Effect of Cusps in Time-Dependent Quantum Mechanics

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Within nonrelativistic quantum mechanics, spatial cusps in initial wave functions can lead to non-analytic behavior in time. We suggest a method for calculating the short-time behavior in such situations. For these cases, the density does not match its Taylor expansion in time, but the Runge-Gross proof of time-dependent density functional theory still holds, as it requires only the potential to be time analytic.

Within the Born-Oppenheimer (BO) approximation and nonrelativistic quantum mechanics, a vast amount of useful information (such as geometry, thermodynamics, and vibrations) of a molecule or solid can be extracted from the electronic ground state. But electronic excitations are important for many areas, from photochemistry to photoemission spectra [1]. Ground-state density functional theory (DFT) [2–4] has been very successful for the former problem, and its time-dependent analog (TDDFT) [5] has become popular for the latter [6]. Within linear response, TDDFT yields useful predictions for the excited states of many molecules [1], and extensions to solids are a keen area of research [7,8].

All density functional theories rely on a one-to-one correspondence between the one-body potential, such as $-Z/r$ for an atom, and the density $n(\mathbf{r})$, under some restrictions. For ground-state DFT, the particle statistics and interaction are fixed. For the time-dependent case, one also specifies the initial wave function. The original proof in the ground-state case of Hohenberg and Kohn [2] has been refined over the decades [9–11], but its essence remains unchanged. In the time-dependent (TD) problem, after pioneering works by others [12–18], Runge and Gross [5] gave a proof assuming the one-body potential is time analytic, i.e., equals its Taylor expansion in time around the initial time, for a finite time interval. Despite recent attempts [19–23], no generally applicable proof has been found that avoids this expansion.

Modern DFT calculations employ the Kohn-Sham (KS) scheme [3], in which a fictitious set of noninteracting electrons reproduces the one-electron density of the real system. If we assume that time-analytic potentials yield time-analytic densities, van Leeuwen [24] gave a constructive procedure for finding the TD KS potential for a given system, a problem that has not yet been generally solved for the ground-state case. But, in the usual treatment, matter has cusps in its ground-state electronic wave functions at the nuclei, and the resulting spatial nonanalyticities are coupled to the time dependence in the TD Schrödinger equation (TDSE) [21]. Even in the most mundane example, a hydrogen atom in a suddenly switched electric field, this coupling leads to nonanalytic short-time dynamics, and its density is not time analytic.

We develop a method for extracting the exact nonanalytic short-time behavior of the Schrödinger equation in the presence of cusps. There are distinct spatial regions with different asymptotic behavior for short times, and by "asymptotic behavior" we mean a series expansion around the initial time $t = 0$, whose error vanishes as $t \to 0_+$. We calculate the exact short-time behavior for a hydrogen atom in an electric field, and demonstrate agreement with linear response theory in the limit of weak fields. The constructive procedure for the TD KS potential fails for our examples. (In DFT speak, the ν-representability question is not solved.) Nonetheless, the original proof of Runge and Gross remains valid.

Consider a single particle prepared in a field-free ground state, ψ_0, placed in a static field which is turned on at $t = 0$, and remains on indefinitely. The exact TD wave function is [atomic units (a.u.) $e^2 = \hbar = m_e = 1/(4\pi\epsilon_0) = 1$ are used if not mentioned otherwise]

$$\psi(\mathbf{r}, t) = \sum_j c_j \exp(-i\epsilon_j t)\phi_j(\mathbf{r}), \qquad (1)$$

where ϵ_j and $\phi_j(\mathbf{r})$ are the eigenvalues and functions of the Hamiltonian operator $\hat{H}$, and $c_j = \langle\phi_j|\psi_0\rangle$. We define the time-Taylor series

$$\psi^{\text{TE}}(\mathbf{r}, t) = \sum_{p=0}^{\infty} c_p(\mathbf{r})t^p,$$

$$c_p(\mathbf{r}) = \sum_n c_n \frac{(-i\epsilon_n)^p}{p!} \phi_n(\mathbf{r}), \qquad (2)$$

which is the result of the usual practice of Taylor expanding (TE) the time-evolution operator:

$$\hat{U}(t) = 1 - i\hat{H}t - \hat{H}^2 t^2/2 + \cdots. \qquad (3)$$

In many cases, the solutions agree, but not necessarily when the wave function has nonanalyticities in space. Although ψ^{TE} *formally* solves the TDSE, it may not be a valid solution. Holstein and Swift [25] reported failure of the TE solution in a model system, in which ψ_0 has compact support (all space derivatives of ψ_0 vanish at the boundary). However, such cases do not occur in routine electronic structure calculations, and may not be of concern in practice. For the rest of this Letter, we focus on the ubiquitous cusp in $\psi_0(\mathbf{r})$ at a nucleus.

