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Nonexistence of a Taylor expansion in time due to cusps

Zeng-hui Yang
Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA

Kieron Burke
Department of Chemistry, University of California-Irvine, Irvine, California 92697, USA

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In the usual treatment of electronic structure, all matter has cusps in the electronic density at nuclei. Cusps can produce nonanalytic behavior in time, even in response to perturbations that are time analytic. We analyze these nonanalyticities 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].

However, 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 noninteracting 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 noninteracting v representable [2,3]). Groundbreaking 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 latter 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 nonexpandability 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 noninterchangeability 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 that 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 one-dimensional (1D) disappearing nucleus, from many different viewpoints. Although this is not a 3D 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 that 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 wave function, finding its behavior 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 TDDFT.

II. WHEN NUCLEI VANISH

Here we study the failure of the Taylor series in the simplest possible case, first studied in Ref. [12]. In 1D, we begin at $t = 0$ with a wave function,

$$\psi_0(x) = \exp(-|x|), \tag{1}$$

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

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} \tag{2}$$

and find

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

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

$$\exp[-i\hat{H}t] \overset{?}{=} 1 - i\hat{H}t - \hat{H}^2t^2/2 + \cdots. \tag{4}$$

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 wave function with the Taylor-expanded time-evolution operator,

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

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 wave function 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 Runge-Gross theorem.

In this case, it is simple to find the true wave function. The free-particle propagator in 1D is

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

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

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

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. Figure 1 confirms that the wave function 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 nonanalyticity throughout the paper. We analyze the time nonanalyticity in detail in Sec. III.

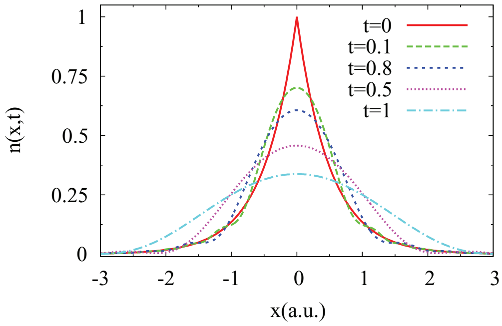

FIG. 1. (Color online) Time-dependent density of an exponential that propagates freely after $t = 0$. The Taylor expansion fails to change from its $t = 0$ value.

In practice, we observe that the t-TE wave function works when the initial wave function is space analytic, from which wave functions 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 wave function requires the initial wave function to be differentiable to infinite order at any space point. However, infinite-order differentiable does not guarantee the validity of the t-TE wave function: The wave function is differentiable in the distributional sense in the case of cusps; in another case [17], one can construct a nontrivial wave packet where the space derivative of all orders vanishes at certain points; t-TE fails in both cases. The analyticity of the initial wave function in space is linked to the analyticity of the TD wave function in time. We provide more evidence and a heuristic derivation of time nonanalyticities originating from cusps in Sec. 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],

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

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

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

which is obtained by interchanging the order of the two summations. If the initial wave function 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,

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

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

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

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 wave function does not have a cusp in momentum space,

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

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 wave function in momentum space as

$$\Psi^{\mathrm{TE}}(k,t) = \sum_{n=0}^{\infty}\frac{(-ik^2/2)^n}{n!}\Psi_0(k)t^n = \frac{2}{k^2+1}\exp(-ik^2t/2), \tag{13}$$

which is exactly the Fourier transform of Eq. (7), the correct TD wave function. 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 Sec. 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 Sec. 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].

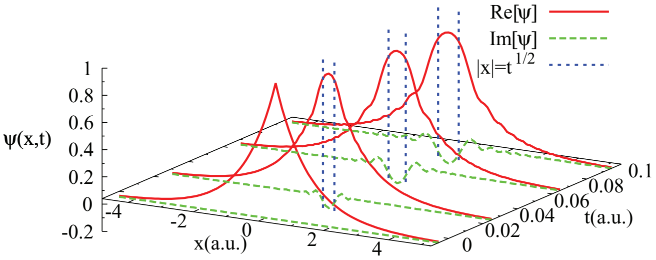

FIG. 2. (Color online) The time-dependent wave function after the nucleus vanishes.

B. Inner and outer regions

Here we define carefully the inner and outer regions, each of which has a distinct asymptotic expansion. Figure 2 shows that 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 origin is nonoscillatory, resembling the spread-out cusp. By carefully taking the $t \to 0_+$ limit as below, we notice that $t \to 0_+$ 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.

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

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

Figure 3 shows that such a change of variables effectively zooms in to the inner region, and the cusp in the initial wave function is removed in the reduced variables.

