

## Perturbative approach in the WKB analysis: Application to the Stark effect

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We have considered a perturbative approach in the WKB framework. Based on an expression for  $\partial E/\partial\lambda$ , we have calculated perturbatively the Stark energy shifts for two important systems, a particle in a one-dimensional power-law potential and the hydrogen atom. The results provide important insight into the properties of these systems. [S1050-2947(99)00904-X]

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### I. INTRODUCTION

The WKB approach [1] provides an important and useful description of the energy eigenvalues and wave functions of quantum systems. It is an eikonal expansion in powers of  $\hbar$ , and is therefore described as a quasiclassical or semiclassical approximation, and is particularly useful for the description of a particle in large quantum number states. It has provided [2,3] simple expressions for the energy eigenvalues for many potentials and for transmission across a potential barrier. It allows us to obtain [4] an expression for the electron density in a Thomas-Fermi atom and large- $\ell$  partial wave phase shifts [5] in electron-atom scattering. It has also been used to obtain simple expressions [2,6] for the expectation values and matrix elements of many operators. As such, the WKB approach is an important component in our understanding of the quantum properties of atoms, molecules, and nuclei.

There is one aspect of the WKB framework which has not received adequate attention. This concerns the analysis of perturbation effects in the WKB approach. Of course, one could use the WKB wave functions to evaluate the expectation values of the perturbing interaction, which may be taken to be the first-order perturbation in the energy. However, it is desirable that one has a systematic, self-contained procedure for the evaluation of the perturbed energy in the WKB approach, to successive orders in the perturbation.

Here we consider an expression for  $\partial E/\partial\lambda$  in the WKB framework where  $E$  is the energy and  $\lambda$  is a parameter in the Hamiltonian, which is analogous to the usual Feynman-Hellmann relation. We suggest that this expression can be expanded in powers of  $\lambda$  to obtain the energy correct to successive orders in the perturbation. We illustrate the idea by evaluating the Stark energy shift in two important systems. We calculate the second-order Stark energy and the dipolar polarizabilities for the one-dimensional power-law potentials. This result is relevant for the discussion of polarizabilities of long-chain molecules. We also calculate the first-, second-, and third-order Stark energy shifts in the hydrogen atom. These shifts should be particularly useful in the description of the Stark effect in an excited hydrogen atom. It is expected that this approach will be useful in the analysis of perturbative effects in other systems as well.

### II. PERTURBATIONS IN THE WKB ENERGIES

Consider a particle of mass  $m$  in a one-dimensional potential, described by the Hamiltonian

$$H = \frac{1}{2m} p^2 + V(\lambda, x), \quad (2.1)$$

where  $\lambda$  is a parameter. Then the WKB energies are given by

$$\int_{x_1}^{x_2} (2m)^{1/2} [E_n - V(\lambda, x)]^{1/2} dx = [n + c_1 + c_2] \hbar \pi, \quad (2.2)$$

$$n = 1, 2, \dots,$$

where  $x_1$  and  $x_2$  are the turning points,  $c_i = -\frac{1}{4}$  for the case where the potential varies linearly at the turning point, and  $c_i = 0$  for the case where the potential shoots up to infinity at the turning point. Taking the derivative of Eq. (2.2) with respect to  $\lambda$ , we get

$$p(x_2) \frac{\partial x_2}{\partial \lambda} - p(x_1) \frac{\partial x_1}{\partial \lambda} + \int_{x_1}^{x_2} \frac{1}{p} (2m) \left[ \frac{\partial E_n}{\partial \lambda} - \frac{\partial V}{\partial \lambda} \right] dx = 0, \quad (2.3)$$

$$p(x) = (2m)^{1/2} [E_n(\lambda) - V(\lambda, x)]^{1/2}. \quad (2.4)$$

Since  $p(x)$  vanishes at the turning points, this leads to

$$\frac{\partial E_n}{\partial \lambda} = \int_{x_1}^{x_2} \frac{1}{p} \left( \frac{\partial V}{\partial \lambda} \right) dx \bigg/ \int_{x_1}^{x_2} \frac{1}{p} dx. \quad (2.5)$$

