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Non-existence of Taylor expansion in time due to cusps

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In the usual treatment of electronic structure, all matter has cusps in the electronic density at nuclei. Cusps can produce non-analytic behavior in time, even in response to perturbations that are time-analytic. We analyze these non-analyticities in a simple case from many perspectives. We describe a method, the s -expansion, that can be used in several such cases, and illustrate it with a variety of examples. These include both the sudden appearance of electric fields and disappearance of nuclei, in both one and three dimensions. When successful, the s -expansion yields the dominant short-time behavior, no matter how strong the external electric field, but agrees with linear response theory in the weak limit. We discuss the relevance of these results to time-dependent density functional theory.

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I. INTRODUCTION

Time-dependent quantum mechanics is used to calculate the response of systems to time-varying external potentials[1], but can be computationally demanding for many particles. Among practical methods, time-dependent density functional theory (TDDFT) excels as a computationally inexpensive method for dealing with the interactions between electrons in time-dependent quantum mechanics[2, 3]. In the last two decades, use of TDDFT has grown tremendously, especially for calculations of transition frequencies of electronic excitations in molecules[4] and solids[5, 6]. The relative computational ease with which TDDFT handles electron-electron interaction make it the only viable quantum tool for systems with several hundred atoms[2–4].

But the validity of TDDFT relies on the celebrated Runge-Gross theorem[7] which proves, under certain circumstances, that the time-dependent one-body potential of an interacting electronic system is a functional of the one-electron density. Modern TDDFT calculations also use a Kohn-Sham scheme, in which fictitious non-interacting fermions are propagated in a time-dependent multiplicative potential, defined to reproduce the time-dependent density of the interacting system. Use of such a scheme implicitly supposes that such a potential exists (in technical jargon, that the density is non-interacting v -representable[2, 3]). Ground-breaking work by van Leeuwen[8] showed that, under quite general assumptions, such a potential can always be found, apparently ending this question within TDDFT.

However, nature can occasionally be both subtle and malicious. The Runge-Gross theorem assumes time-Taylor expandability(t -TE) of the time-dependent potential, while van Leeuwen’s proof requires such expandability of the density also. In recent work[9], we gave a very simple, realistic case (a hydrogen atom in a suddenly-switched static electric field) in which the lat-

ter fails, thus reopening the issue of v -representability in TDDFT. This could only be done convincingly by creating a methodology for explicitly extracting the short-time asymptotic behavior in such cases, and demonstrating the non-expandability of the density. This has reopened the question of the existence of a KS potential in the common case of Coulomb attraction to the nuclei, and recent work has focused on avoiding the Taylor expansion in time[10, 11].

These results were quite unexpected, as they are due to the non-interchangeability of two commonly interchanged limits. In fact, as we demonstrate explicitly here, the time-dependent density in such cases, $n(\mathbf{r}, t)$, has *no* well-defined short time expansion. For finite distances from a cusp, one asymptotic expansion applies, while for distances less than \sqrt{t} from a cusp, a different expansion dominates. (Atomic units $e = \hbar = m_e = 1/(4\pi\epsilon_0) = 1$ are used throughout.) A related statement is that we find the radius of expansion of the time-Taylor series is 0. However, even if the density has no well-defined expansion, integrals over the density, such as the time-dependent dipole moment, *are* well-defined, but can contain fractional powers of t . Here we give further examples of the method developed in Ref. [9] for calculating some of these quantities for several cases. We also show how these features appear in various alternative approaches to this problem.

Our work here is far from a complete analysis of these behaviors, and we make no attempt at a general treatment of this problem. Instead, we merely scratch the surface of the very thorny issues created by the coupling between space and time in the Schrödinger equation. We hope this work will inspire more comprehensive study of these questions, and perhaps lead to a more straightforward computational scheme.

The paper is divided as follows. We begin by analyzing a very simple illustration, the 1D disappearing nucleus, from many different viewpoints. Although this is not a

three-dimensional Coulomb potential problem, this illustration is chosen because we have closed analytic results. We next present the s -expansion as a general method for extracting the short-time behavior of these systems. We then revisit 1D. We check our method reproduces the analytic results of the disappearing nucleus problem, and show what it produces for a nucleus in an electric field. We then turn to 3D, applying the method to the two previous cases, but in 3D. There are specific complications for the H atom in an electric field. In the following section, we examine the time-dependent dipole moment, rather than just the wavefunction, finding its behaviour entirely in the disappearing nucleus case, and partially in the electric-field problem. Then we discuss more general potentials in space and time (but not any general class of potentials). We close with a discussion of the implications of these results for many-electron systems and time-dependent density functional theory.

II. WHEN NUCLEI VANISH

Here we study the failure of the Taylor series in the simplest possible case, first studied in Ref. [12]. In one dimension, we begin at $t = 0$ with a wavefunction:

$$\psi_0(x) = \exp(-|x|), \quad (1)$$

which has a cusp at $x = 0$. We propagate with the free-particle Hamiltonian

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2}, \quad (2)$$

and find

$$\psi(x, t > 0) = \hat{U}(t) \psi_0(x), \quad (3)$$

where the time-propagation operator $\hat{U}(t) = \exp(-i\hat{H}t)$ because the Hamiltonian is t -independent. The common trick of t -TE uses:

$$\exp[-i\hat{H}t] \stackrel{?}{=} 1 - i\hat{H}t - \hat{H}^2 t^2 / 2 + \dots \quad (4)$$

Many textbooks either use the t -TE interchangeably with the correct spectral definition of the propagator[13–16], or introduce the t -TE as a formal propagation method without further discussion of the implications[1]. For the 1D example system, we evaluate the time-dependent wavefunction with the Taylor-expanded time-evolution operator:

$$\begin{aligned} \psi^{\text{TE}}(x, t > 0) &= \left[\sum_{j=0}^{\infty} (-i\hat{H})^j t^j / j! \right] \psi_0(x) \\ &= \exp(-|x| + it/2), \quad (x \neq 0). \end{aligned} \quad (5)$$

yielding the remarkable result that (for $x \neq 0$), the density appears to remain stationary!

We refer to this example as a 1d vanishing nucleus, because the initial wavefunction is the eigenstate of $v(x) = -\delta(x)$, and decays exponentially like that of a hydrogen atom. According to the Taylor expansion, we can instantly remove this potential at $t = 0$, and the density does not change. Obviously, if we do nothing to the potential, the density will not change either, in apparent contradiction of the RG theorem.

In this case, it is simple to find the true wavefunction. The free-particle propagator in 1d is

$$\begin{aligned} U(x, x', t > 0) &= \frac{i}{2\pi} \int_{-\infty}^{\infty} dk \exp[iku - ik^2 t / 2] \\ &= \frac{\exp[iu^2 / (2t)]}{\sqrt{2\pi i t}}, \end{aligned} \quad (6)$$

where $u = x - x'$, and convolution with $\psi_0(x)$ yields

$$\psi(x, t > 0) = \mathcal{S}_x \left[\exp(x + it/2) \operatorname{erfc} \left(\frac{x + it}{\sqrt{2it}} \right) \right] \quad (7)$$

and $\mathcal{S}_x f = [f(x) + f(-x)]/2$ extracts the spatially symmetric part of a function. We choose $\sqrt{i} = (1 + i)/\sqrt{2}$ and use this branch through the paper for square roots. Fig. 1 confirms that the wavefunction spreads and the cusp vanishes for $t > 0$, as intuition demands. An important feature of Eq. (7) is that $\psi(x, t)$ is not an analytic function at $t = 0$ with respect to t , and we denote this as time-non-analyticity throughout the paper. We analyze the time-non-analyticity in detail in Sect. III.

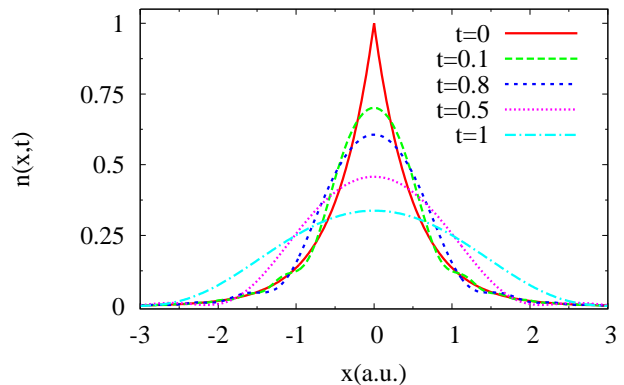


FIG. 1. (Color online) Time-dependent density of an exponential that propagates freely after $t = 0$. The Taylor expansion fails to change from its $t = 0$ value.

In practice, we observe that the t -TE wavefunction works when the initial wavefunction is space-analytic, from which wavefunctions with cusps are excluded. We define ‘cusp’ in a general sense as a discontinuity in the space derivatives of a certain order of the concerned function. No matter what the external potential is, a Hamiltonian always contains the kinetic energy operator - a differential operator in space. According to Eq. (5), the existence of a t -TE wavefunction requires the initial

wavefunction being differentiable to infinite order at any space point. However, infinite-order differentiable does not guarantee the validity of the t -TE wavefunction: the wavefunction is differentiable in the distributional sense in the case of cusps; in another case[17], one can construct a non-trivial wavepacket where the space derivative of all orders vanish at certain points; t -TE fails in both cases. The analyticity of the initial wavefunction in space is linked to the analyticity of the TD wavefunction in time. We provide more evidence and a heuristic derivation of time-non-analyticities originating from cusps in Sect. VII A.

For simplicity of notations, all time variables are greater than 0 unless otherwise specified.

A. Interchanging orders of limits

The failure of t -TE is due to the interchange of the order of limiting operations. For a time-independent Hamiltonian[9],

$$\psi(\mathbf{r}, t) = \sum_j c_j \left(\sum_{p=0}^{\infty} \frac{(-i\epsilon_j)^p}{p!} t^p \right) \phi_j(\mathbf{r}), \quad (8)$$

in which $c_j = \langle \phi_j | \psi_0 \rangle$, while

$$\psi^{\text{TE}}(\mathbf{r}, t) = \sum_{p=0}^{\infty} \left(\sum_j c_j \frac{(-i\epsilon_j)^p}{p!} \phi_j(\mathbf{r}) \right) t^p, \quad (9)$$

which is obtained by interchanging the order of the two summations. If the initial wavefunction is composed of a finite number of eigenstates, such an interchange is valid. More generally, one requires uniform convergence for two summations of infinite number of terms to be interchangeable.