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

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

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

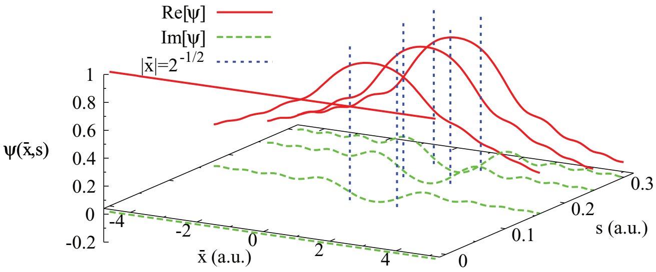

FIG. 3. (Color online) Same as Fig. 2, but as a function of $s = \sqrt{t}$ and $\bar{x} = x/\sqrt{2t}$.

The TD wave function Eq. (7) is then

$$\psi(x,t) = \tfrac{1}{2} e^{\frac{is^2}{2}} [\mathrm{E_c}(s,\bar{x}) - i\mathrm{F}^*(s,\bar{x})]. \tag{16}$$

For the wave function, the $\mathrm{E_c}$ part is smooth, and the $-i\mathrm{F}^*$ 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],

$$\begin{aligned}\mathrm{F}(s,\bar{x}) = ie^{\sqrt{2}s\bar{x}} \Bigg\{ &\mathrm{erf}\left[\sqrt{i}\left(\bar{x} - \frac{is}{\sqrt{2}}\right)\right] \\ &- \mathrm{erf}\left(\frac{s + \sqrt{2}\bar{x}}{2}\right)\Bigg\}.\end{aligned} \tag{17}$$

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

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

$$\begin{aligned}\psi^{\mathrm{inner}}(s,\bar{x}) \overset{s\to 0_+}{\sim}\ & 1 + s[-\sqrt{2i/\pi}\exp(i\bar{x}^2) \\ & - \sqrt{2}\bar{x}\,\mathrm{erf}(\sqrt{i}^*\bar{x})] + O(s^2) \\ =\ & 1 + \frac{x^2}{2} - x\,\mathrm{erf}\left(\sqrt{\frac{i}{2t}}^*\, x\right) \\ & - \sqrt{\frac{2i}{\pi}}\exp\left(\frac{ix^2}{2t}\right)\sqrt{t} + \cdots.\end{aligned} \tag{18}$$

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

$$\begin{aligned}\psi^{\mathrm{outer}}(s,\bar{x}) \overset{\bar{x}\to\pm\infty}{\sim}\ & \exp(-\sqrt{2}s|\bar{x}| + is^2/2) \\ & + \sqrt{\frac{i}{2\pi}}^*\exp(i\bar{x}^2)s\bar{x}^{-2} + O(\bar{x}^{-4}) \\ =\ & \exp(-|x|)\left(1 + \frac{it}{2}\right) \\ & + \sqrt{\frac{2i}{\pi}}^*\frac{\exp[ix^2/(2t)]}{x^2}t^{3/2} + \cdots.\end{aligned} \tag{19}$$

The truncated inner-region and outer-region expansions are plotted in Fig. 4. These two together define the correct short-time behavior of the wave function. It should be noted that the usual $t \to 0_+$ limit corresponds only to the outer region, and thus it does not contain all the information of the system at $t \to 0_+$. Since these two expansions both contain time nonanalyticities, such as half-powers in t and $\exp[ix^2/(2t)]$, the t-TE cannot describe the correct short-time behavior.

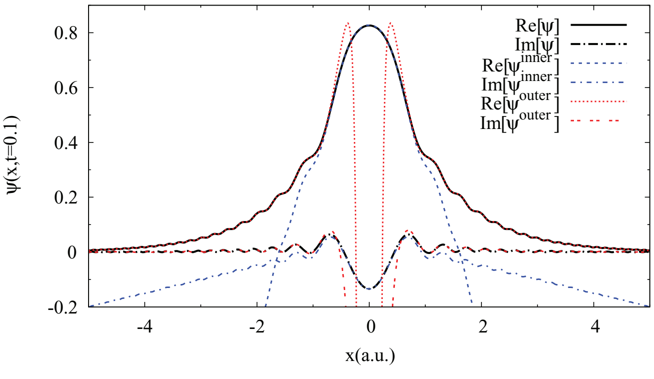

FIG. 4. (Color online) $\psi(x,t = 0.1)$ after the nucleus vanishes, plotting the truncated inner-region expansion and the outer-region expansion.

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

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

Write out the time-dependent wave function using the Green's function [21],

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

where the time-domain Green's function G is related to the time-propagation operator introduced in Sec. 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. Equation (21) is equivalent to Eq. (3).