This relation is essentially a WKB realization of the Feynman-Hellmann theorem. In particular, for

$$V(\lambda, x) = V_0(x) + \lambda V_1(x) \quad (2.6)$$

we have

$$\frac{\partial E_n}{\partial \lambda} = \int_{x_1}^{x_2} \frac{1}{p} V_1(x) dx \bigg/ \int_{x_1}^{x_2} \frac{1}{p} dx, \quad (2.7)$$

$$p = (2m)^{1/2} [E_n(\lambda) - V_0(x) - \lambda V_1(x)]^{1/2}. \quad (2.8)$$

One can then expand the various terms in powers of  $\lambda$  and deduce successive terms in the perturbed energy. For the leading term, we have

$$\left. \frac{\partial E_n}{\partial \lambda} \right|_{\lambda=0} = \int_{x_1}^{x_2} \frac{1}{p} V_1(x) dx \Big/ \int_{x_1}^{x_2} \frac{1}{p} dx, \quad (2.9)$$

$$p = (2m)^{1/2} [E_n(0) - V_0(x)]^{1/2}, \quad (2.10)$$

which gives us the first-order shift in the energy,

$$\delta E_n^{(1)} = \lambda \left( \frac{\partial E_n}{\partial \lambda} \right) \Big|_{\lambda=0}. \quad (2.11)$$

We can also obtain the first-order perturbation in the wave function. Starting from the expression

$$\psi(x) = \frac{1}{p^{1/2}} \sin \left[ \frac{1}{\hbar} \int_{x_1}^{x_2} p(x') dx' + c_1 \frac{\pi}{4} \right] \quad (2.12)$$

with  $p(x)$  given in Eq. (2.8), we get for the first-order perturbation in the wave function

$$\begin{aligned} \delta \psi^{(1)}(x) &= \frac{m\lambda V_1}{2p^{5/2}} \sin \left[ \frac{1}{\hbar} \int_{x_1}^x p(x') dx' + c_1 \frac{\pi}{4} \right] \\ &\quad - \frac{1}{2p^{1/2}\hbar} \int_{x_1}^x \frac{2m(\lambda V_1 - \delta E^{(1)})}{p(x'')} dx'' \\ &\quad \times \cos \left[ \frac{1}{\hbar} \int_{x_1}^x p(x') dx' + c_1 \frac{\pi}{4} \right]. \end{aligned} \quad (2.13)$$

Here the inadequacy of the WKB wave function at the turning points gets enhanced and the wave function is not normalizable, except for the special case  $c_1=0$ . It may be mentioned that for a particle in a box, with  $c_1=0$ , and a linear potential perturbation, Eq. (2.13) does give the correct first-order perturbation to the wave function. However, for the general case when  $c_1 \neq 0$ , it is not very useful.

Here we consider the perturbations in the energy, and illustrate the procedure for obtaining higher-order perturbation energies from Eqs. (2.7) and (2.8), by considering two important examples.

### III. STARK SHIFTS IN A POWER-LAW POTENTIAL

A charged particle in an even, power-law potential and an external electric field is governed by a potential

$$V(x) = A|x|^a + \lambda x, \quad A > 0, \quad a > 0, \quad (3.1)$$

where  $\lambda$  is proportional to the electric field. In this case, Eq. (2.7) can be written in the form

$$\frac{\partial E}{\partial \lambda} = \frac{I_1(\lambda) - I_1(-\lambda)}{I_0(\lambda) + I_0(-\lambda)}, \quad (3.2)$$

where

$$I_n(\lambda) = \int_0^{x_t} \frac{x^n dx}{[E - Ax^a - \lambda x]^{1/2}} \quad (3.3)$$

with  $x_t$  being the turning point,

$$E - Ax_t^a - \lambda x_t = 0. \quad (3.4)$$

We solve for the  $x_t$  iteratively and get

$$x_t = x_0 \left( 1 - \frac{\lambda}{Ea} x_0 + \dots \right), \quad (3.5)$$

$$x_0 = (E/A)^{1/a}. \quad (3.6)$$

The integral in Eq. (3.3) can now be obtained in powers of  $\lambda$ , and to order  $\lambda$  we get

$$\begin{aligned} I_n(\lambda) &= \frac{x_0^{n+1-a/2}}{A^{1/2}a} \left[ B \left( \frac{1}{2}, \frac{n+1}{a} \right) \left\{ 1 - (n+1-a/2) \frac{\lambda}{Ea} x_0 \right\} \right. \\ &\quad \left. - \lambda \frac{x_0^{1-a}}{2A} \left\{ B \left( -\frac{1}{2}, \frac{n+1}{a} \right) - B \left( -\frac{1}{2}, \frac{n+2}{a} \right) \right\} \right], \end{aligned} \quad (3.7)$$