Begin with a simple example. Start from the ground-state wave function of the hydrogen atom,

$$\psi_0(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{\pi}} \exp(-Zr). \qquad (4)$$

Our potential for $t \geq 0$ is simply zero: the nucleus has been instantaneously vaporized. The exact TD wave function can be found by applying the free-particle TD Green's function to $\psi_0(\mathbf{r})$, yielding

$$\psi(\mathbf{r}, t) = \frac{Z^{3/2} e^{iZ^2 t/2}}{2\sqrt{\pi}r}[f(r, t) - f(-r, t)], \qquad (5)$$

where $f(r, t) = (r + iZt) \exp(Zr) \mathrm{erfc}[(r + iZt)/\sqrt{2it}]$. Figure 1 shows the exact solution and the power-series solution as in Eq. (2), which can be summed to all orders:

$$\psi^{TE}(\mathbf{r}, t) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr + iZ^2 t/2}\left(1 - i\frac{Zt}{r}\right), \qquad r > 0. \quad (6)$$

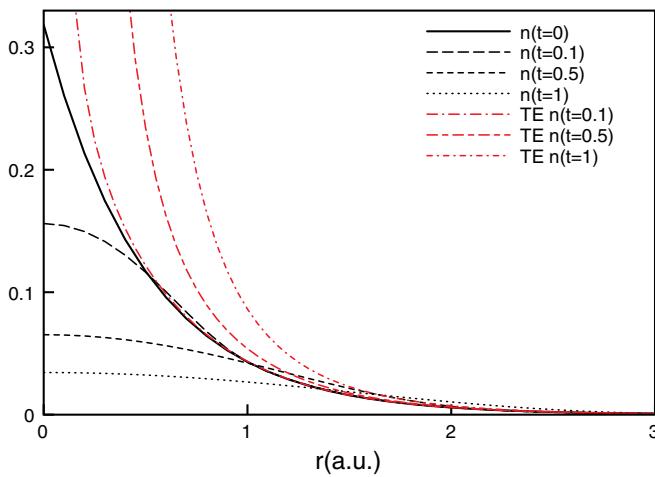The TE density diverges as $r \to 0$ and so is invalid.

FIG. 1 (color online). TD exact density and TE density of the ground-state wave function of hydrogen atom under free propagation.

Our method begins with introducing reduced variables:

$$s = Z\sqrt{t}, \qquad \bar{\mathbf{r}} = \frac{\mathbf{r}}{\sqrt{2t}}, \qquad (7)$$

where the powers are motivated by the previous example, and constants chosen for convenience. The form of these reduced variables is closely connected to the Schrödinger equation being first order in time but second order in space [26]. These reduced variables are appropriate if the system contains only one nucleus placed at the origin. In reduced variables, the TDSE becomes

$$\{\mathcal{L} - is\partial/\partial s + 2s^2 v/Z^2\}\psi = 0, \qquad (8)$$

where

$$\mathcal{L} = -\bar{\nabla}^2/2 + i\bar{\mathbf{r}} \cdot \bar{\nabla}, \qquad (9)$$

Z is the nuclear charge, and v is the external potential. In the disappearing-nucleus case, ψ is equal to its Taylor expansion in powers of s for fixed $\bar{\mathbf{r}}$, and thus we try

$$\psi(\bar{\mathbf{r}}, s) = \sum_{p=0}^{\infty} \psi_p(\bar{\mathbf{r}})s^p, \qquad (10)$$

yielding

$$\{\mathcal{L} - mi\}\psi_m(\bar{\mathbf{r}}) = -\frac{2}{Z^2}\sum_{p=0}^{m} v_{p-2}(\bar{\mathbf{r}})\psi_{m-p}(\bar{\mathbf{r}}), \qquad (11)$$

where $v(\mathbf{r}, t) = \sum_p v_p(\bar{\mathbf{r}})s^p$. Each power of s in ψ produces a second-order differential equation for a function of $\bar{\mathbf{r}}$. The initial wave function in reduced variables is $\psi_0(\sqrt{2}\bar{\mathbf{r}}s/Z)$. For finite values of $\mathbf{r}$, as $s \to 0$, $\bar{r} \to \infty$, so its expansion as $s \to 0$ determines the large $\bar{r}$ behavior of the $\psi_m(\bar{\mathbf{r}})$.