The first term in the integral gives the t-TE wave function, 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 nonanalyticity:

$$\psi(x,t) \overset{x/\sqrt{2t}\to\infty}{\sim} \cdots + \sqrt{\frac{2i}{\pi}}^*\frac{\exp[ix^2/(2t)]}{x^2}t^{3/2} + \cdots. \tag{22}$$

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

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

Equation (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 $x^2/(2t) \to \infty$ 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 wave function in the vanishing nucleus problem, beginning at t_0 *after* the nucleus vanishes. This wave function has no cusp and has a well-behaved Taylor expansion.

The t-TE of the time-evolution operator is

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

The exact TD wave function 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

$$\frac{\partial^{2n}\psi(x,t)}{\partial x^{2n}} \propto (-1)^{n+1}\frac{x^{2n-2}}{t_0^{2n-3/2}}C, \quad x \gg \sqrt{t_0}, \tag{25}$$

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

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

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

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

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

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 with a change of variables:

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

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

$$\bar{\nabla}^2\psi - 4s^2 V\,\psi + 2i\left\{s\frac{\partial\psi}{\partial s} - \bar{\mathbf{r}}\cdot\bar{\nabla}\psi\right\} = 0. \tag{29}$$

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:

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

This yields a set of differential equations,

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

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 $\bar{\mathbf{r}}$. Equation (31) requires proper boundary conditions for the solution to be well defined. Equation (31) is equivalent to the TDSE whenever the wave-function ansatz Eq. (30) is applicable. This requires the boundary conditions to be derived from the initial condition of the TDSE, which is the initial wave function $\psi_0(\mathbf{r}) \equiv \psi_0(\sqrt{2}\bar{\mathbf{r}}s)$. For finite argument $\mathbf{r}$, $s \to 0$ implies $\bar{r} \to \infty$, so the expansion of the initial wave function at $s \to 0$ determines the large $\bar{\mathbf{r}}$ behavior of the $\psi_{(m)}(\bar{\mathbf{r}})$, 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

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

and Eq. (31) becomes

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

Equation (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

$$\begin{aligned}\psi(\bar{\mathbf{r}},s) = {} & \phi(0) + \sqrt{2}\bar{\mathbf{r}}\phi'(0)s \\ & + [-iE\phi(0) + \bar{\mathbf{r}}^2\phi''(0)]s^2 + \cdots,\end{aligned} \tag{34}$$

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

Several examples of using the method are provided in Secs. IV A, IV B, and V B. For the 1D vanishing nucleus case, we solve Eq. (31) directly in Sec. 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 Secs. 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-nonanalytic 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 Sec. IV A). The correction from the t-TE is expressed as asymptotic series. By performing the Borel summation as in Sec. 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 wave function, which is not an observable. It is usually more important to be able to predict nonanalyticities 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 nonanalyticity of the TD wave function is sufficient to determine that of a desired observable. Sections 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

$$\psi''_{(n)} - 2i\bar{x}\psi'_{(n)} + 2in\psi_{(n)} = 0, \tag{35}$$

with general solution

$$\psi_{(n)}(\bar{x}) = a_n \mathrm{H}_n(\sqrt{i}\bar{x}) + b_n f_n(\bar{x}), \tag{36}$$

where

$$f_n(\bar{x}) = \begin{cases} \mathrm{H}_n(\sqrt{i}\bar{x}) \int_0^{\bar{x}} d\bar{x}' \ \frac{\exp[i(\bar{x}')^2]}{\mathrm{H}_n(\sqrt{i}\bar{x}')^2} & n \ \text{ even}, \\ {}_1\mathrm{F}_1\left(-\frac{n}{2},\frac{1}{2},i\bar{x}^2\right) & n \ \text{ odd}, \end{cases} \tag{37}$$

H is the Hermite polynomial, and ${}_1\mathrm{F}_1$ is Kummer's confluent hypergeometric function [20].

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

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

Thus, the boundary conditions for Eq. (36) are

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

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

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

With Eqs. (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 wave function is described by the inner-region and the outer-region expansions together. The inner-region expansion corresponds to expanding the exact time-dependent wave function at $s \to 0$ 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 $\bar{\mathbf{r}} \to \infty$. For the 1D vanishing nucleus case, expanding Eq. (30) for $|\bar{x}| \to \infty$ yields

$$\begin{aligned} \psi^{\text{outer}}(s,\bar{x}) \overset{|\bar{x}|\to\infty}{\sim} & (1 - \sqrt{2}s|\bar{x}| + s^2\bar{x}^2 + \cdots) \\ & + \frac{is^2}{2}(1 - \sqrt{2}s|\bar{x}| + \cdots) \\ & + \sqrt{\frac{i}{2\pi}}^* \frac{s\exp(i\bar{x}^2)}{\bar{x}^2} + \cdots \\ = & \left(1 - |x| + \frac{x^2}{2} + \cdots\right) + \frac{it}{2}(1 - |\bar{x}| + \cdots) \\ & + \sqrt{\frac{2i}{\pi}}^* \frac{\exp[ix^2/(2t)]}{x^2} t^{3/2} + \cdots. \end{aligned} \tag{41}$$

