lambda Zr + 2\lambda^2 r^2. \quad (1)$$

A simple change of scale, $r \rightarrow r/Z$, shows that

$$H(Z, \lambda) = Z^2 H(\mu) \quad E(Z, \lambda) = Z^2 E(\mu) \quad (2)$$

where

$$H(\mu) = -\frac{1}{2}\nabla^2 - 1/r + \mu r + \frac{1}{2}\mu^2 r^2 \quad \mu = 2\lambda/Z^2. \quad (3)$$

As noted earlier by Killingbeck (1978, 1980), the exact solution and corresponding eigenvalue of $H(\mu)$

$$\psi(\mu) = \exp(-r - \frac{1}{2}\mu r^2) \quad E(\mu) = -\frac{1}{2} + \frac{3}{2}\mu \quad (4)$$

describe a *bound* ground-state only if $\mu \geq 0$, whereas, when $\mu < 0$, $\psi(\mu)$ is not square integrable. On the other hand, $\psi(-\mu)$ is an eigenfunction of $H(-\mu)$, *not* of $H(\mu)$. Since both $H(\mu)$ and $H(-\mu)$ approach a common limit as $\mu \rightarrow 0$, it is hardly surprising that Rayleigh–Schrödinger (RS) perturbation theory expansions in powers of μ cannot converge for both positive and negative μ . Killingbeck (1980) has verified convergence to very high order when $\mu \geq 0$.

The case $\mu < 0$ has been treated by Saxena and Varma (1982) by means of a perturbation expansion in powers of $|\mu|^{-1/2}$. This allows a unified treatment of both $\mu > 0$ and $\mu < 0$, but fails for small $|\mu|$. A variational extension of their procedure seems more appropriate. To this end, we rewrite $H(\mu)$ and $E(\mu)$

$$H(\mu) = k[H_0 + p H_1(q, s)] \quad E(\mu) = k\left(E_0 + \sum p^n E_n(q, s)\right) \quad (5a, b)$$

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where

$$H_0 = -\frac{1}{2}\nabla^2 + \frac{1}{2}r^2 \quad H_1(q, s) = -1/r + qr + sr^2. \quad (5c, d)$$

The *scale factor* k is to be chosen optimally for each μ , while p , q and s are related to k by means of

$$p = k^{-1/2} \quad q = \mu/k \quad s = (q^2 - 1)/2p \quad (6)$$

and p plays the role of formal RS expansion parameter. As we show below, even a simple zero-order treatment yields quite different results for $\mu \geq 0$ and $\mu < 0$.

2. Variational perturbation theory

We follow the procedure of Dalgarno and Stewart (1961), adopting as variational trial function

$$\psi_t = \psi_0 + \eta p \psi_1(q, s) \quad (7)$$

where ψ_0 is an eigenfunction of H_0 , $\psi_1(q, s)$ is the first-order correction due to $H_1(q, s)$ and is conveniently chosen orthogonal to ψ_0 , while η is a linear variational parameter. When η is chosen optimally for any given k , the optimised energy is given by the upper bound formula

$$E_u = k[E_0 + pE_1(q, s) + \eta p^2 E_2(q, s)] \quad (8)$$

where η satisfies the equation

$$p^2 \langle \psi_1 | \psi_1 \rangle \eta^2 + (1 - pE_3/E_2)\eta - 1 = 0. \quad (9)$$

Thus, provided that $p^2 \langle \psi_1 | \psi_1 \rangle$ is sufficiently small, equation (9) furnishes a theoretical justification for the so-called geometric approximation to the truncated RS expansion (actually the [2/1] Padé approximant)

$$E_G = E_u(\eta^*) \quad \eta^* = (1 - pE_3/E_2)^{-1}. \quad (10)$$

3. Solutions

The normalised ground-state solution of H_0 is simply

$$\psi_0 = (\frac{1}{2}\alpha)^{3/2} \exp(-\frac{1}{2}r^2) \quad \alpha = 2/\pi^{1/2} \quad (11)$$

and yields the following expectation values:

$$\langle r^{2n} \rangle_0 = \langle \psi_0 | r^{2n} | \psi_0 \rangle = (2n + 1)! / 2^{2n} n! \quad (n \geq 0) \quad (12a)$$

$$\langle r^{2n+1} \rangle_0 = \langle \psi_0 | r^{2n+1} | \psi_0 \rangle = (n + 1)! \alpha \quad (n \geq -1). \quad (12b)$$