where  $B(p, q)$  is the beta function,

$$B(p, q) = \frac{\Gamma(p) \Gamma(q)}{\Gamma(p+q)}, \quad (3.8)$$

with  $\Gamma(p)$  being the gamma function. Some of the details of the integration are given in Appendix A. Substituting this expression in Eq. (3.2), we get

$$\frac{\partial E}{\partial \lambda} = -\lambda \left( \frac{x_0^2}{E} \right) \frac{\Gamma \left( \frac{1}{2} + \frac{1}{a} \right) \Gamma \left( \frac{3}{a} \right)}{\Gamma \left( \frac{1}{a} \right) \Gamma \left( -\frac{1}{2} + \frac{3}{a} \right)}. \quad (3.9)$$

Since this expression is correct to order  $\lambda$ , using the expression for  $x_0$  in Eq. (3.6), we get

$$\left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} = 0, \quad (3.10)$$

$$\left. \frac{\partial^2 E}{\partial \lambda^2} \right|_{\lambda=0} = -E^{2/a-1} A^{-2/a} \frac{\Gamma \left( \frac{1}{2} + \frac{1}{a} \right) \Gamma \left( \frac{3}{a} \right)}{\Gamma \left( \frac{1}{a} \right) \Gamma \left( -\frac{1}{2} + \frac{3}{a} \right)}, \quad (3.11)$$

with the corresponding Stark energy shift

$$\delta E^{(2)} = -\frac{1}{2} \lambda^2 E^{2/a-1} A^{-2/a} \frac{\Gamma \left( \frac{1}{2} + \frac{1}{a} \right) \Gamma \left( \frac{3}{a} \right)}{\Gamma \left( \frac{1}{a} \right) \Gamma \left( -\frac{1}{2} + \frac{3}{a} \right)} \quad (3.12)$$

correct to order  $\lambda^2$ . With the energy shift related to the dipolar polarizability  $\alpha$  as  $\delta E^{(2)} = -(1/2)\alpha\lambda^2$ , the dipolar polarizability is given by

$$\alpha = E^{2/a-1} A^{-2/a} \frac{\Gamma\left(\frac{1}{2} + \frac{1}{a}\right) \Gamma\left(\frac{3}{a}\right)}{\Gamma\left(\frac{1}{a}\right) \Gamma\left(-\frac{1}{2} + \frac{3}{a}\right)}. \quad (3.13)$$

We can also express the polarizability in terms of the quantum number  $n$  in Eq. (2.2),

$$2 \int_0^{x_0} (E - Ax^a)^{1/2} dx = \frac{\pi \hbar}{(2m)^{1/2}} n, \quad n = 1, 2, \dots, \quad (3.14)$$

where we have ignored the additive constant  $c_1 + c_2$  in Eq. (2.2). Using the substitution

$$y = \frac{A}{E} x^a \quad (3.15)$$

one can carry out the integration and obtain [7] for the unperturbed energy,

$$E = n^{2a/(2+a)} A^{2/2+a} \left[ \frac{\hbar \pi a}{(2m)^{1/2}} \frac{\Gamma(3/2 + 1/a)}{\Gamma(1/2)\Gamma(1/a)} \right]^{2a/2+a}. \quad (3.16)$$

Substituting this in Eq. (3.13), we have for the polarizabilities  $\alpha$ ,

$$\alpha = n^{2(2-a)/(2+a)} A^{-4/2+a} g(a), \quad (3.17)$$

$$g(a) = \left[ \frac{\hbar \pi a}{(2m)^{1/2}} \frac{\Gamma(3/2 + 1/a)}{\Gamma(1/2)\Gamma(1/a)} \right]^{2(2-a)/(2+a)} \times \frac{\Gamma\left(\frac{1}{2} + \frac{1}{a}\right) \Gamma\left(\frac{3}{a}\right)}{\Gamma\left(\frac{1}{a}\right) \Gamma\left(-\frac{1}{2} + \frac{3}{a}\right)}. \quad (3.18)$$

It has been suggested [8] on the basis of numerical calculations that the polarizability  $\alpha$  for large  $n$  changes sign roughly at  $a \approx 6$ . Our closed analytical expressions in Eqs. (3.13) and (3.17) establish that  $\alpha$  vanishes at exactly  $a = 6$ , is positive for  $a < 6$ , and is negative for  $a > 6$ .