This result agrees with Eq. (19), except that the $\exp(-|x|)$ envelope of the regular terms in Eq. (19) is expanded at $x \to 0$ 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 nonanalyticity is in $\psi_{(1)}(\bar{x})$. We use the following ansatz for $\psi_{(1)}$:

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

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

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

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),

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

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

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

into Eq. (43), which yields

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

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

$$\psi_1(\bar{x}) = c_1\exp[P(\bar{x})] \sim c\frac{\exp(i\bar{x}^2)}{\bar{x}^2}. \tag{47}$$

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

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

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

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

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

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

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,

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

The Borel sum of the series is defined as

$$S_{\mathrm{B}}(p) \equiv \int_0^{\infty} d\xi \ \exp(-\xi)\phi(p\xi), \tag{52}$$

in which

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

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

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

The Borel sum of Eq. (54) is

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

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

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

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

$$c_1 = \sqrt{\frac{i}{\pi}}^{\,*}, \quad c_2 = -\sqrt{2}. \tag{57}$$

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 one-electron case. Consider a system with the following potential:

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

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 wave function for this system, the first-order perturbative wave function (sans $\mathcal{E}$) $\psi^{\langle 1\rangle}$ [21] is exactly solvable and is given in Sec. VI C. Its outer expansion to the leading time-nonanalytic order is

$$\begin{aligned} \psi^{\langle 1\rangle}(x,t) \overset{t\to 0_+}{\sim} &\left\{-ixt + \frac{x - \mathrm{sgn}(x)}{2}t^2 + \frac{i[x-\mathrm{sgn}(x)]}{8}t^3 \right. \\ &\left. - \frac{x-\mathrm{sgn}(x)}{48}t^4\right\}\exp(-|x|) \\ &- 4\sqrt{\frac{2i}{\pi}}\frac{\exp[ix^2/(2t)]}{x^5}t^{9/2} + O(t^5), \end{aligned} \tag{59}$$

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

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

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

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

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 nonanalyticity occurs at fourth order in s, and we solve for $\psi_{(4)}(\bar{x})$ for this time nonanalyticity. 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 nonanalyticity, 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 wave function does not have the correct short-time behavior, it can be used to facilitate the process of obtaining the leading-order time nonanalyticity in $\psi(x,t)$, as described below.

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

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

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

$$\begin{aligned} \psi^{\mathrm{TE}}_{(n=0,1,2)}(\bar{x}) &= \psi^{\mathrm{TE}}_{(n),\mathcal{E}=0}(\bar{x}), \\ \psi^{\mathrm{TE}}_{(3)}(\bar{x}) &= \psi^{\mathrm{TE}}_{(3),\mathcal{E}=0}(\bar{x}) - i\sqrt{2}\mathcal{E}\bar{x}, \\ \psi^{\mathrm{TE}}_{(4)}(\bar{x}) &= \psi^{\mathrm{TE}}_{(4),\mathcal{E}=0}(\bar{x}) - \mathcal{E}\,\mathrm{sgn}(\bar{x})\left(\tfrac{1}{2} - 2i\bar{x}^2\right), \end{aligned} \tag{63}$$

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

$\psi^{\mathrm{TE}}_{(0)}(\bar{x})$ to $\psi^{\mathrm{TE}}_{(3)}(\bar{x})$ satisfy both the differential equations Eq. (61) and the boundary conditions Eq. (39), which is expected since the outer-expansion Eq. (59) suggests that the leading-order time nonanalyticity does not occur until $\psi_{(4)}$. Inserting $\psi^{\mathrm{TE}}_{(4)}(\bar{x})$ into the left-hand side of Eq. (61) yields $-\mathcal{E}\delta'(\bar{x})$, showing that $\psi^{\mathrm{TE}}_{(4)}(\bar{x})$ 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 $\psi^{\mathrm{TE}}_{(4)}$ as

$$\Delta(\bar{x}) = \psi_{(4)}(\bar{x}) - \psi^{\mathrm{TE}}_{(4)}(\bar{x}). \tag{64}$$

Then Eq. (61) in terms of Δ becomes

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

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

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

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 $\Delta_g(\bar{x})$:

$$\Delta_g(\bar{x}) = c_1(\bar{x}^4 + 3i\bar{x}^2 - 3/4) + c_2\left[-\frac{1}{3}\exp(i\bar{x}^2)\bar{x}(5i + 2\bar{x}^2) + \frac{1-i}{6}\sqrt{\frac{\pi}{2}}(-3 + 12i\bar{x}^2 + 4\bar{x}^4)\,\mathrm{erfc}(\sqrt{i}^*\bar{x})\right]. \tag{67}$$