Consequently, we have

$$E_0 = \frac{3}{2} \quad E_1(q, s) = (q - 1)\alpha + \frac{3}{2}s \quad (13)$$

and, in view of the form of $H_1(q, s)$, we write

$$\psi_1(q, s) = \psi_0(-f_{-1} + qf_1 + sf_2) \quad (14)$$

where $\psi_0 f_n$ is the well behaved solution of

$$(H_0 - E_0)(\psi_0 f_n) + (r^n - \langle r^n \rangle_0)\psi_0 = 0. \tag{15}$$

The integral identity (valid separately for n even and n odd)

$$\langle r^n \rangle_0 = \frac{1}{2}(n + 1)\langle r^{n-2} \rangle_0 \tag{16}$$

may now be used to show that, for all $n \geq 1$,

$$f_n = \frac{1}{2}(n + 1)f_{n-2} - (1/n)r^n. \tag{17}$$

Since we may clearly take $f_0 = 0$, we have at once from (17) that $f_2 = -\frac{1}{2}r^2$ and $f_1 = f_{-1} - r$, so that we need only f_{-1} or f_1 to complete the calculation of ψ_1 , E_2 and E_3 .

The function f_{-1} was obtained in a recent calculation of the effects of strong magnetic fields on a hydrogen atom (Cohen and Herman 1981). Its derivative may be expressed in closed form:

$$f'_{-1} = (\alpha r - 1 + e^{r^2} \operatorname{erfc} r)/r^2 \tag{18}$$

where $\operatorname{erfc} r$ is the complementary error function defined by (Abramowitz and Stegun 1964)

$$\operatorname{erfc} r = \alpha \int_r^\infty e^{-x^2} dx. \tag{19}$$

f_{-1} itself cannot be written simply in terms of elementary functions, but expansion of (18) followed by term-by-term integration yields two convergent infinite series:

$$f_{-1} = \sum_{n=0}^\infty \left(\frac{r^{2n+1}}{(2n+1)(n+1)!} - \frac{2^{2n+1}n!\alpha}{(2n+3)!} r^{2n+2} \right). \tag{20}$$

A variational approximation to f_{-1} was employed in our earlier work (Cohen and Herman 1981).

Several of the integrals which contribute to $\langle \psi_1 | \psi_1 \rangle$, E_2 and E_3 involve infinite sums, some of which may be useful in other connections, and are gathered for convenient reference in the appendix. Note that all necessary integrals were obtained analytically, with the sole exception of

$$V_1 = \int_0^1 \frac{x}{1+x^2} \ln(1+x) dx = 0.162\ 865\ 007. \tag{21}$$

Some comments on *methods* of solution of the perturbation equations, such as our equation (15) for f_{-1} , may be in order here. The method of Dalgarno and Lewis (1955) essentially involves a direct solution (i.e. it avoids the infinite sum-over-states inherent in the classic form of RS perturbation theory). Furthermore, as noted by Young and March (1958) and emphasised by Hirschfelder *et al* (1964), any perturbation equation may be reduced to an inhomogeneous linear differential equation of *first order* in the derivative (or gradient) of an appropriate function, in our case f_{-1} . The procedure is completely general, and is not restricted to perturbation equations of first order, but the first-order solution must be available in *explicit* form in order to proceed conveniently to second order. Our derived form of f_{-1} is too cumbersome to allow us to calculate the second-order correction to $\psi(\mu)$ in closed form, although a variational approximation of high accuracy can be obtained fairly easily.

