Divergent perturbative series and Oppenheimer's formula

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Abstract: We present a derivation of the decay rate of a Hydrogen-type atom subjected to an external electrical field, the so-called Oppenheimer's formula. The perturbative approach to this problem yields a divergent result, so we introduce the necessary mathematical tools to obtain a finite answer, and we illustrate them with two toy models. The result obtained agrees with the answer obtained originally by a WKB analysis.

I. INTRODUCTION

Quantum mechanics is one of the cornerstones of modern physics: its impact in our understanding of the world and in technology are hard to overemphasize.

Being able to solve quantum mechanical problems is thus of paramount importance, but problems with known exact solution are very rare. For this reason, many approximation techniques have been developed over the years: perturbation theory, WKB, variational methods...

Perturbation theory is perhaps the most popular method. However, for many problems of physical interest, perturbation theory displays a number of limitations: it can fail to capture qualitative features (for example, existence or number of ground states), and the resulting perturbative series can even diverge.

On the other hand, the perturbative series can display some subtle connections with other methods. The goal of this bachelor thesis is to illustrate some of these points in a physically relevant example related to the Stark effect.

Recall that the Stark effect is the shifting and splitting of spectral lines of atoms in the presence of an external electric field. In this work, we will focus on the fate of the ground state of a Hydrogen-type atom in the presence of a constant and homogeneous external electric field. This problem was tackled by Schrödinger in his first paper on perturbative methods in quantum mechanics [1]. He missed an important qualitative feature: the system is metastable and there is a non-zero decay rate Γ.

This was noticed first by Oppenheimer [2], who made some mistakes later corrected by Lanczos [3]. They found an estimate of the decay rate of the ground state of the hydrogen atom using WKB techniques for small electric fields, given by the so-called formula of Oppenheimer, that reads in atomic units

$$\Gamma \sim \frac{4}{\mathcal{E}} \exp\left(-\frac{2}{3\mathcal{E}}\right), \quad \mathcal{E} \ll 1, \tag{1}$$

where $\mathcal{E}$ is the modulus of the electric field in atomic units. Note that this decay rate is not analytic in the electric field.

Throughout the work we will use atomic units. Recall [4] that the atomic unit of electric field is given by $\frac{E_h}{ea_0}$ and that the atomic unit of time is given by $\frac{\hbar}{E_h}$, where $E_h = \frac{\hbar^2}{m_e a_0^2}$ is the Hartree energy, a_0 is the Bohr radius, e is the charge of the electron and m_e is the mass of the electron.

This work is structured as follows. In Section II we start motivating the study of divergent perturbative series by presenting two toy models related to the harmonic oscillator, namely, the quartic anharmonic 1D oscillator and the metastable 1D minimum. In Section III we introduce mathematical tools to make sense of factorially divergent power series. Such tools are able to give an approximation of the ground energy of the quartic anharmonic 1D oscillator and an approximation of the decay rate of the metastable 1D minimum. It turns out that the results for both models can be derived from an alternative approach using instantons: a brief comment on this is made in Section IV. Finally, in Section V we generalize Oppenheimer's formula (1) for Hydrogen-type atoms using the methods learned in the previous sections.

II. INTRODUCTORY MODELS

To set the stage of this work, let us start presenting two toy models in which perturbation theory fails. In the first model we will see that perturbation theory fails quantitatively, and in the second model we will see that perturbation theory fails qualitatively.

In both examples, the potential studied depends on a coupling constant $g > 0$ that measures the anharmonicity of the system. Then, perturbation theory gives the ground energy of the system as a series of the form

$$E_0 = \sum_{n=0}^{\infty} a_n g^n, \quad a_n \in \mathbb{R}. \tag{2}$$

A. The quartic anharmonic 1D oscillator

In 1969 Bender and Wu [5] studied the quartic anharmonic oscillator, whose Hamiltonian in one dimension is

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(H and x are dimensionless in what follows)

$$H^Q = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 + \frac{1}{4}gx^4, \quad g > 0.$$

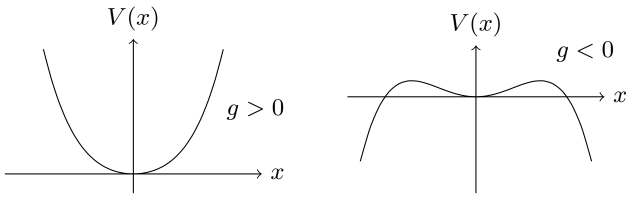

FIG. 1: Potential of the quartic anharmonic 1D oscillator in the stable ($g > 0$) and metastable ($g < 0$) regimes.