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

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

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

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

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

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 wave function can be written out, and the exact leading-order time-nonanalytic term is

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

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

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

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 wave function, and the other one is determined by the δ well whose strength has changed. The simple boundary-layer analysis in Sec. 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 wave functions 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 wave function equals the ground-state wave function of the hydrogen atom:

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

Free propagation of this wave function 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 wave function Eq. (72) as

$$\psi(s,\bar{r}) \overset{s\to 0_+}{\sim} 1 - s\sqrt{2}\bar{r} + s^2\bar{r}^2 + \cdots, \tag{73}$$

We only obtain one boundary condition $[\psi_{(n)}(\bar{r} \to \infty)]$ for Eq. (31) instead of two boundary conditions as in 1D cases $[\psi_{(n)}(\bar{x} \to \pm\infty)]$. Equation (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 wave function is

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

Unlike in the 1D examples, all $\psi^{\mathrm{TE}}_{(n)}(\bar{\mathbf{r}})$ satisfy Eq. (31), but $\psi^{\mathrm{TE}}_{(1)}(\bar{\mathbf{r}})$ diverges at $\bar{r} = 0$ for any nonzero time. Thus, the other boundary condition for Eq. (31) is that $\psi_{(n)}(\bar{\mathbf{r}})$ 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 wave functions more complicated than their 1D counterparts.

The system has the following potential:

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

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

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

The external potential in these reduced variables is

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

Inserting the wave function ansatz Eq. (30) into Eq. (31) yields

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

where

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

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

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

In the presence of the electric field,

$$\psi^{\mathrm{TE}}_{(n)}(\bar{\mathbf{r}}) = \psi^{\mathrm{TE}}_{(n),\mathcal{E}=0}(\bar{\mathbf{r}}) + i\mathcal{E}\bar{z}f_{(n)}(\bar{r}), \quad n \leqslant 4, \tag{81}$$

with

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

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

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

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

As $\bar{r} \to 0$, the divergence in $\psi^{\mathrm{TE}}_{(4)}$ 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:

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

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

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

Performing the Borel sum, we find

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

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

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

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

$$\psi^{\mathrm{outer}}(\mathbf{r},t) \overset{\bar{r}\to\infty}{\sim} \cdots - \frac{8\sqrt{2i}^{*}\mathcal{E}z}{\sqrt{\pi}r^8}\exp\left(\frac{ir^2}{2t}\right)t^{11/2}. \tag{88}$$

Although $\psi_{(4)}(s,\bar{\mathbf{r}})$ contains the leading-order time nonanalyticity in the wave function, that knowledge 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 wave function, 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-nonanalytic term in the outer-region expansion of this system by applying the stationary phase approximation (as in Sec. II B) to first order in $\delta V^{\langle 1\rangle}(\mathbf{r}',t') = z'\theta(t')$. The change in the wave function (sans $\mathcal{E}$) is

$$\psi^{\langle 1\rangle}(\mathbf{r},t) = i\int d^3r'\; G^{\langle 1\rangle}(\mathbf{r},\mathbf{r}',t)\psi^{\langle 0\rangle}(\mathbf{r}',0), \tag{89}$$

in which $\psi^{\langle 0\rangle}$ is the ground-state wave function of 3D hydrogen, and

$$\begin{aligned} G^{\langle 1\rangle}(\mathbf{r},\mathbf{r}',t) = {} & \int d^3r''\int_0^t dt''\; G^{\langle 0\rangle}(\mathbf{r},\mathbf{r}'',t-t'') \\ & \times \delta V^{\langle 1\rangle}(\mathbf{r}'',t'')G^{\langle 0\rangle}(\mathbf{r}'',\mathbf{r}',t'') \end{aligned} \tag{90}$$

is the first-order change of the Green's function, with

$$G^{\langle 0\rangle}(\mathbf{r},\mathbf{r}',t) = -i\sum_n \exp(-i\epsilon_n t)\psi_n(\mathbf{r})\psi_n^{*}(\mathbf{r}'), \tag{91}$$

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 nonanalyticity in $\psi^{\langle 1\rangle}$, and the sum in Eq. (91) becomes an integration for unbound orbitals. Applying the stationary phase approximation (as in Sec. II B) to this integration, we obtain the leading nonanalytic short-time behavior shown in Eq. (88).