We now perform a t -TE on the integrand of Eq. (6) and interchange the order of the integration and the summing of t -TE:

$$\begin{aligned} U^{\text{TE}}(x, x', t) &= \frac{i}{2\pi} \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} dk \exp[iku] \frac{(-ik^2/2)^n}{n!} t^n \\ &= \sum_{n=0}^{\infty} \frac{i^n}{2^n n!} \delta^{(2n)}(u) t^n, \end{aligned} \quad (10)$$

where $u = x - x'$, and $\delta^{(2n)}$ denotes the $2n$ th order derivative of the δ -function with respect to u . Thus U^{TE} only exists in a distributional sense. Applying $\hat{U}^{\text{TE}}(t)$ to Eq. (1) generates an ill-defined wavefunction, even in the dis-

tributional sense:

$$\begin{aligned} \psi^{\text{TE}}(x, t > 0) &= \psi_0(x) - it \left[-\frac{1}{2} + \delta(x) \right] \psi_0(x) \\ &\quad - \frac{t^2}{2} \left\{ \left[\frac{1}{4} - \frac{1}{2} \delta''(x) - \delta(x) + \delta^2(x) \right] \psi_0(x) \right. \\ &\quad \left. - \delta'(x) \psi_0'(x) \right\} + O(t^3), \end{aligned} \quad (11)$$

t -TE does not apply to systems with cusps due to the problematic interchange of limiting operations. In many cases, one can recover the correct result by introducing another interchange of limiting operations. Here, we notice that the initial wavefunction does not have a cusp in momentum space:

$$\begin{aligned} \Psi_0(k) &= \int_{-\infty}^{\infty} dx \psi_0(x) \exp[-ikx] \\ &= \frac{2}{k^2 + 1}, \end{aligned} \quad (12)$$

where we denote the Fourier transform of ψ with respect of x as Ψ and the conjugate variable of x as k .

According to our previous argument, t -TE should be valid for this case. By applying U^{TE} to Eq. (12) and performing the summation to infinite order of the t -TE, we obtain the t -TE wavefunction in momentum space as

$$\begin{aligned} \psi^{\text{TE}}(k, t) &= \sum_{n=0}^{\infty} \frac{(-ik^2/2)^n}{n!} \psi_0(k) t^n \\ &= \frac{2}{k^2 + 1} \exp(-ik^2 t/2), \end{aligned} \quad (13)$$

which is exactly the Fourier transform of Eq. (7), the correct TD wavefunction. Taking the t -TE in momentum space is equivalent to performing a Fourier transform on Eq. (11), and then interchanging the order of the Fourier transform with the summation of the t -TE series. By introducing this extra interchange of orders, the correct TD behaviors are recovered. The Borel summation of asymptotic series(as in Sect. IV A) is another example of correcting the wrong result from interchanging the order of limiting operations by introducing another interchange of orders, and we develop in Sect. III a method based on the Borel summation to obtain short-time behaviors for systems with cusps. Unfortunately, there is no general theorem about the applicability of such techniques, and this topic remains under active research.[18, 19]

B. Inner and outer regions

Here we define carefully the inner and outer regions, each of which has a distinct asymptotic expansion. Fig. 2 shows the region far from the origin becomes oscillatory, showing the plane-wave nature of the eigenstates of the free-particle Hamiltonian; yet the region near the

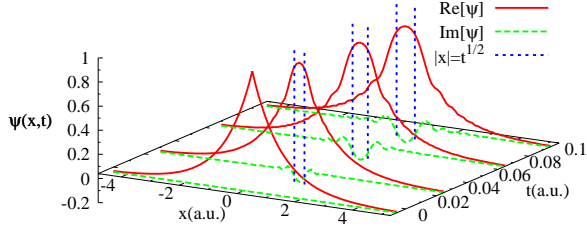


FIG. 2. (Color online) The time-dependent wavefunction after the nucleus vanishes.

origin is non-oscillatory, resembling the spread-out cusp. By carefully taking the $t \rightarrow 0_+$ limit as below, we notice $t \rightarrow 0_+$ actually corresponds to two different limits, with $|x| \gg \sqrt{t}$ and $|x| \ll \sqrt{t}$ respectively. We denote the $|x| \gg \sqrt{t}$ region as the outer region, and the $|x| \ll \sqrt{t}$ region as the inner region. The correct short-time behavior is composed of the short-time behaviors of these two regions.

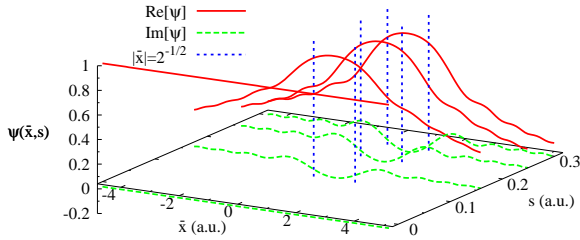


FIG. 3. (Color online) Same as Fig 2, but as a function of $s = \sqrt{t}$ and $\bar{x} = x/\sqrt{2t}$.

The short-time series expansions for these two regions can be obtained by changing the variables from (x, t) to the following reduced variables:

$$s = \sqrt{t}, \quad \bar{x} = \frac{x}{\sqrt{2t}}. \quad (14)$$

Fig. 3 shows such a change-of-variables effectively zooms in to the inner region, and the cusp in the initial wavefunction is removed in the reduced variables.

We can analytically extract the functions describing the smooth and oscillatory parts of the wavefunction. Define the following special functions:

$$\begin{aligned} E_c(s, \bar{x}) &= \mathcal{S}_{\bar{x}} \left[e^{\sqrt{2}s\bar{x}} \operatorname{erfc} \left(\frac{s_+}{2} \right) \right], \\ F(s, \bar{x}) &= \mathcal{S}_{\bar{x}} \left[\frac{2}{\sqrt{\pi}} e^{-s^2/4} \int_0^{s_-/2} dt e^{t^2 + is_+ t} \right], \end{aligned} \quad (15)$$

where $s_{\pm} = s \pm \sqrt{2}\bar{x}$.

The TD wavefunction Eq. (7) is then

$$\psi(x, t) = \frac{1}{2} e^{\frac{is^2}{2}} [E_c(s, \bar{x}) - iF^*(s, \bar{x})]. \quad (16)$$

For the wavefunction, the E_c part is smooth, and the $-iF^*$ part oscillates. Since at $t = 0$ the oscillatory part does not exist, it must be the effect of the vanishing cusp. In terms of error functions[20]:

$$F(s, \bar{x}) = ie^{\sqrt{2}s\bar{x}} \left\{ \operatorname{erf} \left[\sqrt{i} \left(\bar{x} - \frac{is}{\sqrt{2}} \right) \right] - \operatorname{erf} \left(\frac{s + \sqrt{2}\bar{x}}{2} \right) \right\}. \quad (17)$$

If $|x| \gg \sqrt{t}$ as $t \rightarrow 0_+$, the arguments of the error functions in Eq. (17) approach ∞ . On the other hand, when $|x| \ll \sqrt{t}$ as $t \rightarrow 0_+$, these arguments approach 0.

The inner-region expansion can be obtained by Taylor-expanding $\psi(s, \bar{x})$ as $s \rightarrow 0_+$ while holding \bar{x} fixed:

$$\begin{aligned} \psi^{\text{inner}}(s, \bar{x}) &\stackrel{s \rightarrow 0_+}{\sim} 1 + s \left[-\sqrt{2i/\pi} \exp(i\bar{x}^2) \right. \\ &\quad \left. - \sqrt{2}\bar{x} \operatorname{erf} \left(\sqrt{i}^* \bar{x} \right) \right] + O(s^2) \\ &= 1 + \frac{x^2}{2} - x \operatorname{erf} \left(\sqrt{\frac{i}{2t}} x \right) - \sqrt{\frac{2i}{\pi}} \exp \left(\frac{ix^2}{2t} \right) \sqrt{t} + \dots \end{aligned} \quad (18)$$

The outer-region expansion can be obtained by expanding $\psi(s, \bar{x})$ as $\bar{x} \rightarrow \pm\infty$ while holding s fixed:

$$\begin{aligned} \psi^{\text{outer}}(s, \bar{x}) &\stackrel{\bar{x} \rightarrow \pm\infty}{\sim} \exp(-\sqrt{2}s|\bar{x}| + is^2/2) \\ &\quad + \sqrt{\frac{i}{2\pi}} \exp(i\bar{x}^2) s \bar{x}^{-2} + O(\bar{x}^{-4}) \\ &= \exp(-|x|) \left(1 + \frac{it}{2} \right) + \sqrt{\frac{2i}{\pi}} \frac{\exp[ix^2/(2t)]}{x^2} t^{3/2} + \dots \end{aligned} \quad (19)$$

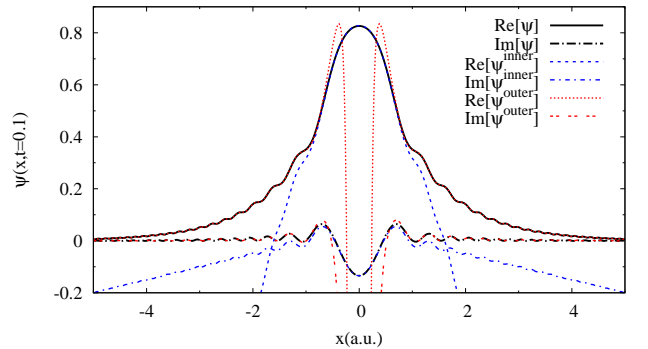


FIG. 4. (Color online) $\psi(x, t = 0.1)$ after the nucleus vanishes, plotting the truncated inner-region expansion and the outer-region expansion.

The truncated inner-region and outer-region expansions are plotted in Fig. 4. These two together define

the correct short-time behavior of the wavefunction. It should be noted that the usual $t \rightarrow 0_+$ limit only corresponds to the outer region, and thus it does not contain all the information of the system at $t \rightarrow 0_+$. Since these two expansions both contain time-non-analyticities, such as half-powers in t and $\exp[ix^2/(2t)]$, the t -TE cannot describe the correct short-time behavior.

Note that the outer region expansion can also be found via the stationary phase approximation[18], applied to the propagated wavefunction in momentum space. The stationary phase approximation is a method yielding the leading asymptotic behavior (as $\xi \rightarrow \infty$) of integrals of the following form:

$$I(\xi) = \int_a^b d\zeta f(\zeta) \exp[i\xi g(\zeta)]. \quad (20)$$

Write out the time-dependent wavefunction using the Green's function[21]:

$$\begin{aligned} \psi(x, t) &= \frac{i}{2\pi} \int k dk \int dx' \exp(-ik^2 t/2) \tilde{G}(x, x', \frac{k^2}{2}) \psi_0(x') \\ &= \frac{1}{\pi} \int_0^\infty dk \left[\frac{ik \exp(-|x|)}{k^2 + 1} + \frac{\exp(ik|x|)}{k^2 + 1} \right] \\ &\quad \times \exp(-ik^2 t/2), \end{aligned} \quad (21)$$

where the time-domain Green's function G is related to the time-propagation operator introduced in Sect. II by $G(x, x', t) = -i \langle x | \hat{U}(t) | x' \rangle$, and \tilde{G} is its Fourier transform with respect to t . Eq. (21) is equivalent to Eq. (3).