To find the leading nonanalytic behavior in t due to a cusp, we rearrange the TE solution of Eq. (2) in terms of the reduced variables s and $\bar{\mathbf{r}}$, and test its validity power by power in s. Each ψ_m^{TE} must satisfy the differential equation, the boundary condition derived from the initial wave function as $\bar{r} \to \infty$, and remain finite at the nucleus (m being the order of the s expansion). We do this recursively, until we find k, the lowest value of m for which ψ_k^{TE} fails. Define

$$\xi(\bar{\mathbf{r}}, s) = \psi(\bar{\mathbf{r}}, s) - \psi^{TE}(\bar{\mathbf{r}}, s) \qquad (12)$$

and solve the differential equation for $\xi_k(\mathbf{r})$ to find the leading nonanalytic behavior due to the cusp.

This can be quite demanding as, in 3D, the equation is a partial differential equation. A simple approach is to perform a local analysis using the method of dominant balance [27] to generate an asymptotic series in inverse powers of $\bar{r}$. Repeated application yields the series to all orders, but this is insufficient to ensure that ψ remains finite at the $r = 0$. This difficulty can be overcome by performing a Borel resummation of the asymptotic series [27] to find the exact solution. The conditions where Borel resummation works are discussed in [28].

As a second example, we consider a hydrogen atom in a suddenly switched electric field which stays on indefinitely, the initial wave function is that of Eq. (4), and the potential after $t = 0$ is

$$v(r) = -Z/r + \mathcal{E}z, \qquad (13)$$

where $\mathcal{E}$ is the amplitude of the electric field. This situation is covered by the Runge-Gross theorem as a potential that is analytic in time (in fact, constant) with an initial wave function that is not its instantaneous ground state. The time-dependent dipole moment $\mu(t)$ determines the photoabsorption of the atom via

$$\sigma(\omega) = \frac{4\pi\omega}{c} \int_0^\infty d\tau \left[\frac{\partial \mu(t)}{\partial t} \bigg|_{t=\tau} \right] \sin(\omega\tau), \qquad (14)$$

known analytically [29,30] for the H atom as $\mathcal{E} \to 0$.

To apply our method, we first calculate the TE wave function order by order. We find each term satisfies both the differential equation and boundary conditions until the fourth order:

$$\psi_4^{\mathrm{TE}} = \frac{Z^{3/2}}{24\sqrt{\pi}}(-3 + 12i\bar{r}^2 + 4\bar{r}^4)$$

$$+ \mathcal{E}\frac{i\bar{z}}{12\sqrt{\pi}Z^{3/2}\bar{r}^3}(1 + 6i\bar{r}^2 + 24\bar{r}^4), \qquad (15)$$

which works except that it diverges at the nucleus. Assume a correction of the form

$$\xi_4 = \exp(S(\bar{r}))\bar{z}, \qquad (16)$$

because the applied field is linear in z. This yields an ordinary differential equation for S:

$$S'' + (S')^2 - 2i\bar{r}S' + 4S'/\bar{r} + 6i = 0, \qquad (17)$$

and applying the method of dominant balance recursively, one finds the asymptotic expansion:

$$\xi_4 = c_1\left(\bar{r}^3 + \frac{9i\bar{r}}{2} - \frac{9}{4\bar{r}} + \frac{3i}{8\bar{r}^3}\right)$$

$$+ c_2\frac{e^{i\bar{r}^2}}{\bar{r}^8}\left[1 + \frac{1}{\bar{r}^2}\sum_{m=0}^\infty \frac{(-i)^{m+1}(m+4)(2m+6)!}{(m+1)!2^{2m+5}\times 9\bar{r}^{2m}}\right]. \qquad (18)$$