VI. DIPOLE MOMENTS

Our results so far, using the s expansion, have been for the time-dependent wave function. 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 wave functions *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 wave function 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 (first-order) change in the density $\delta n(\mathbf{r},t)$ is described by the linear-response function χ and its Fourier transform $\tilde{\chi}$:

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

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

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

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:

$$\tilde{\chi}(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0_+}\sum_j \left\{\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_j\rangle\langle\Psi_j|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega-\omega_j+i\eta} + \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_j\rangle\langle\Psi_j|\hat{n}(\mathbf{r})|\Psi_0\rangle}{-\omega-\omega_j-i\eta}\right\}, \tag{94}$$

where Ψ is the many-body eigen-wave-function 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 $\omega \to \infty$ for each separate term, yielding $O(\omega^{-2})$ high-frequency behavior [25]. However, when the system has a continuum, the sum must be performed before taking the $\omega \to \infty$ limit, and this produces fractional decay.

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

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

and its transform, the polarizability in x direction, is

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

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

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 Imα decays as $\omega^{-9/2}$ (Im denotes the imaginary part). For a hydrogen atom, Im[$\alpha(\omega\to\infty)$] is [26]

$$\mathrm{Im}[\alpha(\omega)] \overset{\omega\to\infty}{\sim} \frac{4\sqrt{2}}{3\omega^{9/2}}, \tag{97}$$

where α is a spherical average. Thus,

$$\mu^{\langle 1\rangle}(t) \overset{t\to 0_+}{\sim} \frac{2}{\pi}\int_0^t dt' \int_{\omega_c}^{\infty} d\omega\ \mathrm{Im}[\alpha(\omega)]\sin[\omega(t-t')], \tag{98}$$

where $\omega_c \gg 1$ is a cutoff, yielding

$$\mu^{\langle 1\rangle}(t) \overset{t\to 0_+}{\sim} \int_0^t dt' \left\{\frac{16\sqrt{2}(t-t')}{15\pi\omega_c^{5/2}} - \frac{8\sqrt{2}(t-t')^3}{9\pi\omega_c^{1/2}} + \frac{128(t-t')^{7/2}}{315\sqrt{\pi}}\right\} + \cdots. \tag{99}$$

As $\omega_c \to \infty$, we find the leading time-nonanalytic term in $\mu^{\langle 1\rangle}(t \to 0_+)$:

$$\mu^{\langle 1\rangle}(t) \overset{t\to 0_+}{\sim} \cdots + \frac{256}{2835\sqrt{\pi}}t^{9/2} + \cdots. \tag{100}$$

C. Origins of nonanalyticity and relation to time dependence

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

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

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

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

Even for a free particle, there are nonanalytic 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

$$G^{\mathrm{1DH}}(x,x',\tau) = -i\sqrt{\frac{1}{2\pi i\tau}}\exp\left[\frac{iu^2}{2\tau}\right] - \frac{i}{2}\exp\left(\frac{i\tau}{2} - X\right) \times \mathrm{erfc}\left(\frac{X}{\sqrt{2i\tau}} - \sqrt{\frac{i\tau}{2}}\right), \tag{103}$$

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

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

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

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

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

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

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

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

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

$$\begin{aligned}\mu^{\langle 1\rangle}(t) = &-\frac{t^2}{12}(t^2+6)+\frac{\sqrt{t}\cos(t/2)}{12\sqrt{\pi}}(t^3-3t^2+7t+15)\\ &-\frac{\sqrt{t}\sin(t/2)}{12\sqrt{\pi}}(t^3+3t^2+7t-15)\\ &+2\mathrm{Re}\left\{\frac{1}{24}(t^4-4it^3+6t^2+12it-15)\right.\\ &\left.\times\,\mathrm{erf}\left(\sqrt{\frac{it}{2}}\right)\right\}. \end{aligned} \tag{107}$$

The leading short-time behavior is

$$\mu^{\langle 1\rangle}(t) \overset{t\to 0_+}{\sim} -\frac{t^2}{2}+\frac{32}{105\sqrt{\pi}}t^{7/2}-\frac{t^4}{12}+O(t^{9/2}). \tag{108}$$

To see the connection with the s expansion in this case, we note simply that the fourth-order contribution Eq. (68), inserted in Eq. (106), recovers the same leading nonanalytic behavior. Thus, here the leading-order nonanalyticity in the wave function is sufficient to determine the leading-order nonanalyticity 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 nonanalyticities originate from the specific form of the TDSE and show that the time nonanalyticity of the time-dependent wave function is determined by the space nonanalyticity of the initial wave function.