An alternative method (Aharonov and Au 1979, Au and Aharonov 1979) achieves a similar reduction of order in the perturbation equations by first transforming to the *logarithm* of the perturbed wavefunction ψ . Unfortunately, this method rapidly encounters the same difficulties as the more direct procedure followed here.

4. Choice of scale factor: zero-order approximation

If the zero-order ψ_0 is itself regarded as a variational trial function, the upper bound energy is simply $k[E_0 + pE_1(q, s)]$ and may be optimised as a function of k . (Recall that p , q and s are all functions of k .) The optimal k and energy are then found to depend on both the sign and magnitude of μ , as follows:

$$\mu \geq -\frac{1}{9}\alpha^2: k_{\text{opt}}^{1/2} = \frac{1}{3}\alpha + (\frac{1}{9}\alpha^2 + \mu)^{1/2} \quad (22a)$$

$$E_{\text{opt}} = -\frac{1}{3}\alpha^2 + \frac{3}{2}\mu \quad (22b)$$

$$\mu < -\frac{1}{9}\alpha^2: k_{\text{opt}} = -\mu \quad (23a)$$

$$E_{\text{opt}} = -\frac{3}{2}\mu - 2\alpha\sqrt{-\mu}. \quad (23b)$$

Thus, for almost all negative μ , the optimised energy is obtained for what is the *asymptotic* scale factor ($k = -\mu$), whereas for positive μ the corresponding asymptotic scale factor is never optimal. In the following, we confine our attention to negative μ , since an exact solution is available for $\mu > 0$.

5. First-order calculations

After orthogonalising $\psi_1(q, s)$ of equation (14) to ψ_0 , we obtain exact expressions for $\langle \psi_1 | \psi_1 \rangle$, E_2 and E_3 in the form of polynomials in q and s . When $\mu < -\frac{1}{9}\alpha^2$ (so that $q = -1$, $s = 0$) we have explicitly

$$\langle \psi_1 | \psi_1 \rangle = (\frac{11}{2} - 4\pi) - \alpha^2(5 - \frac{4}{3}\pi^2 + 16V_1) \quad (24a)$$

$$E_2 = \frac{7}{2} - 4\alpha^2 \ln 2 \quad (24b)$$

$$E_3 = 2\alpha(5 - 4\pi - 8 \ln 2) - 4\alpha^3[1 - \frac{2}{3}\pi^2 + 2(\ln 2)^2 + 8V_1 - 2\beta(2)] \quad (24c)$$

where V_1 is given by equation (21) above, while $\beta(2)$ denotes *Catalan's constant* (cf Abramowitz and Stegun 1964)

$$\beta(2) = \sum_{k=0}^{\infty} (-1)^k / (2k+1)^2 = 0.915\,965\,594 \dots \quad (25)$$

Note that our E_2 reproduces the result of Saxena and Varma (1982) but that E_3 differs from their semi-empirical estimate in both magnitude and sign.

For smaller negative μ , the analogues of equations (24) contain more terms, and need not be given here.

It is now a straightforward calculation to determine the optimal values of η and the corresponding upper bounds to the energy. Table 1 contains a summary of our results.

Table 1. Calculated energies for negative λ .

$-\lambda$	Perturbation sums					
	First order	Second order	Third order	Upper bound	Geom approx	Accurate \ddagger
0.02 \dagger	-0.484 413	-0.532 232	-0.548 426	-0.554 022	-0.556 720	-0.560 000
0.05 \dagger	-0.574 413	-0.617 619	-0.634 460	-0.641 416	-0.645 218	-0.649 107
0.1	-0.709 253	-0.739 423	-0.752 935	-0.760 206	-0.763 206	-0.765 827
1	-0.191 538	-0.221 708	-0.225 981	-0.226 574	-0.226 686	-0.226 773
2	1.486 483	1.456 314	1.453 292	1.453 005	1.452 956	1.452 917
5	7.863 504	7.833 334	7.831 423	7.831 311	7.831 294	7.831 279
40	99.814 940	99.784 770	99.784 095	99.784 081	99.784 079	99.784 077
320	902.908 028	902.877 859	902.877 620	902.877 618	902.877 618	902.877 618

\dagger Optimised k from equation (22a).