Observe that the potential is stable for $g > 0$ and has an absolute minimum at the origin, so we expect to have bound states with well-defined energies.

Using the recurrence relations introduced by Bender and Wu [5], we find that the large order behaviour of the coefficients of the perturbative series of the ground energy is of the form

$$a_n^Q \sim (-1)^{n+1}\frac{\sqrt{6}}{\pi^{3/2}}\left(\frac{3}{4}\right)^n \Gamma\left(n + \frac{1}{2}\right), \quad n \gg 1. \qquad (3)$$

Note that the coefficients grow factorially fast with n, so the perturbative series diverges for all (non-zero) values of the coupling constant g.

B. The metastable 1D cubic minimum

The simplest example of a system having a metastable minimum is given by a Hamiltonian of the form

$$H^C = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 - gx^3, \; g > 0,$$

and we expect a non-zero decay rate Γ^C for the ground state.

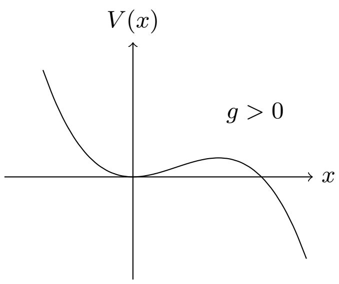

FIG. 2: Potential of the metastable 1D cubic minimum.

Following Álvarez [6], we find that the large order behaviour of the coefficients of the perturbative series is of the form

$$a_n^C \sim -\frac{\sqrt{60}}{(2\pi)^{3/2}}\left(\frac{15}{2}\right)^n \Gamma\left(n + \frac{1}{2}\right), \quad n \gg 1. \qquad (4)$$

Again, the coefficients grow factorially fast with n, but the difference now is that the coefficients do not alternate in sign. Disturbingly, perturbation theory at first sight seems to miss the fact that, strictly speaking, this potential has no true bound states.

III. BOREL TRANSFORMS

Motivated by the above examples, we present a way to make sense of series that are factorially divergent. For such purpose, consider the following formal power series

$$\varphi(z) = \sum_{n=0}^{\infty} a_n z^n, \qquad (5)$$

with the coefficients a_n growing factorially fast with n,

$$a_n \sim A^{-n} n!, \quad n \gg 1.$$

The Borel transform of $\varphi(z)$ is defined to be

$$\hat{\varphi}(\zeta) := \sum_{n=0}^{\infty} \frac{a_n}{n!}\zeta^n. \qquad (6)$$

Observe that $\hat{\varphi}(z)$ defines an analytic function in the $\zeta-$complex disk $|\zeta| < |A|$.

A. Borel resummation and Borel summability

If in some region of the $z-$complex plane exists (and is finite) the quantity

$$s(\varphi)(z) := \int_0^{\infty} \hat{\varphi}(z\zeta)e^{-\zeta} d\zeta, \qquad (7)$$

the formal power series $\varphi(z)$ is said to be Borel summable with Borel resummation $s(\varphi)(z)$.

Substituting, formally, (5) in (7), it is straightforward to check that

$$s(\varphi)(z) = \sum_{n=0}^{\infty} a_n z^n. \qquad (8)$$

This equation allows the following interpretation. Suppose that the perturbative series of the ground energy, $\varphi(g)$, is factorially divergent but Borel summable, with well-defined Borel resummation, $s(\varphi)(g)$, on the positive real axis, $g > 0$. Then, the right hand side of (8) can be identified to be such perturbative series, $\varphi(g)$, and equation (8) says that the ground energy is given by the Borel resummation, $E_0 = s(\varphi)(g)$.

This is precisely what happens in the quartic anharmonic one dimensional oscillator, as we shall see now.

1. *Example: the quartic anharmonic 1D oscillator*

Estimating the perturbative series of the ground energy of the quartic anharmonic 1D oscillator, using the large order behaviour (3), as the series

$$\sum_{n=0}^{\infty} a_n^Q g^n \approx \sum_{n=0}^{\infty} (-1)^{n+1} \frac{\sqrt{6}}{\pi^{3/2}} \left(\frac{3}{4}\right)^n \Gamma\left(n+\frac{1}{2}\right) g^n,$$

we can estimate its Borel transform as the Borel transform of the series of the right hand side, that is

$$\hat{\varphi}^Q(\zeta) \approx \frac{-\sqrt{6}}{\pi}\left(1+\frac{3\zeta}{16}\right)^{-1/2}, \qquad (9)$$

which is well-defined on the positive real axis and induces a well-defined Borel resummation on the positive real axis.