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

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

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

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

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 nth-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 wave function. 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 wave function by dropping all derivative terms [18],

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

yielding

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

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

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

Though the form of the TDSE implies time nonanalyticities, such nonanalyticities do not show up in every system. If the initial wave function is analytic in space, then the time-dependent wave function of the system described by Eq. (109) is analytic in time; if the initial wave function has cusps, the time-dependent wave function is not time analytic, and the time nonanalyticities have the form $t^{n/2}$ and $\exp[ix^2/(2t)]$.

The inverse Laplace transform of Eq. (112) is

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

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

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

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

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

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

$$t^{(j-l)/2}\,{}_1\mathrm{F}_1\left(\frac{l-j}{2};\frac{1}{2}+l;\frac{ix^2}{2t}\right),\quad l=\frac{1-(-1)^j}{2}, \tag{117}$$

where ${}_1\mathrm{F}_1$ is Kummer's confluent hypergeometric functions [20]. The ${}_1\mathrm{F}_1$'s in Eq. (117) are polynomials that involve only positive integer powers of t, so there are no time nonanalyticities starting from a space-analytic initial wave function for the model system Eq. (109).

For initial wave functions with cusps, we modify Eq. (116) to be

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

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

$$t^{m/2}\,{}_1\mathrm{F}_1\left(-\frac{m}{2};\frac{1}{2};\frac{ix^2}{2t}\right)+t^{(m-1)/2}\,{}_1\mathrm{F}_1\left(\frac{1-m}{2};\frac{3}{2};\frac{ix^2}{2t}\right). \tag{119}$$

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. Equation (119) contains t half powers for all values of m, and thus the initial wave function with cusps has time nonanalyticities in its short-time behavior for the model system Eq. (109).

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

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

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

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

Equation (121) has no time nonanalyticities at the initial time. The radius of convergence of the t-TE at the initial time is σ^2. In the limit of $\sigma \to 0$, 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 Sec. II C).

B. Different time dependence

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

$$V(x,t) = -\delta(x) + V_a(x) + \mathcal{E}\delta V^{\langle 1\rangle}(x,t), \tag{122}$$

where $V_a(x)$ is an analytic potential, $\delta V^{\langle 1\rangle}(x,t) = x^n f(t)$, 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 wave function is approximated by an envelope function for all $x \neq 0$. Write

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

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

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

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

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

where ψ_{k_ω} is the continuum wave function whose energy difference to the ground state is ω, and $\delta V^{\langle 1\rangle}(x,\omega)$ is the Fourier transform of $\delta V^{\langle 1\rangle}(x,t)$. Inserting Eq. (125) into Eq. (98), we find that there is one term of the result which does not depend on the cutoff ω_c and the envelope parameter a, which is the term of the leading time nonanalyticity. This result does not depend on what 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 nonanalyticity 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 $\mu^{\langle 1\rangle}$ as

$$\begin{aligned}\mu^{\langle 1\rangle}(t \to 0_+) \sim \cdots &+ 2[\psi_0'(0_+) - \psi_0'(0_-)]^2\Gamma(-2-n/2) \\ &\times \Gamma(n+2)t^{2+n/2}2^{-3-n/2}[-1+(-1)^n] \\ &\times (-1+i^n)\exp(-3in\pi/4) + \cdots.\end{aligned} \tag{126}$$

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

$$\begin{aligned}\mu^{\langle 1\rangle}(t \to 0_+) \sim \cdots &- 2\frac{[\psi'(0_+) - \psi'(0_-)]^2\csc(n\pi/2)}{\Gamma(4+m+n/2)} \\ &\times t^{3+m+n/2}2^{-3-n/2}[-1+(-1)^n](-1+i^n) \\ &\times \Gamma(1+m)\Gamma(2+n)\exp(-3in\pi/4) + \cdots.\end{aligned} \tag{127}$$

It is clear that the effect of different turning-on method only changes the order of the nonanalytic behavior, so the previously shown time-nonanalytic 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 $\delta V^{\langle 1\rangle}(x,t) = \sin(kx - \omega_0 t)\theta(t)$ also has time nonanalyticities in the short-time behavior of the wave function.

C. Onset of nonanalytic 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 Sec. IV B $-\delta(x) + \mathcal{E}x\theta(t)$ with

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

We set $\mathcal{E} = 1$ for the numerical calculation. In the limit of $\sigma \to 0$, the case in Sec. IV B is recovered. We solve the ground-state wave function of this system for $t < 0$ on an unevenly distributed grid, which has more points near $x = 0$ to ensure that the cusplike structure in the wave function is well resolved. We propagate the TD wave function with the