\ddagger Hill determinant values from Saxena and Varma (1982).

6. Results and discussion

Perturbation sums through first, second and third orders, the variational upper bounds of equation (8), and the results of using the geometric approximation of equation (10), are compared with accurate results based on the method of Hill determinants (Biswas *et al* 1973) and quoted by Saxena and Varma (1982). There is satisfactory convergence for all values of λ (we have taken $Z = 1$ for simplicity of comparison with the earlier work), although higher-order corrections are evidently required to achieve greater accuracy for $\lambda = -0.02$ and $\lambda = -0.05$. However, our perturbation results are already much better than those of Saxena and Varma (1982) at these λ values, emphasising the essential role of the scale factor k . We note that at $\lambda = -0.02$, the RS parameter $p = 1.44$ results from the optimal choice of k (equation (22a)) whereas the asymptotic choice adopted by Saxena and Varma yields $p = 5$. The perturbation is clearly much smaller when the scale factor is chosen correctly.

It is probable that slightly better upper bounds can be obtained for small negative λ by a *simultaneous* variation of k and η , but such a choice cannot be guaranteed to improve either the convergence of the perturbation sums or the accuracy of the geometric approximation.

For larger negative λ , where our second-order perturbation results reproduce those of Saxena and Varma, the slight improvement obtained by including the third-order energy coefficient makes the perturbation results competitive in accuracy with refined variational calculations, and there seems little to be gained from an elaborate higher-order calculation.

Appendix. Some infinite sums

In the course of the present calculations, a number of infinite sums were evaluated by a variety of analytical procedures. In particular, we note the following:

$$S_1 = \sum_{n=1}^{\infty} \frac{(2n-1)!}{2^{2n}(n!)^2} = \ln 2 \tag{A1}$$

$$S_2 = \sum_{n=0}^{\infty} \frac{(2n)!}{2^{2n+1} n! (n+1)!} = 1 \quad (\text{A2})$$

$$S_3 = \sum_{n=0}^{\infty} \frac{(2n)!}{2^{2n} (2n+1)n! (n+1)!} = \pi - 2 \quad (\text{A3})$$

$$S_4 = \sum_{n=0}^{\infty} \frac{2^{2n+1} n! (n+1)!}{(2n+3)!} = 1 \quad (\text{A4})$$

$$S_5 = \sum_{n=0}^{\infty} \frac{2^{2n} (n!)^2}{(2n+3)!} = \frac{\pi^2}{8} - 1 \quad (\text{A5})$$

$$S_6 = \sum_{n=0}^{\infty} \frac{2^{2n-1} (n!)^2}{(2n+1)(2n+1)!} = \beta(2) \quad (\text{A6})$$

where $\beta(2)$ is Catalan's constant.

References

- Abramowitz M and Stegun I 1964 *Handbook of Mathematical Functions* (New York: Dover)
 Aharonov Y and Au C K 1979 *Phys. Rev. Lett.* **42** 1582-5
 Au C K and Aharonov Y 1979 *Phys. Rev. A* **20** 2245-50
 Biswas S N, Datta K K, Saxena R P, Srivastava P K and Varma V S 1973 *J. Math. Phys.* **14** 1190-5
 Cohen M and Herman G 1981 *J. Phys. B: At. Mol. Phys.* **14** 2761-7
 Dalgarno A and Lewis J T 1955 *Proc. R. Soc. A* **233** 70-4
 Dalgarno A and Stewart A L 1961 *Proc. Phys. Soc.* **77** 467-70
 Hirschfelder J O, Byers Brown W and Epstein S T 1964 *Adv. Quantum Chem.* **1** 255-374
 Killingbeck J 1978 *Phys. Lett.* **67A** 13-5
 ——— 1980 *J. Phys. A: Math. Gen.* **13** L393-5
 Saxena R P and Varma V S 1982 *J. Phys. A: Math. Gen.* **15** L149-53
 Young W H and March N H 1958 *Phys. Rev.* **109** 1854-5