The first term in the integral gives the t -TE wavefunction, and we apply the stationary phase approximation[18]. The stationary point is $k = |x|/t$, and the second term of Eq. (21) correctly yields the leading time-non-analyticity:

$$\psi(x, t) \underset{x/\sqrt{2t} \rightarrow \infty}{\sim} \dots + \sqrt{\frac{2i}{\pi}} \frac{\exp[ix^2/(2t)]}{x^2} t^{3/2} + \dots \quad (22)$$

By change-of-variables, one can see the limit that the stationary phase approximation corresponds to. Letting $k = (|x|/t)\zeta$, the second term in Eq. (21) becomes

$$\int_0^\infty d\zeta \exp \left[i \frac{x^2}{2t} (-\zeta^2 + 2\zeta) \right] \frac{|x| t}{x^2 \zeta^2 + t^2}. \quad (23)$$

Eq. (23) is in the form of Eq. (20), with $x^2/(2t)$ as ξ in Eq. (20). Thus the stationary phase approximation Eq. (22) corresponds to the $x^2/(2t) \rightarrow \infty$ limit, i.e., the outer-region expansion.

C. Radius of convergence

Next we consider the radius of convergence of the Taylor expansion. We study the wavefunction in the vanishing nucleus problem, beginning at t_0 after the nucleus

vanishes. This wavefunction has no cusp, and has a well-behaved Taylor expansion.

The t -TE of the time-evolution operator is

$$\text{TE} [e^{-iHt}] = \sum_j \frac{(it/2)^j}{j!} \frac{\partial^{2j}}{\partial x^{2j}}. \quad (24)$$

The exact TD wavefunction is Eq. (7). Instead of t -TE at $t = 0$, we pick a later time t_0 as the expansion point, and derive the radius of convergence of this t -TE.

In the outer region ($x \gg \sqrt{t_0}$), it is easy to show that

$$\frac{\partial^{2n} \psi(x, t)}{\partial x^{2n}} \propto -\frac{x^{2n-2}}{t_0^{2n-3/2}} C, \quad x \gg \sqrt{t_0}, \quad (25)$$

where $C = (i-1)e^{ix^2/(2t_0)}/\sqrt{\pi}$. In the inner region ($x \ll \sqrt{t_0}$), we have

$$\frac{\partial^{2n} \psi(x, t)}{\partial x^{2n}} \propto \frac{i^{n-1} (2n-1)!!}{t_0^{n-1/2}} C, \quad x \ll \sqrt{t_0}. \quad (26)$$

Then the radii of convergence for the inner and outer regions are given by

$$R_{\text{outer}} = \infty, \quad R_{\text{inner}} = t_0, \quad (27)$$

separately. Thus the radius of convergence for the inner region vanishes as $t_0 \rightarrow 0$.

III. THE s -EXPANSION

Here we introduce the s -expansion method[9]. Our notation is for 3D problems, but the method applies equally to 1D problems. Based on the previous analysis, we begin by a change-of-variables:

$$s = \sqrt{t}, \quad \bar{\mathbf{r}} = \frac{\mathbf{r}}{\sqrt{2t}}. \quad (28)$$

With these reduced variables, we can describe the time-non-analyticities which are not covered by the form of the t -TE. The time-dependent Schrödinger equation becomes

$$\bar{\nabla}^2 \psi - 4s^2 v \psi + 2i \left\{ s \frac{\partial \psi}{\partial s} - \bar{\mathbf{r}} \cdot \bar{\nabla} \psi \right\} = 0. \quad (29)$$

In the vanishing nucleus case, ψ is equal to its Taylor expansion in powers of s for fixed $\bar{\mathbf{r}}$, and thus we assume the following s -expansion ansatz in the more general case:

$$\psi(\bar{\mathbf{r}}, s) = \sum_{n=0}^{\infty} \psi_{(n)}(\bar{\mathbf{r}}) s^n. \quad (30)$$

This yields a set of differential equations:

$$\bar{\nabla}^2 \psi_{(n)} - 2i \bar{\mathbf{r}} \cdot \bar{\nabla} \psi_{(n)} + 2ni \psi_{(n)} - 4 \sum_{p=-2}^{n-2} v_{(p)} \psi_{(n-p-2)} = 0, \quad (31)$$

in which we assume the potential has a simple form of $v(\mathbf{r}, t) = \sum_{p=-2}^{\infty} v_{(p)}(\bar{\mathbf{r}}) s^p$. Thus each power of s produces a second-order differential equation for a function of $\bar{\mathbf{r}}$. Eq. (31) requires proper boundary conditions for the solution to be well-defined. Eq. (31) is equivalent to the TDSE whenever the wavefunction ansatz Eq. (30) is applicable. This requires the boundary conditions to be derived from the initial condition of the TDSE, which is the initial wavefunction $\psi_0(\mathbf{r}) \equiv \psi_0(\sqrt{2}\bar{\mathbf{r}}s)$. For finite argument \mathbf{r} , $s \rightarrow 0$ implies $\bar{\mathbf{r}} \rightarrow \infty$, so the expansion of the initial wavefunction at $s \rightarrow 0$ determines the large $\bar{\mathbf{r}}$ behavior of the $\psi_{(n)}(\bar{\mathbf{r}})$, i.e., provides the boundary conditions of Eq. (31).

We first check that for the trivial case where a system stays in an eigenstate, the s -expansion reduces to the t -TE result. Assume the system stays in an eigenstate $\phi(\mathbf{r})$ with eigenvalue E , Eq. (29) becomes

$$-4s^2 E\psi + 2i \left\{ s \frac{\partial \psi}{\partial s} - \bar{\mathbf{r}} \cdot \bar{\nabla} \psi \right\} = 0, \quad (32)$$

and Eq. (31) becomes

$$-4E\psi_{(n-2)} + 2ni\psi_{(n)} - 2i\bar{\mathbf{r}} \cdot \bar{\nabla} \psi_{(n)} = 0. \quad (33)$$

Eq. (33) can be trivially solved, and the coefficients originating from the differential equations are determined by the initial condition of the TDSE. Inserting $\psi_{(n)}$'s into Eq. (30), we obtain

$$\psi(\bar{\mathbf{r}}, s) = \phi(0) + \sqrt{2}\bar{\mathbf{r}}\phi'(0)s + [-iE\phi(0) + \bar{\mathbf{r}}^2\phi''(0)]s^2 + \dots, \quad (34)$$

where the derivatives of ϕ are taken with respect of \mathbf{r} . Eq. (34) is identical to the t -TE result.

Several examples of using the method are provided in Sect. IV A, IV B, and V B. For the 1D vanishing nucleus case, we solve Eq. (31) directly in Sect. IV A. Partial differential equations as in Eq. (31) are difficult to solve exactly except for the most simple systems. For the 1D/3D hydrogen in turned-on static electric field shown in Sect. IV B and V B, we are not able to solve Eq. (31) directly. For these more general cases, we find that although t -TE does not describe the correct short-time behaviors as a whole, it works fine before the occurrence of the first time-non-analytic term. Thus instead of solving the short-time behaviors directly, we solve for the simpler corrections from the t -TE with the method of dominant balance (described in Sect. IV A). The correction from the t -TE is expressed as asymptotic series. By performing the Borel summation as in Sect. IV A, we obtain the short-time behavior in closed form.

This method is not intended to be applied to all systems. The formulation only applies to one-electron systems. Second, although the theory is applicable for short-time behaviors to any order, the method depends on the ability to solve differential equations analytically in closed form - either directly or through the use of Borel summation - which requires asymptotic expansions in closed form. The requirement of closed-form

solutions makes numerical approximation difficult. Although several approximation methods exist for the Borel summation [18] requiring only part of the asymptotic series, it is not clear to us whether they are applicable in this case. Third, the short-time behavior obtained from the method is that of the TD wavefunction, which is not an observable. It is usually more important to be able to predict non-analyticities in observables, such as the $\omega^{-7/2}$ in the high frequency oscillator strengths of atoms. However, there is no guarantee that the leading order time-non-analyticity of the TD wavefunction is sufficient to determine that of a desired observable. Sec. V B and VI demonstrate such a situation for the 3D hydrogen atom in a turned-on static electric field. Aside from these restrictions, a more subtle restriction of the method is related to having more than one time-scale introduced by cusps, and is discussed in Sec. IV C.

IV. APPLICATIONS IN 1D

Here we show how the s -expansion works, by applying it to several different problems. We already have the exact solution for a vanishing nucleus, so this works as a demonstration of our method.

A. Vanishing nucleus revisited

In this case, Eq. (31) becomes:

$$\psi_{(n)}'' - 2i\bar{x}\psi_{(n)}' + 2in\psi_{(n)} = 0. \quad (35)$$

with general solution

$$\psi_{(n)}(\bar{x}) = a_n H_n(\sqrt{i}\bar{x}) + b_n f_n(\bar{x}), \quad (36)$$

where

$$f_n(\bar{x}) = \begin{cases} H_n(\sqrt{i}\bar{x}) \int_0^{\bar{x}} d\bar{x}' \frac{\exp[i(\bar{x}')^2]}{H_n(\sqrt{i}\bar{x}')^2} & n \text{ even,} \\ {}_1F_1\left(-\frac{n}{2}, \frac{1}{2}, i\bar{x}^2\right) & n \text{ odd,} \end{cases} \quad (37)$$

H is the Hermite polynomial, and ${}_1F_1$ is Kummer's confluent hypergeometric function [20].

Expanding Eq. (1) at $s \rightarrow 0_+$ yields

$$\psi_0(x) = \exp(-\sqrt{2}s|x|) = \sum_{n=0}^{\infty} \frac{(-\sqrt{2})^n |\bar{x}|^n}{n!} s^n. \quad (38)$$

Thus the boundary conditions for Eq. (36) are

$$\psi_{(n)}(\bar{x}) \sim (-\sqrt{2})^n |\bar{x}|^n / n!, \quad |\bar{x}| \rightarrow \infty. \quad (39)$$

With Eq. (39), we find $a_{2n+1} = b_{2n} = 0$ and

$$a_{2n} = \frac{(-i)^n}{(2n)!2^n}, \quad b_{2n+1} = -\frac{\sqrt{2}i^{n+1/2}}{(2n+1)!!\sqrt{\pi}}. \quad (40)$$

With Eq. (36) and (40), we obtain the inner-region expansion from Eq. (30). It agrees with the previously

shown Eq. (18), which is obtained from exactly solving the entire TDSE.