By the previous reasoning, we conclude that the ground energy of the quartic anharmonic 1D oscillator is given by the Borel resummation of its perturbative series, which can be approximated using (9) in (7) as

$$E_0 \approx 4\sqrt{\frac{2}{\pi}}\frac{1}{\sqrt{g}} \exp\left(\frac{16}{3g}\right) \operatorname{erfc}\left(\frac{4}{\sqrt{3g}}\right),$$

where erfc is the complementary error function.

Note that the Borel transform has a singularity on the negative real axis, although this does not affect the previous argument.

2. *Example: the metastable 1D cubic minimum*

An analogous argument shows that the Borel transform of the perturbative series of the ground energy of the metastable 1D cubic potential is approximately

$$\hat{\varphi}^C(\zeta) \approx \frac{-\sqrt{60}}{\pi}\left(1-30\zeta\right)^{-1/2},$$

which has a singularity on the positive real axis, on which the quantity (7) is ill-defined. Thus, the previous argument does not apply and, a priori, we can not say anything about the system from its Borel transform. To fix this, we shall study the behaviour of Borel transforms around their singularities.

B. Singularities of the Borel transform

If the Borel transform $\hat{\varphi}(\zeta)$ has a singularity on the real axis, at $\zeta = A \neq 0$, then $s(\varphi)(z)$ has a discontinuity when integrated, on the one hand, following a complex path avoiding the singularity from above and, on the other hand, when integrated following a complex path avoiding the singularity from below, as shown in Figure 3.

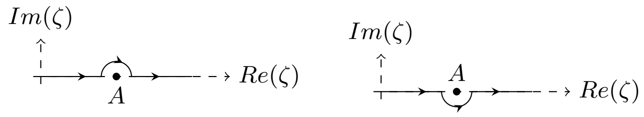

FIG. 3: Paths of integration avoiding the singularity from above (left) and from below (right).

It can be shown (see [7, pgs. 85–87]) that such discontinuity is of the form

$$\begin{aligned} disc(\varphi)(z) &:= s_{above}(\varphi)(z) - s_{below}(\varphi)(z) \\ &= ie^{-|A|/z} z^{-b}\left(c_0 + O(z)\right), \quad b, c_0 \in \mathbb{R}. \end{aligned} \qquad (10)$$

Observe that if the Borel resummation is intended to give the ground state energy and moreover has a discontinuity of the form (10), we can claim that the ground energy has an imaginary part given by a half of (10), that is,

$$Im(E_0) = \frac{1}{2} e^{-|A|/z} z^{-b}\left(c_0 + O(z)\right). \qquad (11)$$

This imaginary part may be physically interpretable. For example, for metastable potentials we expect the ground state to have a non-zero decay rate Γ: in this situation, this imaginary part can be interpreted to be such decay rate, since the time evolution of the ground state is given by

$$e^{-iE_0 t} = e^{-itRe(E_0)} e^{-\Gamma t/2}, \quad \Gamma = 2|Im(E_0)|. \qquad (12)$$

This is precisely what happens in the metastable 1D cubic minimum. To prove it, we still need one last ingredient, which we explain next.

1. *Large order behaviour from Borel transforms*

The coefficients a_n of the formal power series (5) can be recovered from its Borel transform (6) through Cauchy's formula,

$$\frac{a_n}{n!} = \frac{1}{2\pi i}\int_{\mathcal{C}} \frac{\hat{\varphi}(\zeta)}{\zeta^{n+1}} d\zeta,$$

where $\mathcal{C}$ is a closed path containing the origin and avoiding the singularity $\zeta = A \in \mathbb{R}\setminus\{0\}$ of $\hat{\varphi}(z)$, as shown in Figure 4.

Indeed, it can be shown (see [7, pgs. 89–91]) that

$$a_n = \frac{1}{2\pi} A^{-b-n}\Gamma(n+b)\left(c_0 + O(n^{-1})\right), \quad n \gg 1. \qquad (13)$$

Observe that the parameters b, A and c_0 are the same as in (10). Hence, from the discontinuity of the Borel resummation (10), or equivalently from the imaginary part (11), the asymptotic growth of the coefficients of the perturbative series can be recovered from (13), and vice versa.