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

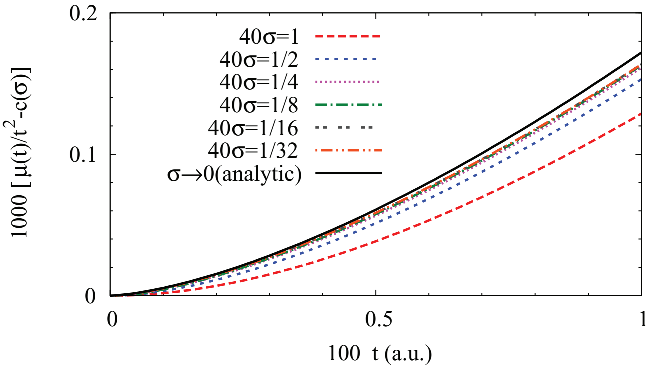

FIG. 5. (Color online) $1000[\mu(t)/t^2 - c(\sigma)]$ for σ listed in Table I and $\sigma \to 0$. $[32000t^{3/2}/(105\sqrt{\pi})$ is plotted for the $\sigma \to 0$ curve.] The errors between the exact $\sigma \to 0$ curve and the fit curves show systematic behavior.

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

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

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

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 $\sigma \to 0$ 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. Figure 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 nonanalyticity is still relevant in numerical situations. On the atomic time scale, the time evolution is indistinguishable from that with a cusp.

VIII. DISCUSSION: MANY-ELECTRON SYSTEMS AND TDDFT

The original motivation for this study was concern about the fundamentals of 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 wave function 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 nth derivative at $t = 0$ differ for some finite n.

The present and previous [9] works show that, in the case of a hydrogen atom in a suddenly switched electric field, the time-dependent density has nonanalytic contributions, so that the Taylor series does not converge. Nonetheless, if two densities differ in their jth 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 that 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 known general conditions on densities 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 that 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 show convincingly that such effects are generic, rather than unusual, once the ground-state wave function contains spatial cusps. In the past 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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[1] D. J. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (University Science Books, South Orange, NJ, 2007).

[2] M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio, eds., *Fundamentals of Time-Dependent Density Functional Theory*, Lecture Notes in Physics (Springer, Berlin, 2012).

[3] C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford University Press, Oxford, 2012).

[4] P. Elliott, F. Furche, and K. Burke, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and T. R. Cundari (Wiley, Hoboken, NJ, 2009).

[5] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[6] S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining, Rep. Prog. Phys. **70**, 357 (2007).

[7] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[8] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).

[9] Z.-H. Yang, N. T. Maitra, and K. Burke, Phys. Rev. Lett. **108**, 063003 (2012).

[10] M. Ruggenthaler and R. van Leeuwen, Eur. Phys. Lett. **95**, 13001 (2011).

[11] M. Ruggenthaler, K. J. H. Giesbertz, M. Penz, and R. van Leeuwen, Phys. Rev. A **85**, 052504 (2012).

[12] N. T. Maitra, T. N. Todorov, C. Woodward, and K. Burke, Phys. Rev. A **81**, 042525 (2010).

[13] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Dover, New York, 1975).

[14] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, New York, 2003).

[15] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).

[16] H. Bruus and K. Flensberg, *Many-body Quantum Theory in Condensed Matter Physics* (Oxford University Press, New York, 2004).

[17] B. R. Holstein and A. R. Swift, Am. J. Phys. **40**, 829 (1972).

[18] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers-Asymptotic Methods and Perturbation Theory* (Springer, New York, 1999).

[19] R. B. White, *Asymptotic Analysis of Differential Equations* (Imperial College Press, London, 2010).

[20] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions* (Dover, New York, 1972).

[21] E. N. Economou, *Green's Functions in Quantum Physics* (Springer, Berlin, 2006).

[22] H. J. Silverstone, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995).

[23] H. Friedrich, *Theoretical Atomic Physics*, 3rd ed. (Springer, Berlin, 2006).

[24] N. T. Maitra, A. Wasserman, and K. Burke, in *Electron Correlations and Materials Properties 2*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Kluwer Academic/Plenum, New York, 2003).

[25] R. van Leeuwen, Int. J. Mod. Phys. B **15**, 1969 (2001).

[26] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two-Electron Atoms* (Springer, Berlin, 1957).

[27] U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

[28] Z.-H. Yang, M. van Faassen, and K. Burke, J. Chem. Phys. **131**, 114308 (2009).

[29] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[30] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, 3rd ed. (Cambridge University Press, New York, 2007).

[31] K. Burke, J. Chem. Phys. **136**, 150901 (2012).

[32] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

[33] M. E. Casida, in *Recent Developments and Applications in Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).

[34] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[35] S. Sharma, J. K. Dewhurst, A. Sanna, and E. K. U. Gross, Phys. Rev. Lett. **107**, 186401 (2011).

[36] E. M. Stoudenmire, L. O. Wagner, S. R. White, and K. Burke, Phys. Rev. Lett. **109**, 056402 (2012).