The short-time behavior of the time-dependent wavefunction is described by the inner-region and the outer-region expansion together. The inner-region expansion corresponds to expanding the exact time-dependent wavefunction at $s \rightarrow 0$ while holding $\bar{\mathbf{r}} = \mathbf{r}/\sqrt{2t}$ constant, but there is no requirement on the magnitude of the constant. Therefore the outer-region expansion is obtained by expanding the inner-region expansion Eq. (30) for $\bar{\mathbf{r}} \rightarrow \infty$. For the 1D vanishing nucleus case, expanding Eq. (30) for $|\bar{x}| \rightarrow \infty$ yields

$$\begin{aligned} \psi^{\text{outer}}(s, \bar{x}) &\stackrel{|\bar{x}| \rightarrow \infty}{\sim} (1 - \sqrt{2}s|\bar{x}| + s^2\bar{x}^2 + \dots) \\ &+ \frac{is^2}{2}(1 - \sqrt{2}s|\bar{x}| + \dots) + \sqrt{\frac{i}{2\pi}} \frac{s \exp(i\bar{x}^2)}{\bar{x}^2} + \dots \\ &= (1 - |\bar{x}| + \frac{\bar{x}^2}{2} + \dots) + \frac{it}{2}(1 - |\bar{x}| + \dots) \\ &+ \sqrt{\frac{2i}{\pi}} \frac{\exp[ix^2/(2t)]}{x^2} t^{3/2} + \dots \end{aligned} \quad (41)$$

This result agrees with Eq. (19), except that the $\exp(-|x|)$ envelope of the regular terms in Eq. (19) is expanded at $x \rightarrow 0$, as the price paid for obtaining the outer-region expansion from the inner-region expansion. The same result is obtained with the stationary phase approximation[18].

To find the asymptotic behavior without solving TDSE, we use the method of dominant balance[18]. For this case the leading-order time-non-analyticity is in $\psi_{(1)}(\bar{x})$. We use the following ansatz for $\psi_{(1)}$:

$$\psi_{(1)}(\bar{x}) = \exp[P(\bar{x})] \quad (42)$$

Inserting Eq. (42) into Eq. (35) yields

$$P''(\bar{x}) + [P'(\bar{x})]^2 - 2i\bar{x}P'(\bar{x}) + 2i = 0 \quad (43)$$

One consistent balance is assuming $P''(\bar{x}) \ll [P'(\bar{x})]^2$. We obtain the reduced differential equation corresponding to this balance by removing $P''(\bar{x})$ from Eq. (43):

$$P(\bar{x}) \sim i\bar{x}^2, \quad (44)$$

which is the first order in the asymptotic series of $P(\bar{x} \rightarrow \infty)$, corresponding to this balance. The next order is found by inserting

$$P(\bar{x}) \sim i\bar{x}^2 + C(\bar{x}) \quad (45)$$

into Eq. (43), which yields

$$C(\bar{x}) \sim -2 \ln(\bar{x}) \quad (46)$$

Thus $\psi_{(1)}$ has the following asymptotic behavior from the balance $P''(\bar{x}) \ll [P'(\bar{x})]^2$:

$$\psi_{(1)}(\bar{x}) = c_1 \exp[P(\bar{x})] \sim c \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \quad (47)$$

More terms are obtained by iteration, and inserting results of Eq. (46) yields $\psi_{(1)}$ as

$$\psi_{(1)}(\bar{x}) \sim c_1 \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \sum_{n=0}^{\infty} \frac{(2n+1)!(-i)^n}{2^n} \bar{x}^{-2n}. \quad (48)$$

Another consistent balance is assuming $-2i\bar{x}P'(\bar{x}) \gg P''(\bar{x}), [P'(\bar{x})]^2$. The asymptotic series corresponding to this balance is

$$\psi_{(1)}(\bar{x}) \sim c_2 \bar{x}. \quad (49)$$

The complete asymptotic behavior is then a summation of Eq. (48) and Eq. (49):

$$\psi_{(1)}(\bar{x}) \sim c_1 \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \left(1 - \frac{3i}{2\bar{x}^2} - \frac{15}{4\bar{x}^4} + \dots\right) + c_2 \bar{x}. \quad (50)$$

Borel summation is a method of extracting information and yields the closed-form formula of a function from its asymptotic series under certain restrictions[18, 22]. Consider a divergent series

$$S(p) = \sum_{n=0}^{\infty} \beta_n p^n. \quad (51)$$

The Borel sum of the series is defined as

$$S_B(p) \equiv \int_0^{\infty} d\xi \exp(-\xi) \phi(p\xi), \quad (52)$$

in which

$$\phi(p) = \sum_{n=0}^{\infty} \frac{\beta_n p^n}{n!}. \quad (53)$$

As an example, we do the Borel sum of the series in Eq. (50). The original divergent series is

$$S(\bar{x}) = \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \sum_{n=0}^{\infty} \frac{(2n+1)!(-i)^n}{2^n} \bar{x}^{-2n}. \quad (54)$$

The Borel sum of Eq. (54) is

$$\begin{aligned} S_B(\bar{x}) &= \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \int_0^{\infty} d\xi \exp(-\xi) \sum_{n=0}^{\infty} \frac{(2n+1)!(-i)^n \xi^n}{2^n n! \bar{x}^{2n}} \\ &= \frac{\exp(i\bar{x}^2)}{\bar{x}^2} \int_0^{\infty} d\xi \exp(-\xi) \frac{1}{(1 + i\xi/\bar{x}^2)^{3/2}} \\ &= -2i \exp(i\bar{x}^2) + 2\sqrt{i\pi\bar{x}} \operatorname{erfc}\left(\sqrt{i^* \bar{x}}\right), \end{aligned} \quad (55)$$

which is the exact form of $\psi_{(1)}$ as in Eq. (36):

$$\psi_{(1)}(\bar{x}) = c_2 \bar{x} + c_1 \left[-2i \exp(i\bar{x}^2) + 2\sqrt{i\pi\bar{x}} \operatorname{erfc}\left(\sqrt{i^* \bar{x}}\right)\right], \quad (56)$$

and c_1, c_2 are obtained by matching with Eq. (39).

$$c_1 = \sqrt{\frac{i}{\pi}}, \quad c_2 = -\sqrt{2}. \quad (57)$$

This result agrees with Eq. (36), so the method worked.

B. Suddenly switched electric field

Next we apply the method on a more complicated 1D 1-electron case. Consider a system with the following potential:

$$V(x, t) = -\delta(x) + \mathcal{E}x\theta(t). \quad (58)$$

The initial state is Eq. (1), the ground state of the ‘1D hydrogen’. The system stays in that state for $t < 0$, and a static linear electric field with field strength \mathcal{E} is turned on at $t = 0$. Though we cannot obtain the full analytic wavefunction for this system, the 1st order perturbative wavefunction (sans \mathcal{E}) $\psi^{<1>}$ [21] is exactly solvable and is given in Sect. VI C. Its outer expansion to the leading time-non-analytic order is

$$\begin{aligned} \psi^{<1>}(x, t) \stackrel{t \rightarrow 0^+}{\sim} & \left\{ -ixt + \frac{x - \text{sgn}(x)}{2}t^2 \right. \\ & \left. + \frac{i[x - \text{sgn}(x)]}{8}t^3 - \frac{x - \text{sgn}(x)}{48}t^4 \right\} \exp(-|x|) \\ & - 4\sqrt{\frac{2i}{\pi}} \frac{\exp[ix^2/(2t)]}{x^5} t^{9/2} + O(t^5), \quad (59) \end{aligned}$$

Below we show that the s -expansion method reproduces the $t^{9/2}$ term in Eq. (59).

Although V has no explicit time-dependence for $t > 0$, the potential in the reduced variables has explicit s -dependence, which is

$$V(x, t > 0) = -\delta(x) + \mathcal{E}x = -\frac{\delta(\bar{x})}{s\sqrt{2}} + \mathcal{E}s\bar{x}\sqrt{2}. \quad (60)$$

With the s -dependent potential Eq. (60), the differential equations Eq. (31) become a system of inhomogeneous differential equations:

$$\psi''_{(n)} - 2i\bar{x}\psi'_{(n)} + 2in\psi_{(n)} + 2\sqrt{2}\delta(\bar{x})\psi_{(n-1)} - 4\sqrt{2}\mathcal{E}\bar{x}\psi_{(n-3)} = 0. \quad (61)$$

The boundary conditions for Eq. (61) is the same as Eq. (39), since the initial condition of TDSE does not change from Eq. (1). A general formula for $\psi_{(n)}(\bar{x})$ like Eq. (36) is not available in this case.

Converting the $t^{9/2}$ term in Eq. (59) to (s, \bar{x}) variables, we observe the leading-order time-non-analyticity occurs at fourth order in s , and we solve for $\psi_{(4)}(\bar{x})$ for this time-non-analyticity. Since $\psi_{(4)}(\bar{x})$ depends on all the previous $\psi_{(n)}(\bar{x})$'s as shown in Eq. (61), we need $\psi_{(0)}(\bar{x})$ to $\psi_{(3)}(\bar{x})$ to solve for $\psi_{(4)}$.

In this case, $\psi_{(0)}(\bar{x})$ and $\psi_{(3)}(\bar{x})$ can be obtained easily from Eq. (61). For a more complicated system, there may be more such extra work to do before reaching the leading-order time-non-analyticity, and it is cumbersome having to solve for the first few $\psi_{(n)}$'s which are analytic in time. We observe that though the t -TE wavefunction does not have the correct short-time behavior, it can be used to facilitate the process of obtaining the leading-order time-non-analyticity in $\psi(x, t)$, as described below.

$\psi^{\text{TE}}(x, t)$ of this system is

$$\begin{aligned} \psi^{\text{TE}}(x, t) = \psi_0(x) & \left[1 - it \left(-\frac{1}{2} + \mathcal{E}x \right) \right. \\ & \left. - \frac{t^2}{2} \left(\frac{1}{4} + \mathcal{E} \text{sgn}(x) - \mathcal{E}x + \mathcal{E}^2 x^2 \right) \right] + O(t^3). \quad (62) \end{aligned}$$

Converting Eq. (62) to (s, \bar{x}) variables and collecting the s^n terms gives a set of $\psi_{(n)}^{\text{TE}}(\bar{x})$. $\psi_{(n)}^{\text{TE}}$ for $n = 0 \sim 4$ are listed below:

$$\begin{aligned} \psi_{(n=0,1,2)}^{\text{TE}}(\bar{x}) & = \psi_{(n), \mathcal{E}=0}^{\text{TE}}(\bar{x}) \\ \psi_{(3)}^{\text{TE}}(\bar{x}) & = \psi_{(3), \mathcal{E}=0}^{\text{TE}}(\bar{x}) - i\sqrt{2}\mathcal{E}\bar{x}, \\ \psi_{(4)}^{\text{TE}}(\bar{x}) & = \psi_{(4), \mathcal{E}=0}^{\text{TE}}(\bar{x}) - \mathcal{E} \text{sgn}(\bar{x}) \left(\frac{1}{2} - 2i\bar{x}^2 \right), \quad (63) \end{aligned}$$

with $\psi_{(n), \mathcal{E}=0}^{\text{TE}}(\bar{x}) = (n!)^{-1} \partial^n [\psi_0(s, \bar{x}) \exp(is^2/2)] / \partial s^n |_{s=0}$.