Now we can complete the argument for the metastable 1D cubic minimum.

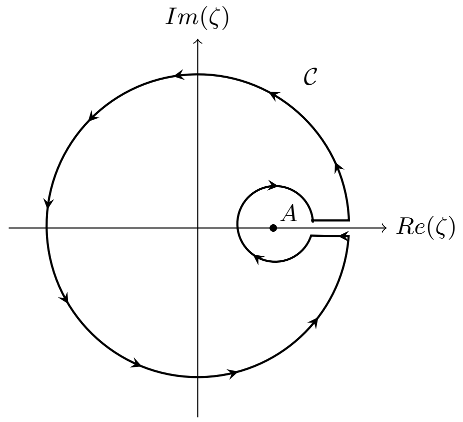

FIG. 4: Contour avoiding the singularity at $A \in \mathbb{R} \setminus \{0\}$.

2. Example (revisited): the metastable 1D cubic minimum

Comparing the large order behaviour (4) with (13), we identify

$$b^C = \frac{1}{2},\ A^C = \frac{2}{15},\ c_0^C = \frac{-2}{\sqrt{\pi}}.$$

Then, using (11) and (12), we find that the metastable 1D cubic minimum has a non-zero decay rate given by

$$\Gamma^C \approx \frac{2}{\sqrt{\pi}g} \exp\left(-\frac{2}{15g^2}\right).$$

IV. BRIEF COMMENT ON INSTANTONS

It is worth mentioning that there is an alternative approach to derive these results, based on the evaluation of solutions of the classical equations of motion in imaginary time, the so-called instantons. See [7, Sections 1.4, 1.5, 3.2, 3.3] for a detailed exposition of the relationship between instantons and the asymptotic behaviours (10) and (13). Such approach is cleanest working with the path integral formalism: see [8, Section 2] for a detailed presentation.

Using instantons, I have explicitly reproduced the large order behaviours (3) and (4) of the introductory models.

V. OPPENHEIMER'S FORMULA

Let's apply the previous tools to reproduce Oppenheimer's formula (1). As before, we work in atomic units.

Recall that for a Hydrogen-type atom, with atomic number Z, in presence of an external electric field $(0, 0, \mathcal{E})$, the Hamiltonian is

$$H^S = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \mathcal{E}z, \quad r := \sqrt{x^2 + y^2 + z^2}.$$

Observe that the unperturbed Hamiltonian is

$$H^{\text{unpert.}} = -\frac{1}{2}\nabla^2 - \frac{Z}{r},$$

for which we know that the ground energy is

$$E_0^{\text{unpert.}} = -\frac{Z^2}{2}. \tag{14}$$

It turns out that the Schrödinger equation $H^S\psi(x, y, z) = E\psi(x, y, z)$ is separable in squared parabolic coordinates,

$$\begin{cases} x = \xi\eta\cos\phi \\ y = \xi\eta\sin\phi \\ z = \frac{1}{2}(\xi^2 - \eta^2) \end{cases} \quad \text{with } r = \frac{1}{2}(\xi^2 + \eta^2),$$

with solutions of the form

$$\psi(\xi, \eta, \phi) = \frac{g_1(\xi)}{\sqrt{\xi}} \frac{g_2(\eta)}{\sqrt{\eta}} e^{im\phi},$$

g_1 being an eigenfunction of eigenvalue $\mu_n^{(m)}(-2E, \mathcal{E})$ of

$$A_m = -\frac{d^2}{d\xi^2} + \left(m^2 - \frac{1}{4}\right)\frac{1}{\xi^2} - 2E\xi^2 + \mathcal{E}\xi^4,$$

g_2 being an eigenfunction of eigenvalue $\mu_n^{(m)}(-2E, -\mathcal{E})$ of

$$A'_m = -\frac{d^2}{d\eta^2} + \left(m^2 - \frac{1}{4}\right)\frac{1}{\eta^2} - 2E\eta^2 - \mathcal{E}\eta^4,$$

and such that

$$\mu_n^{(m)}(-2E, \mathcal{E}) + \mu_n^{(m)}(-2E, -\mathcal{E}) = 4Z. \tag{15}$$