We can extend our calculations to the case of potentials with negative powers,

$$V(x) = -B|x|^{-b} + \lambda x, \quad B > 0, \quad b > 0. \quad (3.19)$$

Since the analysis is similar to that for the positive powers, we only present the results. We get

$$\alpha = |E|^{-1-2/b} B^{2/b} \frac{\Gamma\left(1 + \frac{1}{b}\right) \Gamma\left(\frac{3}{2} + \frac{3}{b}\right)}{\Gamma\left(\frac{1}{2} + \frac{1}{b}\right) \Gamma\left(1 + \frac{3}{b}\right)}, \quad (3.20)$$

$E =$

$$-n^{2b/(b-2)} B^{2/(2-b)} \left[ \frac{\hbar \pi b}{(2m)^{1/2}} \frac{\Gamma(1 + 1/b)}{\Gamma(1/2)\Gamma(1/b - 1/2)} \right]^{2b/(b-2)}. \quad (3.21)$$

This result is valid for  $0 < b < 2$ .

#### IV. STARK EFFECT IN THE HYDROGEN ATOM

As a second application of the WKB perturbative analysis, we consider the energy shifts in different states of the hydrogen atom, in the presence of a constant, external electric field. In this case the potential may be written as

$$V(r, z) = -\frac{1}{r} + \lambda z, \quad (4.1)$$

where  $\lambda$  is the electric field in the  $z$  direction, and we have used atomic units. The Stark shifts in the hydrogen atom are most conveniently described [2] in terms of parabolic coordinates,

$$u = r + z, \quad v = r - z, \quad \phi = \tan^{-1}(y/x). \quad (4.2)$$

In terms of parabolic coordinates, the Schrödinger equation separates into equations

$$\frac{d^2}{du^2} f_1 + \frac{1}{u} \frac{df_1}{du} + \left( \frac{1}{2} E - \frac{m^2}{4u^2} - \frac{1}{4} \lambda u \right) f_1 = -\frac{\beta_1}{u} f_1, \quad (4.3)$$

$$\frac{d^2}{dv^2} f_2 + \frac{1}{v} \frac{df_2}{dv} + \left( \frac{1}{2} E - \frac{m^2}{4v^2} + \frac{1}{4} \lambda v \right) f_2 = -\frac{\beta_2}{v} f_2, \quad (4.4)$$

$$\beta_1 + \beta_2 = 1, \quad (4.5)$$

where  $\beta_1$  and  $\beta_2$  are the separation constants. These equations are similar to the equation in the two-dimensional polar radial coordinate, for which there are no Langer-type corrections. The corresponding WKB equations for the bound states are

$$\int \left[ -\frac{1}{2} \left| E \right| + \frac{\beta_1}{u} - \frac{m^2}{4u^2} + au \right]^{1/2} du = (n_1 + 1/2) \pi, \quad (4.6)$$

$$\int \left[ -\frac{1}{2} \left| E \right| + \frac{\beta_2}{v} - \frac{m^2}{4v^2} - av \right]^{1/2} dv = (n_2 + 1/2) \pi, \quad (4.7)$$

where  $a = -\lambda/4$ . We need to solve these equations for the energy  $E$  subject to the condition in Eq. (4.5), i.e.,  $\beta_1 + \beta_2 = 1$ . However, it is more convenient to treat  $E$  as a fixed parameter, solve for  $\beta_1$  and  $\beta_2$  in terms of  $E$ , and then determine  $E$  by requiring that  $\beta_1$  and  $\beta_2$  satisfy the condition  $\beta_1 + \beta_2 = 1$ . We solve for  $\beta_1$  and  $\beta_2$  as perturbation series in  $a$ , and hence obtain the perturbation series for  $E$ .

To start with, the unperturbed values of  $\beta_{10}$  and  $\beta_{20}$  are obtained from Eqs. (4.6) and (4.7) by evaluating the integrals for  $a = 0$ . The integrals are standard and give

$$\beta_{i0} = (2|E|)^{1/2} \left( n_i + \frac{1}{2} \left| m \right| + \frac{1}{2} \right). \quad (4.8)$$

For obtaining the higher-order terms, we take the derivatives of Eqs. (4.6) and (4.7) with respect to  $a$ . Since the integrand vanishes at the turning points, we get

$$\frac{\partial \beta_1}{\partial a} = -\frac{J_1(a)}{J_{-1}(a)}, \quad (4.9)$$

$$J_n(a) = \int \frac{1}{p_1} u^n du, \quad (4.10)$$

$$p_1 = \left[ -\frac{1}{2} |E| + \frac{\beta_1}{u} - \frac{m^2}{4u^2} + au \right]^{1/2}. \quad (4.11)$$