$\psi_{(0)}^{\text{TE}}(\bar{x})$ to $\psi_{(3)}^{\text{TE}}(\bar{x})$ satisfy both the differential equations Eq. (61) and the boundary conditions Eq. (39), which is expected since the outer-expansion Eq. (59) suggests the leading-order time-non-analyticity does not occur until $\psi_{(4)}$. Inserting $\psi_{(4)}^{\text{TE}}(\bar{x})$ into the left hand side of Eq. (61) yields $-\mathcal{E}\delta'(\bar{x})$, showing that $\psi_{(4)}^{\text{TE}}(\bar{x})$ does not satisfy the differential equation. Then we only need to solve the differential equations starting from $\psi_{(4)}(\bar{x})$.

We define the difference between $\psi_{(4)}$ and $\psi_{(4)}^{\text{TE}}$ as

$$\Delta(\bar{x}) = \psi_{(4)}(\bar{x}) - \psi_{(4)}^{\text{TE}}(\bar{x}). \quad (64)$$

Then Eq. (61) in terms of Δ becomes

$$\Delta'' - 2i\bar{x}\Delta' + 8i\Delta - \mathcal{E}\delta'(\bar{x}) = 0. \quad (65)$$

We obtain the complete asymptotic expansion of the general solution Δ_g for $\bar{x} \rightarrow \infty$ by the method of dominant balance (as described in Sect. IV A):

$$\begin{aligned} \Delta_g(\bar{x}) \sim c_1 & \left(\bar{x}^4 + 3i\bar{x}^2 - \frac{3}{4} \right) \\ & + c_2 \frac{\exp(i\bar{x}^2)}{\bar{x}^5} \left[1 + \frac{1}{3\bar{x}^2} \sum_{m=0}^{\infty} \frac{(2m+6)!(-i)^{m+1}}{(m+1)!2^{2m+5}} \bar{x}^{-2m} \right], \quad (66) \end{aligned}$$

in which c_1 and c_2 are coefficients to be determined later. We apply a Borel summation to Eq. (66), which yields the exact formula for $\Delta_g(\bar{x})$:

$$\begin{aligned} \Delta_g(\bar{x}) = c_1 & (\bar{x}^4 + 3i\bar{x}^2 - 3/4) + c_2 \left[-\frac{1}{3} \exp(i\bar{x}^2) \bar{x} (5i + 2\bar{x}^2) \right. \\ & \left. + \frac{1-i}{6} \sqrt{\frac{\pi}{2}} (-3 + 12i\bar{x}^2 + 4\bar{x}^4) \text{erfc}(\sqrt{i}\bar{x}) \right]. \quad (67) \end{aligned}$$

The coefficients c_1 and c_2 are determined using the boundary conditions Eq. (39), yielding

$$\begin{aligned} \psi_{(4)}(\bar{x}) &= \frac{1}{6}\bar{x}^4 + \frac{1}{2}i\bar{x}^2 - \frac{1}{8} \\ &- \mathcal{E} \left\{ \frac{2}{3}\bar{x}^4 \operatorname{sgn}(\bar{x}) + \frac{\sqrt{i}}{3\sqrt{\pi}} \exp(i\bar{x}^2)\bar{x}(5i + 2\bar{x}^2) \right. \\ &\quad \left. + \left(\frac{2}{3}\bar{x}^4 + 2i\bar{x}^2 - \frac{1}{2} \right) \operatorname{erf}(\sqrt{i}\bar{x}) \right\}. \end{aligned} \quad (68)$$

We obtain the leading time-non-analytic term in the outer-region expansion similarly as in Sect. IV A, which is verified by Eq. (59).

Unlike Eq. (59), no expansion in powers of \mathcal{E} was needed. Eq. (61) shows that $\psi_{(6)}(\bar{x})$ contains the first \mathcal{E}^2 term, and $\psi_{(9)}(\bar{x})$ the first \mathcal{E}^3 term.

C. Time-varying nuclear charge

Here we discuss a more subtle restriction of the method. We study a 1D system with Eq. (1) as the initial wavefunction, and with the following potential:

$$V(x, t) = -[1 + \epsilon\theta(t)]\delta(x). \quad (69)$$

In this system, the strength of the δ -well changes at $t = 0$, causing the shape of the cusp at $x = 0$ to change. The analytic form of the exact wavefunction can be written out, and the exact leading order time-non-analytic term is

$$-\sqrt{\frac{i}{2\pi}} \epsilon [2 + (1 + \epsilon)|x|] e^{ix^2/(2t)} x^{-2} t^{3/2}. \quad (70)$$

However, that derived with the method in Sect. III is

$$-\sqrt{\frac{2i}{\pi}} \epsilon e^{ix^2/(2t)} x^{-2} t^{3/2}, \quad (71)$$

which is only a part of Eq. (70). The reason for this discrepancy is that there are two time-scales in the short-time behavior of this system, one is determined by the cusp in the initial wavefunction, and the other one is determined by the δ -well whose strength has changed. The simple boundary-layer analysis in Sect. I does not apply here, as the boundary layer structure is too complicated here.

V. APPLICATIONS IN 3D

The essential methodology remains the same when turning to 3D, but the equations become substantially more complex. For brevity, we normalize 3D wavefunctions to π instead of 1.

A. Vanishing nucleus

One point needs to be changed for the s -expansion method in 3D. Consider a system whose initial wavefunction equals the ground-state wavefunction of the hydrogen atom:

$$\psi_0(\mathbf{r}) = \exp(-r). \quad (72)$$

Free-propagation of this wavefunction yields a similar situation as in the 1D vanishing nucleus case, as the system is effectively 1D due to the spherical symmetry. By expanding the initial wavefunction Eq. (72) as

$$\psi(s, \bar{r}) \stackrel{s \rightarrow 0^+}{\sim} 1 - s\sqrt{2}\bar{r} + s^2\bar{r}^2 + \dots, \quad (73)$$

We only obtain one boundary condition ($\psi_{(n)}(\bar{r} \rightarrow \infty)$) for Eq. (31) instead of two boundary conditions as in 1D cases ($\psi_{(n)}(\bar{x} \rightarrow \pm\infty)$). Eq. (31) requires another boundary condition to be well-defined, and it is related to how t -TE behaves in 3D cases. For the 3D vanishing nucleus case, the t -TE wavefunction is

$$\begin{aligned} \psi^{\text{TE}}(\mathbf{r}, t) &= \exp(-r + it/2) \left(1 - \frac{it}{r} \right) \\ &= 1 - \frac{i + 2\bar{r}^2}{\sqrt{2}\bar{r}} s + \frac{3i + 2\bar{r}^2}{2} s^2 + O(s^3). \end{aligned} \quad (74)$$

Unlike in the 1D examples, all $\psi_{(n)}^{\text{TE}}(\bar{\mathbf{r}})$ satisfy Eq. (31), but $\psi_{(1)}^{\text{TE}}(\bar{\mathbf{r}})$ diverges at $\bar{r} = 0$ for any non-zero time. Thus the other boundary condition for Eq. (31) is $\psi_{(n)}(\bar{\mathbf{r}})$ must be regular at $\bar{r} = 0$.

B. Suddenly switched electric field

We discussed 3D systems in our previous paper[9]. Here we provide a more detailed derivation for 3D hydrogen atom in a turned-on static electric field. Aside from the dimensionality change, the main change from 1D cases to 3D cases is that the Coulomb potential replaces the δ -function potential as the singular potential. Unlike the δ -function potential, the Coulomb potential is long-ranged, which makes 3D wavefunctions more complicated than their 1D counterparts.

The system has the following potential:

$$V(\mathbf{r}, t) = -\frac{1}{r} + \mathcal{E}z\theta(t). \quad (75)$$

One can easily check with perturbation theory that the t -TE wavefunction of this system does not have a convergent norm, and thus it must have time-non-analyticities. Define reduced variables:

$$s = \sqrt{t}, \quad \bar{r} = \frac{r}{\sqrt{2t}}, \quad \bar{z} = \frac{z}{\sqrt{2t}}. \quad (76)$$

The external potential in these reduced variables is

$$V(\mathbf{r}, t > 0) = -\frac{1}{\sqrt{2}s\bar{r}} + \mathcal{E}\sqrt{2}s\bar{z}. \quad (77)$$

Inserting the wavefunction ansatz Eq. (30) into Eq. (31) yields

$$(\mathcal{L} + 2in)\psi_{(n)} + \frac{2\sqrt{2}}{\bar{r}}\psi_{(n-1)} - 4\sqrt{2}\mathcal{E}\bar{z}\psi_{(n-3)} = 0, \quad (78)$$

where

$$\mathcal{L} = \frac{\partial^2}{\partial \bar{r}^2} + \frac{\partial^2}{\partial \bar{z}^2} + \left(1 + \bar{z} \frac{\partial}{\partial \bar{z}}\right) \frac{2}{\bar{r}} \frac{\partial}{\partial \bar{r}} - 2i \left(\bar{r} \frac{\partial}{\partial \bar{r}} + \bar{z} \frac{\partial}{\partial \bar{z}}\right). \quad (79)$$

For $\mathcal{E} = 0$, the TE is simple, and

$$\psi_{(n), \mathcal{E}=0}^{\text{TE}}(\bar{\mathbf{r}}) = (n!)^{-1} \partial^n [\psi_0(s, \bar{\mathbf{r}}) \exp(is^2/2)] / \partial s^n |_{s=0}. \quad (80)$$

In the presence of the electric field,

$$\psi_{(n)}^{\text{TE}}(\bar{\mathbf{r}}) = \psi_{(n), \mathcal{E}=0}^{\text{TE}}(\bar{\mathbf{r}}) + i\mathcal{E}\bar{z}f_{(n)}(\bar{r}), \quad n \leq 4, \quad (81)$$

with

$$f_{(n \leq 2)} = 0, \quad f_{(3)} = -\sqrt{2}, \quad f_{(4)}(\bar{r}) = 1/(12\bar{r}^3) + 1/(2\bar{r}) + 2\bar{r}. \quad (82)$$

The $\psi_{(n)}^{\text{TE}}(\bar{\mathbf{r}})$'s before the occurring of the leading-order time-non-analyticity are identical to $\psi_{(n)}(\bar{\mathbf{r}})$, and we only need to solve for $\psi_{(n)}(\bar{\mathbf{r}})$ if $\psi_{(n)}^{\text{TE}}(\bar{\mathbf{r}})$ fails to satisfy the differential equation Eq. (78) and the boundary conditions. Since $\psi_{(4)}^{\text{TE}}(\bar{\mathbf{r}})$ diverges as $\bar{r} \rightarrow 0$, the leading-order time-non-analyticity is in $\psi_{(4)}(\bar{\mathbf{r}})$.