In 1970, Simon [9] studied the eigenvalues $\mu_n^{(m)}(\alpha, \beta)$ of the class of operators

$$h(\alpha, \beta) = -\frac{d^2}{dx^2} + \left(m^2 - \frac{1}{4}\right)\frac{1}{x^2} + \alpha x^2 + \beta x^4,$$

of which A_m and A'_m are members, deducing the rescaling formula [9, Theorem II.2.1], for all $\lambda > 0$,

$$\mu_n^{(m)}(\lambda^2\alpha, \lambda^3\beta) = \lambda\mu_n^{(m)}(\alpha, \beta). \tag{16}$$

Moreover, in 1973, Banks, Bender and Wu [10] found, from the study of the quartic anharmonic oscillator in two dimensions, that the ground energy $\mu_0^{(0)}(1, \beta)$ has a perturbative series of the form

$$\mu_0^{(0)}(1, \beta) = \sum_{n=0}^{\infty} a_n\beta^n,\ a_n \underset{n\gg1}{\sim} \frac{8}{\pi}\left(\frac{3}{2}\right)^{n+1}(-1)^n\Gamma(n+1). \tag{17}$$

Comparing (17) with equation (13), we obtain

$$b^S = 1,\ A^S = \frac{2}{3},\ c_0^S = 16, \tag{18}$$

and therefore, using (11), we get

$$Im\left(\mu_0^{(0)}(1,\beta)\right) = \frac{8}{\beta}\exp\left(-\frac{2}{3\beta}\right). \tag{19}$$

Formula (16) allows to rewrite (15) conveniently as

$$\zeta\omega = \mu_n^{(m)}(1,\omega^3) + \mu_n^{(m)}(1,-\omega^3), \tag{20}$$

with $\zeta = 4Z/\mathcal{E}^{1/3}$ and $\omega = \mathcal{E}^{1/3}/\sqrt{-2E}$.

Taking imaginary parts in (20) and expanding in Taylor series at first order in $Im(\omega^3)$ it can be shown that

$$Im\left(\frac{4Z}{(-2E_0)^{1/2}}\right) \approx Im\left[\mu_0^{(0)}\left(1,\frac{\mathcal{E}}{Z^3}\right)\right]. \tag{21}$$

Expanding $4Z/\sqrt{-2E_0}$ in Taylor series at first order in $Im(E_0)$, using, according to (14), that $Re(E_0) \approx -Z^2/2$ and replacing in (21) the behaviour (19), we get

$$\Gamma^S = 2Im(E_0) \approx \frac{4Z^5}{\mathcal{E}}\exp\left(-\frac{2}{3}\frac{Z^3}{\mathcal{E}}\right),\ \mathcal{E} \ll 1, \tag{22}$$

which is in accordance with (1).

Let's put in perspective the magnitude of such decay rate. For a Hydrogen atom ($Z = 1$) in presence of an external, homogeneous and constant electric field of modulus of order $\mathcal{E} \sim 10^8$ V/m, or in atomic units $\mathcal{E} \sim 10^{-3} \ll 1$, using (22) we get that, in atomic units, $\Gamma^S \sim 10^{-286}$. This means that the mean lifetime of the ground state is of the order $\left(\Gamma^S\right)^{-1} \sim 10^{270}$ years, about 10^{260} times the age of the universe. Thus, despite theoretically the state is metastable with non-zero decay rate, for practical purposes we can neglect this metastability, thus justifying the elementary treatment of the Stark effect.

VI. CONCLUSIONS

Perturbation theory is not an exhaustive tool to find the energies of quantum systems because it can fail quantitatively or qualitatively, as we have seen. Thus, other approximation methods are essential to complement perturbation theory.

Nevertheless, we have seen that the study of the divergence of a perturbative series may lead to meaningful results. In particular, in this work we have seen the accordance of the results derived from the study of divergent perturbative series through Borel transforms with the results derived from WKB techniques and instantons. Moreover, these techniques on the study of divergent perturbative series allow to generalize Oppenheimer's formula to Hydrogen-type atoms.

Looking ahead, there is a number of ways this work could be generalized. First, Oppenheimer's formula assumes the electric field to be small; it would be interesting to relax this assumption (and consider electric fields up to the Schwinger limit). More broadly, the interplay between perturbative methods and non-perturbative effects is a topic of ongoing research in Quantum Field Theory.

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