We carry out the integrations as a series in powers of  $a$ , and obtain

$$\begin{aligned} \frac{\partial \beta_1}{\partial a} = & -\left[ \frac{3}{2} \frac{\beta_1^2}{\epsilon^2} - \frac{m^2}{4\epsilon} \right] - a \left[ 13 \frac{\beta_1^3}{\epsilon^4} - 3 \frac{\beta_1 m^2}{\epsilon^3} \right] \\ & - a^2 \left[ \frac{2211}{16} \frac{\beta_1^4}{\epsilon^6} - \frac{651}{16} \frac{\beta_1^2 m^2}{\epsilon^5} + \frac{75}{64} \frac{m^4}{\epsilon^4} \right], \end{aligned} \quad (4.12)$$

where  $\epsilon = |E|$ . Some of the details of the integrations are given in Appendix B. We now expand the two sides of Eq. (4.12) in powers of  $a$ , and equate terms of the same order. The leading term gives

$$\left. \frac{\partial \beta_1}{\partial a} \right|_{a=0} = -\left[ \frac{3}{2} \frac{\beta_{10}^2}{\epsilon^2} - \frac{m^2}{4\epsilon} \right]. \quad (4.13)$$

The terms first order in  $a$  give

$$\left. \frac{\partial^2 \beta_1}{\partial a^2} \right|_{a=0} = -\left[ 13 \frac{\beta_{10}^3}{\epsilon^4} - 3 \frac{\beta_{10} m^2}{\epsilon^3} + 3 \frac{\beta_{10}}{\epsilon^2} \beta'_{10} \right], \quad (4.14)$$

where  $\beta'_{10}$  represents the derivative of  $\beta_1$  at  $a=0$ . Using the expression for the first derivative given in Eq. (4.13), we get

$$\left. \frac{\partial^2 \beta_1}{\partial a^2} \right|_{a=0} = -\left[ \frac{17}{2} \frac{\beta_{10}^3}{\epsilon^4} - \frac{9}{4} \frac{\beta_{10} m^2}{\epsilon^3} \right]. \quad (4.15)$$

The terms which are of order  $a^2$  in Eq. (4.12) give

$$\begin{aligned} \left. \frac{\partial^3 \beta_1}{\partial a^3} \right|_{a=0} = & -2 \left[ \frac{2211}{16} \frac{\beta_{10}^4}{\epsilon^6} - \frac{651}{16} \frac{\beta_{10}^2 m^2}{\epsilon^5} + \frac{75}{64} \frac{m^4}{\epsilon^4} \right. \\ & \left. + \frac{3}{2} \frac{\beta_{10}'^2}{\epsilon^2} - 3 \frac{\beta_{10}' m^2}{\epsilon^3} + 39 \frac{\beta_{10}^2 \beta_{10}'}{\epsilon^4} + \frac{3}{2} \frac{\beta_{10} \beta_{10}''}{\epsilon^2} \right], \end{aligned} \quad (4.16)$$

where  $\beta_{10}''$  represents the second derivative of  $\beta_1$  at  $a=0$ . Using the relations in Eqs. (4.13) and (4.15), we get

$$\left. \frac{\partial^3 \beta_1}{\partial a^3} \right|_{a=0} = -2 \left[ \frac{1125}{16} \frac{\beta_{10}^4}{\epsilon^6} - \frac{387}{16} \frac{\beta_{10}^2 m^2}{\epsilon^5} + \frac{33}{64} \frac{m^4}{\epsilon^4} \right]. \quad (4.17)$$

Collecting these terms, we have for  $\beta_1$  correct to order  $a^3$ ,

$$\begin{aligned} \beta_1 = & \beta_{10} - \left[ \frac{3}{2} \frac{\beta_{10}^2}{\epsilon^2} - \frac{m^2}{4\epsilon} \right] a - \left[ \frac{17}{2} \frac{\beta_{10}^3}{\epsilon^4} - \frac{9}{4} \frac{\beta_{10} m^2}{\epsilon^3} \right] \frac{a^2}{2} \\ & - \left[ \frac{1125}{16} \frac{\beta_{10}^4}{\epsilon^6} - \frac{387}{16} \frac{\beta_{10}^2 m^2}{\epsilon^5} + \frac{33}{64} \frac{m^4}{\epsilon^4} \right] \frac{a^3}{3}. \end{aligned} \quad (4.18)$$