As before, we use the method of dominant balance and Borel summation to solve for $\Delta(\bar{\mathbf{r}}) = \psi_{(4)}(\bar{\mathbf{r}}) - \psi_{(4)}^{\text{TE}}(\bar{\mathbf{r}})$. Since $\psi_{(4)}^{\text{TE}}$ satisfies Eq. (78), the equation can be rewritten as

$$(\mathcal{L} + 8i)\Delta = 0, \quad (83)$$

As $\bar{r} \rightarrow 0$, the divergence in $\psi_{(4)}^{\text{TE}}$ is proportional to \bar{z} , and $\Delta(\bar{\mathbf{r}})$ must cancel this divergence to satisfy the boundary conditions. Therefore $\Delta(\bar{\mathbf{r}})$ has the following form:

$$\Delta(\bar{r}, \bar{z}) = g(\bar{r})\bar{z}. \quad (84)$$

The method of dominant balance(Sect. IV A) yields the entire asymptotic expansion of $g(\bar{\mathbf{r}})$:

$$g(\bar{\mathbf{r}}) = c_1 \left(\bar{r}^3 + \frac{9i\bar{r}}{2} - \frac{9}{4\bar{r}} + \frac{3i}{8\bar{r}^3} \right) + c_2 \frac{\exp(i\bar{r}^2)}{\bar{r}^8} \left[1 + \frac{1}{9\bar{r}^2} \sum_{m=0}^{\infty} \frac{(-i)^{m+1}(m+4)(2m+6)!}{(m+1)!2^{2m+5}\bar{r}^{2m}} \right]. \quad (85)$$

Performing the Borel sum, we find

$$g(\bar{\mathbf{r}}) = c_1 \left(\bar{r}^3 + \frac{9i\bar{r}}{2} - \frac{9}{4\bar{r}} + \frac{3i}{8\bar{r}^3} \right) + c_2 \frac{\sqrt{2i}}{72\bar{r}^3} \left[2\sqrt{2i} \exp(i\bar{r}^2) \bar{r} (-3 + 16i\bar{r}^2 + 4\bar{r}^4) - \sqrt{2\pi} (3i - 18\bar{r}^2 + 36i\bar{r}^4 + 8\bar{r}^6) \operatorname{erfc} \left(\sqrt{i}^* \bar{r} \right) \right]. \quad (86)$$

The coefficients c_1 and c_2 are determined by the boundary conditions as $\bar{r} \rightarrow 0$ and $\bar{r} \rightarrow \infty$, yielding

$$c_1 = 0, \quad c_2 = -\sqrt{\frac{i}{\pi}}^* \mathcal{E}. \quad (87)$$

Expanding $s^4\psi_{(4)}(\bar{r})$ for $\bar{r} \rightarrow \infty$ yields the outer-region expansion:

$$\psi_{(4)}^{\text{outer}}(\mathbf{r}, t) \stackrel{\bar{r} \rightarrow \infty}{\sim} \dots - \frac{8\sqrt{2i}^* \mathcal{E} z}{\sqrt{\pi} r^8} \exp\left(\frac{ir^2}{2t}\right) t^{11/2}. \quad (88)$$

Although $\psi_{(4)}(s, \bar{\mathbf{r}})$ contains the leading order time-non-analyticity in the wavefunction, knowing it is insufficient[9] to derive the correct coefficient of the leading half-power in the TD dipole moment (Sec. VI). Due to the coupling between \mathbf{r} and t in the wavefunction, higher order terms in the s -expansion can contribute to integrated properties such as the TD dipole moment. We have evidence that both $\psi_{(4)}$ and $\psi_{(5)}$ contribute, but we have been unable to find a closed-form expression for $\psi_{(5)}$.

Finally, we obtain the leading-order time-non-analytic term in the outer-region expansion of this system by applying the stationary phase approximation (as in Sect. II B) to 1st order in $\delta V^{<1>}(\mathbf{r}', t') = z'\theta(t')$. The change in the wavefunction(sans \mathcal{E}) is

$$\psi^{<1>}(\mathbf{r}, t) = i \int d^3 r' G^{<1>}(\mathbf{r}, \mathbf{r}', t) \psi^{<0>}(\mathbf{r}', 0) \quad (89)$$

in which $\psi^{<0>}$ is the ground-state wavefunction of 3D hydrogen, and

$$G^{<1>}(\mathbf{r}, \mathbf{r}', t) = \int d^3 r'' \int_0^t dt'' G^{<0>}(\mathbf{r}, \mathbf{r}'', t - t'') \times \delta V^{<1>}(\mathbf{r}'', t'') G^{<0>}(\mathbf{r}'', \mathbf{r}', t''), \quad (90)$$

is the 1st order change of the Green's function, with

$$G^{<0>}(\mathbf{r}, \mathbf{r}', t) = -i \sum_n \exp(-i\epsilon_n t) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}'), \quad (91)$$

where ψ_n and ϵ_n are atomic orbitals and orbital energies of the 3D hydrogen atom respectively. Only the well-known[23] unbound p orbitals in the sum of Eq. (91) contribute to the time-non-analyticity in $\psi^{<1>}$, and the sum in Eq. (91) becomes an integration for unbound orbitals. Applying the stationary phase approximation(as in Sect. II B) to this integration, we obtain the leading non-analytic short-time behavior shown in Eq. (88).

VI. DIPOLE MOMENTS

Our results so far, using the s -expansion, have been for the time-dependent wavefunction. There is no simple result for its short-time dependence, due to the existence of

distinct expansions in the inner and outer regions. However, expectation values over wavefunctions *do* have well-defined expansions for small times, although more complex than a simple Taylor expansion.

In the present section, we extract results for dipole moments induced by turning on an electric field, in both 1D and 3D. Note that our s -expansion is not a perturbation expansion in the applied field, but rather demonstrates that the leading corrections to the wavefunction for short-time behavior are linear in the applied field. On the other hand, we deduce dipole moments only within linear-response theory, but we find consistent results, as shown below.

A. Linear response theory

The linear(1st order) change in the density $\delta n(\mathbf{r}, t)$ is described by the linear response function χ and its Fourier transform $\tilde{\chi}$:

$$\begin{aligned}\chi(\mathbf{r}, \mathbf{r}', t - t') &= \frac{\delta n(\mathbf{r}, t)}{\delta v(\mathbf{r}', t')}, \\ \tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega) &= \int_{-\infty}^{\infty} d\tau \chi(\mathbf{r}, \mathbf{r}', \tau) e^{i\omega\tau}.\end{aligned}\quad (92)$$

For one particle systems, there is a simple relation between $\tilde{\chi}$ and the frequency-domain Green's function \tilde{G} [24]:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sqrt{n(\mathbf{r})n(\mathbf{r}')} \left[\tilde{G}(\mathbf{r}, \mathbf{r}', \omega + \epsilon_0) + \tilde{G}^*(\mathbf{r}, \mathbf{r}', \epsilon_0 - \omega) \right], \quad (93)$$

where ϵ_0 is the ground-state energy of the system. Aside from the definition Eq. (92), the linear response function can also be expressed in the Lehmann representation:

$$\begin{aligned}\tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega) &= \lim_{\eta \rightarrow 0^+} \sum_j \left\{ \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_j \rangle \langle \Psi_j | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{\omega - \omega_j + i\eta} \right. \\ &\quad \left. + \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}') | \Psi_j \rangle \langle \Psi_j | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{-\omega - \omega_j - i\eta} \right\},\end{aligned}\quad (94)$$

where Ψ is the many-body eigen wavefunction of the corresponding system labeled with j , and $\omega_j = \epsilon_j - \epsilon_0$ is the transition frequency between state j and the ground state. For a system with only a discrete spectrum, one can take $\omega \rightarrow \infty$ for each separate term, yielding $O(\omega^{-2})$ high-frequency behavior[25]. But when the system has a continuum, the sum must be performed before taking the $\omega \rightarrow \infty$ limit, and this produces fractional decay.

Consider a perturbation potential $\mathcal{E}x\theta(t)$. The 1st order dipole moment(sans \mathcal{E}) is

$$\mu_x^{<1>}(t) = \int_0^t dt' \int d^3r \int d^3r' xx' \chi(\mathbf{r}, \mathbf{r}', t - t'), \quad (95)$$

and its transform, the polarizability in x direction is

$$\alpha_{xx}(\omega) = \int d^3r \int d^3r' xx' \tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega). \quad (96)$$

The subscripts denotes the direction on which these observables are measured. $\alpha_{xx}(\omega)$ and $\mu_x^{<1>}(t)$ are related by Fourier transform, and the high-frequency behavior of $\alpha_{xx}(\omega)$ depends on the short-time behavior of $\mu_x^{<1>}(t)$.

B. Known results

The high-frequency part of the photoabsorption cross-section of all atoms decays as $\omega^{-7/2}$ [26–28], which means that the $\Im\alpha$ decays as $\omega^{-9/2}$ (\Im denotes the imaginary part). For hydrogen-like atoms, $\Im[\alpha(\omega \rightarrow \infty)]$ is[26]

$$\Im[\alpha(\omega)] \stackrel{\omega \rightarrow \infty}{\sim} \frac{4\sqrt{2}}{3\omega^{9/2}}, \quad (97)$$

where α is a spherical average. Thus

$$\mu^{<1>}(t) \stackrel{t \rightarrow 0^+}{\sim} \frac{2}{\pi} \int_0^t dt' \int_{\omega_c}^{\infty} d\omega \Im[\alpha(\omega)] \sin[\omega(t - t')], \quad (98)$$

where $\omega_c \gg 1$ is a cut-off, yielding

$$\begin{aligned}\mu^{<1>}(t) \stackrel{t \rightarrow 0^+}{\sim} \int_0^t dt' \left\{ \frac{16\sqrt{2}(t - t')}{15\pi\omega_c^{5/2}} - \frac{8\sqrt{2}(t - t')^3}{9\pi\omega_c^{1/2}} \right. \\ \left. + \frac{128(t - t')^{7/2}}{315\sqrt{\pi}} \right\} + \dots,\end{aligned}\quad (99)$$

As $\omega_c \rightarrow \infty$, we find the leading time-non-analytic term in $\mu^{<1>}(t \rightarrow 0_+)$:

$$\mu^{<1>}(t) \stackrel{t \rightarrow 0^+}{\sim} \dots + \frac{256}{2835\sqrt{\pi}} t^{9/2} + \dots \quad (100)$$

C. Origins of non-analyticity and relation to time-dependence

To trace clearly the origin of these non-analytic behaviors, we begin with the simplest case, a free particle in 1D. The green's function is simply

$$\tilde{G}^{\text{free}}(x, x', \omega) = \frac{\exp(iku)}{ik}, \quad (101)$$

where $u = |x - x'|$ and $k = \sqrt{2\omega}$. Insertion into Eq. (93) yields $\tilde{\chi}$:

$$\tilde{\chi}^{\text{free}}(x, x', \omega) = -\frac{\exp(-ku) + i \exp(iku)}{k}. \quad (102)$$

Even for a free particle, there are non-analytic behaviors in the frequency-dependent response due to the continuum, which are not apparent in the Lehmann representation Eq. (94).

Our next example is the 1D H atom. Here

$$\begin{aligned}G^{\text{1DH}}(x, x', \tau) &= -i\sqrt{\frac{1}{2\pi i\tau}} \exp\left[\frac{i u^2}{2\tau}\right] \\ &\quad - \frac{i}{2} \exp\left(\frac{i\tau}{2} - X\right) \operatorname{erfc}\left(\frac{X}{\sqrt{2i\tau}} - \sqrt{\frac{i\tau}{2}}\right),\end{aligned}\quad (103)$$

where $X = |x| + |x'|$, leading to a response function of the form:

$$\tilde{\chi}^{1\text{DH}}(x, x', \omega) = -i \exp(-X) \left[\frac{\exp(iu\kappa_+)}{\kappa_+} - \frac{\exp(iX\kappa_+)}{i\kappa_+^2 + \kappa_+} - \frac{\exp(-iu\kappa_-^*)}{\kappa_-^*} - \frac{\exp(-iX\kappa_-^*)}{i\kappa_-^2 - \kappa_-^*} \right], \quad (104)$$

where $\kappa_{\pm} = \sqrt{\pm 2\omega - 1}$. Eq. (104) clearly has non-analytic behavior for large ω .

For a 1D H atom in a turned-on linear electric field, we can explicitly calculate the 1st order perturbative wavefunction (sans \mathcal{E}):

$$\psi^{<1>}(x, t) = \sqrt{\frac{i}{\pi}} \exp[i\bar{x}^2] \bar{x} t + \frac{\exp(it/2)}{2} \{ h_+(x, t) + h_-(x, t) \} + [(|x| + t^2) \sinh(x) - x(|x| + 2it) \cosh(x)], \quad (105)$$

where $h_{\pm}(x, t) = -\exp(\pm x)(x \mp y_{\pm}^2) \text{erf}[\sqrt{i/(2t)}^* y_{\pm}] / 2$, with $y_{\pm} = \pm x + it$, and $\bar{x} = x/\sqrt{2t}$ as before.

The induced first-order time-dependent dipole moment (sans \mathcal{E}) $\mu^{<1>}$ is related to $\psi^{<1>}$ by

$$\mu^{<1>}(t) = 2\Re \langle \psi^{<0>} | x | \psi^{<1>} \rangle, \quad (106)$$

(\Re denotes the real part) so $\mu^{<1>}$ of this system is then

$$\begin{aligned} \mu^{<1>}(t) = & -\frac{t^2}{12}(t^2 + 6) + \frac{\sqrt{t} \cos(t/2)}{12\sqrt{\pi}}(t^3 - 3t^2 + 7t + 15) \\ & - \frac{\sqrt{t} \sin(t/2)}{12\sqrt{\pi}}(t^3 + 3t^2 + 7t - 15) \\ & + 2\Re \left\{ \frac{1}{24}(t^4 - 4it^3 + 6t^2 + 12it - 15) \text{erf} \left(\sqrt{\frac{it}{2}} \right) \right\}. \end{aligned} \quad (107)$$

The leading short-time behavior is

$$\mu^{<1>}(t) \stackrel{t \rightarrow 0^+}{\sim} -\frac{t^2}{2} + \frac{32}{105\sqrt{\pi}} t^{7/2} - \frac{t^4}{12} + O(t^{9/2}). \quad (108)$$

To see the connection with the s -expansion in this case, we note simply that the 4-th order contribution Eq. (68), inserted in Eq. (106), recovers the same leading non-analytic behavior. Thus, here, the leading-order non-analyticity in the wavefunction is sufficient to determine the leading-order non-analyticity in the dipole moment, at least to first-order in the external electric field.

VII. MORE GENERAL POTENTIALS

Here we explore what happens for other potentials.

A. Different spatial dependence

We provide a heuristic demonstration that the time-non-analyticities originate from the specific form of the TDSE, and show that the time-non-analyticity of the time-dependent wavefunction is determined by the space-non-analyticity of the initial wavefunction.

Consider a perturbed 1D one-electron model system described by the following potential:

$$V(x, t) = V_0(x) + \mathcal{E} x^n \theta(t). \quad (109)$$

The structure of the problem is exposed by taking a space-Fourier transform and a time-Laplace transform of the TDSE:

$$\begin{aligned} \frac{k^2}{2} \tilde{\Psi}(k, \nu) + V_0(k) * \tilde{\Psi}(k, \nu) + \mathcal{E} i^n \tilde{\Psi}^{(n)}(k, \nu) \\ - i\nu \tilde{\Psi}(k, \nu) + i\Psi_0(k) = 0, \end{aligned} \quad (110)$$

where $\tilde{\Psi}(k, \nu)$ is the time-Laplace and spatial Fourier transform of $\psi(x, t)$, $\Psi_0(k)$ is the spatial Fourier transform of $\psi_0(x)$, $*$ denotes convolution, and the superscript (n) denotes n -th order derivative with respect to k . For analytic $V_0(x)$, the $V_0(k) * \tilde{\Psi}(k, \nu)$ term is composed of derivatives of $\tilde{\Psi}(k, \nu)$. Our goal is to find out the short-time behavior of the time-dependent wavefunction. Dividing through by ν and taking ν large, the highest derivative is multiplied by a small parameter, and the solution of such an equation has a so-called boundary layer behavior[18, 19]. This means the solution changes its behavior rapidly in a narrow region whose thickness is determined by the small parameter. Using boundary layer theory, we obtain a very crude estimate of the outer-region expansion of the time-dependent wavefunction by dropping all derivative terms[18]:

$$\frac{k^2}{2} \tilde{\Psi}(k, \nu) - i\nu \tilde{\Psi}(k, \nu) + i\Psi_0(k) = 0, \quad (111)$$

yielding

$$\tilde{\Psi}(k, \nu) = -\frac{2i\Psi_0(k)}{k^2 - 2i\nu}. \quad (112)$$

This specific pole structure is due to the specific form of the TDSE, that of a 2nd order differential equation in space, but a 1st order differential equation in time. This pole structure generates the time-non-analyticities shown in the previous examples. One recognizes this by doing the inverse Laplace/Fourier transform of the pole:

$$\psi(x, t) = \sqrt{\frac{i}{\pi t}}^* \exp\left(\frac{ix^2}{2t}\right), \quad \text{for } \Psi_0(k) = 1. \quad (113)$$

Though the form of the TDSE implies time-non-analyticities, such non-analyticities do not show up in every system. If the initial wavefunction is analytic in space, then the time-dependent wavefunction of the

system described by Eq. (109) is analytic in time; if the initial wavefunction has cusps, the time-dependent wavefunction is not time-analytic, and the time-non-analyticities have the form $t^{n/2}$ and $\exp[ix^2/(2t)]$.

The inverse Laplace transform of Eq. (112) is

$$\Psi(k, t) \sim -\exp(-ik^2 t/2)\Psi_0(k). \quad (114)$$

The outer-region asymptotic behavior of $\psi(x, t \rightarrow 0_+)$ is obtained from the inverse Fourier transform of Eq. (114):

$$\psi(x, t) \sim -\frac{\exp[ix^2/(2t)]}{\sqrt{it}} * \Psi_0(x), \quad (115)$$

in which $*$ denotes convolution. If $\psi(x, t)$ is space-analytic, it equals its Taylor expansion:

$$\psi_0(x) = \sum_{j=0}^{\infty} \frac{\psi_0^{(j)}(0)}{j!} x^j, \quad (116)$$

where $\psi_0^{(j)}$ here denote j -th order space derivative of ψ_0 . Then the convolution in Eq. (115) can be evaluated term by term, with the j -th term being proportional to

$$t^{(j-1)/2} {}_1F_1\left(\frac{l-j}{2}; \frac{1}{2} + l; \frac{ix^2}{2t}\right), \quad l = \frac{1 - (-1)^j}{2}, \quad (117)$$

where ${}_1F_1$ is Kummer's confluent hypergeometric functions[20]. The ${}_1F_1$'s in Eq. (117) are polynomials that involve only positive integer powers of t , so there are no time-non-analyticities starting from a space-analytic initial wavefunction for the model system Eq. (109).

For initial wavefunctions with cusps, we modify Eq. (116) to be:

$$\psi_0'(x) = \sum_{j=0, j \neq m}^{\infty} \frac{\psi_0^{(j)}(0)}{j!} x^j + cx^m[\theta(x) - \theta(-x)], \quad (118)$$

which contains a derivative discontinuity (i.e., 'cusp') in the m -th order. The convolution in Eq. (115) for the $\theta(x)$ part of Eq. (118) is proportional to

$$t^{m/2} {}_1F_1\left(-\frac{m}{2}; \frac{1}{2}; \frac{ix^2}{2t}\right) + t^{(m-1)/2} {}_1F_1\left(\frac{1-m}{2}; \frac{3}{2}; \frac{ix^2}{2t}\right). \quad (119)$$

The convolution with the $\theta(-x)$ part yields a similar result. As in previous case, the ${}_1F_1$'s in Eq. (119) are regular polynomials. Eq. (119) contains t -half-powers for all values of m , and thus the initial wavefunction with cusps has time-non-analyticities in its short-time behavior for the model system Eq. (109).

We provide the free-propagation of a Gaussian initial wavefunction as an example in which there is no non-analytic short-time behavior starting from a smooth initial wavefunction. The initial wavefunction is

$$\psi_0(x) = \frac{\exp[-x^2/(2\sigma^2)]}{\pi^{1/4}\sqrt{\sigma}}, \quad (120)$$

in which σ characterizes the width of the Gaussian. Combining Eq. (114) and Eq. (115) yields

$$\psi(x, t) \sim -\frac{i\sqrt{2\sigma}\pi^{1/4}}{\sqrt{t-i\sigma^2}} \exp\left[\frac{ix^2}{2(t-i\sigma^2)}\right]. \quad (121)$$

Eq. (121) has no time-non-analyticities at the initial time. The radius of convergence of the t -TE at the initial time is σ^2 . In the limit of $\sigma \rightarrow 0$, the Gaussian becomes a δ -function and no longer smooth. The pole in Eq. (121) coincides with $t = 0$, and as a consequence the radius of convergence of the t -TE becomes exactly zero (just as in Sect. IIC).