The corresponding expression for  $\beta_2$  is

$$\begin{aligned} \beta_2 = & \beta_{20} + \left[ \frac{3}{2} \frac{\beta_{20}^2}{\epsilon^2} - \frac{m^2}{4\epsilon} \right] a - \left[ \frac{17}{2} \frac{\beta_{20}^3}{\epsilon^4} - \frac{9}{4} \frac{\beta_{20} m^2}{\epsilon^3} \right] \frac{a^2}{2} \\ & + \left[ \frac{1125}{16} \frac{\beta_{20}^4}{\epsilon^6} - \frac{387}{16} \frac{\beta_{20}^2 m^2}{\epsilon^5} + \frac{33}{64} \frac{m^4}{\epsilon^4} \right] \frac{a^3}{3}. \end{aligned} \quad (4.19)$$

We now add these terms and impose the condition in Eq. (4.5) that  $\beta_1 + \beta_2 = 1$ . Using the relations

$$\beta_{10} + \beta_{20} = n(2\epsilon)^{1/2}, \quad n = n_1 + n_2 + |m| + 1, \quad (4.20)$$

$$\beta_{10} - \beta_{20} = (n_1 - n_2)(2\epsilon)^{1/2}, \quad (4.21)$$

we get

$$\begin{aligned} \frac{1}{n(2\epsilon)^{1/2}} = & 1 - 6 \frac{(n_1 - n_2)}{(2\epsilon)^{3/2}} a \\ & - [17n^2 + 51(n_1 - n_2)^2 - 9m^2] \frac{1}{(2\epsilon)^3} a^2 \\ & - (n_1 - n_2) [1125n^2 + 1125(n_1 - n_2)^2 \\ & - 387m^2] \frac{1}{(2\epsilon)^{9/2}} \frac{2a^3}{3}. \end{aligned} \quad (4.22)$$

We iterate and invert this relation to get

$$\begin{aligned} E = & -\frac{1}{2n^2} + \frac{3}{2}(n_1 - n_2)n\lambda \\ & - \frac{1}{16} [17n^2 - 3(n_1 - n_2)^2 - 9m^2] n^4 \lambda^2 \\ & + \frac{1}{32} (n_1 - n_2) [69n^2 - 3(n_1 - n_2)^2 + 33m^2] n^7 \lambda^3, \end{aligned} \quad (4.23)$$

where we have used  $E = -\epsilon$  and  $a = -\lambda/4$ ,  $\lambda$  being the strength of the electric field.

It is interesting to compare our WKB results with the exact results [2],

$$\begin{aligned} E = & -\frac{1}{2n^2} + \frac{3}{2}(n_1 - n_2)n\lambda \\ & - \frac{1}{16} [17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19] n^4 \lambda^2 \end{aligned} \quad (4.24)$$

to order  $\lambda^2$ . The first two terms are the same. It may be noted that the first term when calculated in the WKB approach with spherical coordinates requires a correction in the angular momentum term, the Langer correction, to get the exact

expression for the hydrogenic energy. However, with the use of parabolic coordinates, the equations are similar to the equation in two-dimensional polar coordinates and give the exact energy expression. What is surprising is that the WKB analysis gives the exact results for the second term as well. For the term which is quadratic in  $\lambda$ , only the constant term 19 is missing in the WKB expression. Consequently for the ground state, the WKB term quadratic in  $\lambda$  is smaller in magnitude by a factor of about 2. For the first excited state it is smaller by about 25% and rapidly approaches the exact value for higher excited states. The WKB perturbative approach provides a simple expression for the third-order term as well.

## V. CONCLUSIONS

We have demonstrated that a perturbative approach in the WKB analysis is a powerful technique. Our approach is based on an expression for  $\partial E/\partial\lambda$ , similar to the usual Feynman-Hellmann theorem. We have used this expression to develop a perturbation series for the Stark energy shift in two important systems. We have calculated the second-order energy shift and hence the polarizability for a particle in a one-dimensional power-law potential. We find that the polarizability vanishes when the power is exactly equal to 6, being positive for powers less than 6 and negative for powers greater than 6. These results could be useful in the analysis of polarizabilities of long-chain molecules. These molecular polarizabilities have been analyzed in terms of a particle in a box [9] It may be useful to consider the higher-order polarizabilities of the molecules in terms of power-law potentials.

We have also calculated the Stark energy for the hydrogen atom to third order in the electric field. It is found that the first-order term agrees with the exact result and the second-order term is close to the exact result for excited states. Our third-order term is a new result.