B. Different time dependence

Next we consider cases other than sudden switching. For ease of discussion, we limit ourselves to 1D systems with the following time-dependent potential:

$$V(x, t) = -\delta(x) + V_a(x) + \mathcal{E}\delta V^{<1>}(x, t), \quad (122)$$

where $V_a(x)$ is an analytic potential, $\delta V^{<1>}(x, t) = x^n f(t)$, and $f(t)$ determines how the perturbation is turned on. At $t = 0$, the system starts in the ground state $\psi_0(x)$ of potential $-\delta(x) + V_a(x)$, which has a cusp at $x = 0$ due to the δ -function part of the potential.

To show that the information at the cusp is enough to determine the leading half-power term in time, we make a drastic approximation: the wavefunction is approximated by an envelope function for all $x \neq 0$. Write

$$\psi_0(x) = g(ax) \sum_{j=0}^{\infty} d_j x^j, \quad (123)$$

where $g(x)$ is some decaying envelope function, a is a positive constant, and d_j 's are the Taylor coefficients of $\psi_0(x)/g(ax)$. Choosing $g(x) = \exp(-|x|)$ and applying Kato's cusp condition[29], we obtain

$$\begin{aligned} \psi_0(x) = \exp(-a|x|) & \left\{ \psi_0'(0_-) - \psi_0'(0_+) \right. \\ & + x[\psi_0'(0_+) + a(\psi_0'(0_-) - \psi_0'(0_+))] \\ & \left. + x^2[a\psi_0'(0_+) + a^2(\psi_0'(0_-) - \psi_0'(0_+)) + \psi_0''(0_+)] + \dots \right\} \end{aligned} \quad (124)$$

We can still use Eq. (98) for the dipole moment even though the potential is more general, by defining $\Im[\hat{\alpha}(\omega)]$ in analog of the dynamic polarizability as

$$\Im[\hat{\alpha}(\omega \rightarrow \infty)] \sim \mathcal{E}\pi \langle \psi_0 | x | \psi_{k_\omega} \rangle \langle \psi_{k_\omega} | \delta V^{<1>}(x, \omega) | \psi_0 \rangle, \quad (125)$$

where ψ_{k_ω} is the continuum wavefunction whose energy difference to the ground state is ω , and $\delta V^{<1>}(x, \omega)$ is the Fourier transform of $\delta V^{<1>}(x, t)$. Inserting Eq. (125) into Eq. (98), we find that there is one term of the result which does not depend on the cut-off ω_c and the envelope

parameter a , which is the term of the leading time-non-analyticity. This result does not depend on which smooth decaying envelope function is chosen for $g(x)$.

In previous examples, the time-dependent perturbation is always turned-on with $f(t) = \theta(t)$, allowing the possibility that the time-non-analyticity is related to this specific turning-on method. Here we test different turn-on functions $f(t)$. If $f(t) = \delta(t)$, we obtain the leading half-power term in $\mu^{<1>}$ as

$$\begin{aligned} \mu^{<1>}(t \rightarrow 0_+) &\sim \dots + 2[\psi'_0(0_+) - \psi'_0(0_-)]^2 \\ &\quad \times \Gamma(-2 - n/2)\Gamma(n+2)t^{2+n/2}2^{-3-n/2} \\ &\quad \times [-1 + (-1)^n](-1 + i^n)\exp(-3in\pi/4) + \dots \end{aligned} \quad (126)$$

In another case, if $f(t) = t^m$, we obtain the leading half-power term as

$$\begin{aligned} \mu^{<1>}(t \rightarrow 0_+) &\sim \dots + -2\frac{[\psi'(0_+) - \psi'(0_-)]^2 \csc(n\pi/2)}{\Gamma(4+m+n/2)} \\ &\quad \times t^{3+m+n/2}2^{-3-n/2}[-1 + (-1)^n](-1 + i^n) \\ &\quad \times \Gamma(1+m)\Gamma(2+n)\exp(-3in\pi/4) + \dots \end{aligned} \quad (127)$$

It is clear that the effect of different turning-on method only changes the order of the non-analytic behavior, so the previously shown time-non-analytic behavior is not the result of the θ -function turning-on. Similarly, the spatial part of the time-dependent perturbation potential also does not need to be in the form of x^n , and it can be easily tested that a perturbation of $\delta V^{<1>}(x, t) = \sin(kx - \omega_0 t)\theta(t)$ also have time-non-analyticities in the short-time behavior of the wavefunction.

C. Onset of non-analytic behavior

A nucleus has a finite radius, and one may argue that the failure of the t -TE due to cusps is artificial. To examine this effect, we provide a numerical example similar to the 1D hydrogen in a turned-on static electric field case, but with a rounded cusp. This is done by substituting the potential in Sect. IV B $-\delta(x) + \mathcal{E}x\theta(t)$ with

$$V(x, t) = -\frac{\exp[-x^2/(2\sigma^2)]}{\sigma\sqrt{2\pi}} + \mathcal{E}x\theta(t). \quad (128)$$

We set $\mathcal{E} = 1$ for the numerical calculation. In the limit of $\sigma \rightarrow 0$, the case in Sect. IV B is recovered. We solve the ground state wavefunction of this system for $t < 0$ on an unevenly distributed grid, which has more points near $x = 0$ to ensure the cusp-like structure in the wavefunction is well-resolved. We propagate the TD wavefunction with the t -TE based Crank-Nicolson method[30], and a sufficiently small time step considering the radius-of-convergence problem. We then calculate the numerical TD dipole moment $\mu(t)$, and fit $\mu(t)$ with

$$\mu(t) \sim ct^2 + \frac{32}{105\sqrt{\pi}}t^{7/2}, \quad (129)$$

which are the first two terms of Eq. (108). In the limit $\sigma \rightarrow 0$, $c = -1/2$; with finite value of σ , we list the corresponding values of c in Table I.

TABLE I. Relation between the coefficient of t^2 in $\mu(t)$ and σ

40σ	1	1/2	1/4	1/8	1/16	1/32
$-1000(c+1/2)$	86.6	41.9	20.1	9.32	3.98	1.32

Table I shows that although the system does not have a cusp, the TD behavior in Sec. IV B heavily influences the TD behavior here. This is hardly surprising as Sec. IV B correspond to the $\sigma \rightarrow 0$ limit. We used the t -TE based propagation scheme in the numerical example, and the $t^{7/2}$ -like behavior is mimicked by all the integer t powers in the t -TE when σ is small. Fig. 5 shows that the $t^{7/2}$ term in Eq. (108) and $\mu(t) - c(\sigma)t^2$ with small σ are nearly identical. Thus the time-non-analyticity is still relevant in numerical situations. On atomic time scale, the time evolution is indistinguishable from that with a cusp.

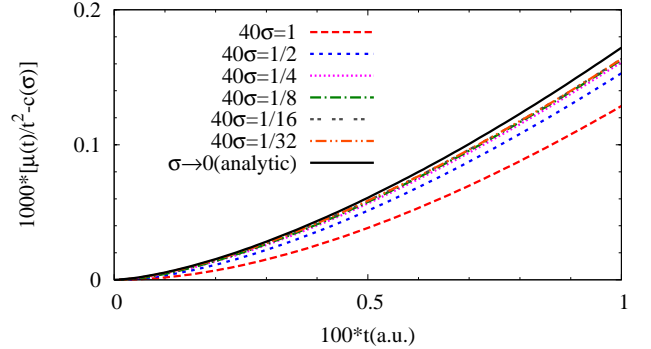


FIG. 5. (Color online) $\mu(t)/t^2 - c(\sigma)$ for σ listed in Table. I and $\sigma \rightarrow 0$. $(32t^{3/2}/(105\sqrt{\pi}))$ is plotted for the $\sigma \rightarrow 0$ curve.) The errors between the exact $\sigma \rightarrow 0$ curve and the fit curves show systematic behavior.

VIII. DISCUSSION: MANY-ELECTRON SYSTEMS AND TDDFT

The original motivation for this study was concern about the fundamentals of time-dependent density functional theory (TDDFT)[2, 3]. Since the proof of a general theorem[7], the number of applications of TDDFT in chemistry and physics has grown phenomenally[31]. In its standard form, TDDFT translates the many-electron problem into a fictitious many-fermion problem *without* interaction between the particles, thereby greatly reducing the computational cost, and allowing calculations with several hundred atoms. While all such applications rely on approximate functionals, their validity as an alternative to solving the time-dependent Schrödinger equation relies on several exact statements and the existence of exact functionals.

The most basic requirement for construction of a formally exact density functional theory is a proof of uniqueness of the one-body potential that can give rise to a given density. The Runge-Gross theorem[7] shows that, for a given initial wavefunction and electron-electron repulsion, there is at most one $v(\mathbf{r}, t)$ that can produce a given $n(\mathbf{r}, t)$ when solving TDSE. Thus $v(\mathbf{r}, t)$ is a functional of $n(\mathbf{r}, t)$. Applying the same logic to the fictitious KS system yields the TD KS equations that can be applied to many-electron systems, once the many-electron effects are approximated in the mysterious exchange-correlation potential. A linear response analysis[32–34] yields an extremely efficient scheme for calculating low-lying electronic excitations in molecules and solids[35].

The proof of Runge-Gross was constructed only for one-body potentials that are analytic in t , and can therefore be Taylor-expanded about $t = 0$. The proof demonstrates that two distinct such potentials must give rise to densities whose n -th derivative at $t = 0$ differ for some finite n .

The present and previous[9] work show that, in the case of a hydrogen atom in a suddenly-switched electric field, the time-dependent density has non-analytic contributions, so that the Taylor series does not converge. Nonetheless, if two densities differ in their j -th time-derivative, they must be different, even if neither matches its Taylor expansion. Thus the uniqueness proof of Runge-Gross remains valid even for such problems.

This suggests these results apply to many-electron atoms, although they have only been proven for one-electron cases. If one considers the TD KS equations for, e.g., a He atom in a suddenly-switched field, in the region of the nucleus, the density, which is a sum of occupied

orbitals, will contain the same features (via the occupied 1s-orbital). However, this argument presupposes the *existence* of such a KS potential for this case.

Even in the simpler ground-state DFT, there are no general conditions on densities known that guarantee that a density is in fact a ground-state density for some electronic problem, although this is rarely a problem in practice, even for strongly correlated systems[36].

A second important theorem in TDDFT was van Leeuwen’s constructive proof of the TD KS potential. Assuming both the density and the potential are Taylor-expandable, a relatively simple procedure yields, power-by-power, a prescription for finding the potential[8]. Clearly, this theorem does not apply to the cases studied here. Since all atoms, molecules and solids have cusps at their nuclei (within the Born-Oppenheimer and point nuclei approximations), this theorem cannot be applied as is to such cases. Earlier work[12] had already shown that such cases could be constructed in 1d, but these could be regarded as pathological. The motivation to develop the s -expansion described here was to convincingly show that such effects are generic, rather than unusual, once the ground-state wavefunction contains spatial cusps. In the last few years, much work toward a proof of existence of the KS potential without a Taylor-expansion has been performed[10, 11].

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