We expect that the perturbative approach in the WKB analysis would be useful in many other situations.

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## APPENDIX A

For evaluating the integral

$$I_n(\lambda) = \int_0^{x_t} \frac{x^n dx}{[E - Ax^a - \lambda x]^{1/2}} \quad (\text{A1})$$

we note that

$$E = Ax_t^a + \lambda x_t. \quad (\text{A2})$$

Substituting this expression for  $E$ , and using the variable  $u$ ,

$$u = x/x_t, \quad (\text{A3})$$

we get

$$I_n(\lambda) = A^{-1/2} x_t^{n+1-a/2} \int_0^1 u^n (1-u^a)^{-1/2} \times \left[ 1 + \lambda A^{-1} x_t^{1-a} \left( \frac{1-u}{1-u^a} \right) \right]^{-1/2} du. \quad (\text{A4})$$

Expanding in powers of  $\lambda$  and keeping the first two terms leads to

$$I_n(\lambda) = A^{-1/2} x_t^{n+1-a/2} \int_0^1 u^n [(1-u^a)^{-1/2} - \frac{1}{2} \lambda A^{-1} x_t^{1-a} \times (1-u)(1-u^a)^{-3/2}] du. \quad (\text{A5})$$

Substituting

$$z = u^a, \quad (\text{A6})$$

we get

$$I_n(\lambda) = A^{-1/2} x_t^{n+1-a/2} a^{-1} \int_0^1 z^{(n+1-a)/a} \times [(1-z)^{-1/2} - \frac{1}{2} \lambda A^{-1} x_t^{1-a} \times (1-z^{1/a})(1-z)^{-3/2}] dz. \quad (\text{A7})$$

This is related to beta functions,

$$I_n(\lambda) = A^{-1/2} x_t^{n+1-a/2} a^{-1} \left[ B\left(\frac{1}{2}, \frac{n+1}{a}\right) - \frac{1}{2} \lambda A^{-1} x_t^{1-a} \left\{ B\left(-\frac{1}{2}, \frac{n+1}{a}\right) - B\left(-\frac{1}{2}, \frac{n+2}{a}\right) \right\} \right], \quad (\text{A8})$$

$$B(p, q) = \frac{\Gamma(p)\Gamma(q)}{\Gamma(p+q)}. \quad (\text{A9})$$

We also substitute for  $x_t$  the expression in Eq. (3.5) correct to order  $\lambda$ , to get

$$I_n(\lambda) = A^{-1/2} x_0^{n+1-a/2} a^{-1} \left[ B\left(\frac{1}{2}, \frac{n+1}{a}\right) \left\{ 1 - (n+1-a/2) \frac{\lambda}{Ea} x_0 \right\} - \frac{1}{2} \lambda A^{-1} x_0^{1-a} \left\{ B\left(-\frac{1}{2}, \frac{n+1}{a}\right) - B\left(-\frac{1}{2}, \frac{n+2}{a}\right) \right\} \right] \quad (\text{A10})$$

correct to order  $\lambda$ .

## APPENDIX B

The integral  $J_n(a)$  may be written in the form

$$J_n(a) = a^{-1/2} \int \frac{u^{n+1} du}{[(u-u_1)(u_2-u)(u_3-u)]^{1/2}}, \quad (\text{B1})$$

where

$$u_1 u_2 u_3 = \frac{m^2}{4a}, \quad (\text{B2})$$

$$u_1 u_2 + u_2 u_3 + u_3 u_1 = \frac{\beta_1}{a}, \quad (\text{B3})$$

$$u_1 + u_2 + u_3 = \frac{\epsilon}{2a}. \quad (\text{B4})$$

Here,  $u_1$  and  $u_2$  are the usual turning points and  $u_3$  is the new zero introduced by the  $au$  term. We can solve for  $u_3$  iteratively by using the relation for the zeros,

$$u = \frac{\epsilon}{2a} - \left(\frac{\beta_1}{a}\right) \frac{1}{u} + \left(\frac{m^2}{4a}\right) \frac{1}{u^2}. \quad (\text{B5})$$

Since  $u_3$  is very large for  $a \rightarrow 0$ , we obtain by iteration

$$u_3 = \frac{\epsilon}{2a} - \frac{2\beta_1}{\epsilon} - \frac{a}{\epsilon^2} \left( \frac{8\beta_1^2}{\epsilon} - m^2 \right) + \dots \quad (\text{B6})$$

correct to the first three orders in  $a$ . Using the relations in Eqs. (B2) and (B3), we get

$$u_1 u_2 = \frac{m^2}{2\epsilon} + a \left( \frac{2\beta_1 m^2}{\epsilon^3} \right) + a^2 \left( \frac{16\beta_1^2 m^2}{\epsilon^5} - \frac{m^4}{\epsilon^4} \right), \quad (\text{B7})$$

$$u_1 + u_2 = \frac{2\beta_1}{\epsilon} + a \left( \frac{8\beta_1^2}{\epsilon^3} - \frac{m^2}{\epsilon^2} \right) + a^2 \left( \frac{64\beta_1^3}{\epsilon^5} - \frac{12\beta_1 m^2}{\epsilon^4} \right), \quad (\text{B8})$$

correct to the first three orders in  $a$ .

For evaluating the integral in Eq. (B1), we note that  $u_3$  is large for  $a \rightarrow 0$ , and expand  $(u_3 - u)^{-1/2}$  in inverse powers of  $u_3$ :

$$J_n(a) = a^{-1/2} \int_{u_1}^{u_2} \frac{u^{n+1} du}{[(u-u_1)(u_2-u)]^{1/2}} u_3^{-1/2} \left( 1 + \frac{1}{2u_3} u + \frac{3}{8u_3^2} u^2 + \dots \right). \quad (\text{B9})$$

One can write the integral in the form

$$J_n(a) = a^{-1/2} u_3^{-1/2} \left( K_{n+1} + \frac{1}{2u_3} K_{n+2} + \frac{3}{8u_3^2} K_{n+3} + \dots \right), \quad (\text{B10})$$

where

$$K_m = \int \frac{u^m du}{[(u-u_1)(u_2-u)]^{1/2}}. \quad (\text{B11})$$

In particular we have

$$K_m = \pi \quad \text{for } m=0,$$

$$= \frac{1}{2} \pi (u_1 + u_2) \quad \text{for } m=1,$$

$$= \pi \left[ \frac{3}{8} (u_1 + u_2)^2 - \frac{1}{2} u_1 u_2 \right] \quad \text{for } m=2,$$

$$= \pi \left[ \frac{5}{16} (u_1 + u_2)^3 - \frac{3}{4} (u_1 + u_2) u_1 u_2 \right] \quad \text{for } m=3,$$

$$= \pi \left[ \frac{35}{128} (u_1 + u_2)^4 - \frac{15}{16} (u_1 + u_2)^2 u_1 u_2 + \frac{3}{8} u_1^2 u_2^2 \right]$$

$$\text{for } m=4. \quad (\text{B12})$$

Using Eqs. (B10), (B11), (B12), we obtain for  $\partial\beta_1/\partial a$  in Eq. (4.9),

$$\begin{aligned} \frac{\partial\beta_1}{\partial a} &= -\frac{J_1(a)}{J_{-1}(a)} \\ &= -\left[ \frac{3}{8} (u_1 + u_2)^2 - \frac{1}{2} u_1 u_2 \right] - \frac{1}{u_3} \left[ \frac{1}{16} (u_1 + u_2)^3 \right. \\ &\quad \left. - \frac{1}{4} (u_1 + u_2) u_1 u_2 \right] \\ &\quad - \frac{1}{u_3^2} \left[ \frac{35}{1024} (u_1 + u_2)^4 - \frac{19}{128} (u_1 + u_2)^2 u_1 u_2 + \frac{3}{64} u_1^2 u_2^2 \right], \end{aligned} \quad (\text{B13})$$

where we have expanded in powers of  $1/u_3 \sim a$  and retained the three leading terms. Finally, substituting the expressions for  $u_3$ ,  $u_1 u_2$ , and  $u_1 + u_2$  given in Eqs. (B6), (B7), (B8), and expanding in powers of  $a$ , we get

$$\begin{aligned} \frac{\partial\beta_1}{\partial a} &= -\left[ \frac{3}{2} \frac{\beta_1^2}{\epsilon^2} - \frac{m^2}{4\epsilon} \right] \\ &\quad - a \left[ 13 \frac{\beta_1^3}{\epsilon^4} - 3 \frac{\beta_1 m^2}{\epsilon^3} \right] \\ &\quad - a^2 \left[ \frac{2211}{16} \frac{\beta_1^4}{\epsilon^6} - \frac{651}{16} \frac{\beta_1^2 m^2}{\epsilon^5} + \frac{75}{64} \frac{m^4}{\epsilon^4} \right]. \end{aligned} \quad (\text{B14})$$

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