Since ψ_4^{TE} satisfies the boundary condition at large $\bar{r}$, ξ_4 must vanish here, and $c_1 = 0$. But this asymptotic series does not yield the small $\bar{r}$ limit. To find this, we perform a Borel resummation, yielding

$$\xi_4 = c_2\frac{1+i}{72\bar{r}^3}\left[(2+2i)e^{i\bar{r}^2}\bar{r}(-3 + 16i\bar{r}^2 + 4\bar{r}^4)\right.$$

$$\left. - \sqrt{2\pi}(3i - 18\bar{r}^2 + 36i\bar{r}^4 + 8\bar{r}^6)\mathrm{erfc}\left(\frac{1-i}{\sqrt{2}}\bar{r}\right)\right]. \qquad (19)$$

Requiring ψ_4 to remain finite yields

$$c_2 = (1 - i)\mathcal{E}/(2\pi Z^{3/2}). \qquad (20)$$

One can easily check analytically that $\psi_4 = \psi_4^{\mathrm{TE}} + \xi_4$ is then the unique solution to Eq. (11) for $m = 4$.

With ψ_4, we find the leading half-power of the wave function by changing the variables back to $(\mathbf{r}, t)$ and taking the asymptotic expansion around the $t = 0$. The leading time-half-power is then

$$-\frac{(8 - 8i)\mathcal{E}Z^{5/2}e^{ir^2/2t}\cos\theta}{\pi r^7}t^{11/2}, \qquad r \gg \sqrt{t}, \qquad (21)$$

and one can show $\psi_{m>4}$ contributes to higher-order time-half-powers by the method of dominant balance. This is also the lowest order in t at which rapid non-time-analytic oscillations of the phase appear.

Our derivation applies for any value of $\mathcal{E}$. The one-body potential appears linearly in our equations for $\psi_n(\bar{\mathbf{r}})$, and only for $n \geq 3$. Thus if $\psi_4(\bar{\mathbf{r}})$ produces the leading non-analytic behavior in t, then this behavior is linear in $\mathcal{E}$, and is determined exactly by linear response theory. (Higher-order effects in $\mathcal{E}$ produce changes in other terms, but not the leading nonanalytic short-time behavior.) To see this, take the Lehmann representation of the Green's function of the hydrogen atom and evaluate the change in the wave function to first order in $\mathcal{E}$. We did not find a closed form, but the stationary phase approximation to the integral over the wave number yields the leading half-power term in agreement with our short-time result Eq. (21).

The leading half-power term in the induced dipole moment calculated using linear response theory yields

$$\mu(t \to 0_+) \sim \cdots - 256Z^5/(2835\sqrt{\pi})t^{9/2} + \cdots. \qquad (22)$$

Its Fourier transform yields the known high-frequency decay of the photoabsorption cross section [29]

$$\sigma(\omega \to \infty) \sim 16\sqrt{2}Z^5\pi/(3c\omega^{7/2}). \qquad (23)$$

Thus the cusp at the nucleus leads to fractional powers in time evolution and fractional powers in frequency decay.

The leading half-power term in $\sigma(\omega \to \infty)$ calculated with ψ_4 differs from Eq. (23) by a factor of 2. In calculating $\sigma(\omega)$ from $\psi(\mathbf{r}, t)$, one must integrate over r, and the coupling between r and t in ψ (as seen in ψ_4) allows higher-order terms in the s expansion to contribute to the leading half-power term in $\sigma(\omega \to \infty)$ as well. In this case, ψ_4 and ψ_5 both contribute to the $\omega^{-7/2}$ term in σ.

Before discussing the consequences for TDDFT, we again consider the simpler, but starker example of the disappearing-nucleus case. Our method correctly shows the error appearing at s^1 order, and produces the correct short-time behavior:

$$\psi(|\mathbf{r}| \gg \sqrt{t}, t \to 0_+) \sim \frac{Z^{3/2}e^{-Zr}}{\sqrt{\pi}} + \frac{iZ^{5/2}(Zr-2)e^{-Zr}}{2\sqrt{\pi}r}t$$
$$- \frac{Z^{9/2}(Zr-4)e^{-Zr}}{8\sqrt{\pi}r}t^2$$
$$- \frac{(2+2i)Z^{5/2}e^{ir^2/(2t)}}{\pi r^4}t^{5/2} + \dots \quad (24)$$

while its TE contains only integer powers of t.

Although less relevant for TDDFT, our method applies equally well in 1D and proves that the short-time behavior for the initial state with cusp example in [21] originates from s^1 order and has fractional power $t^{3/2}$, again with a rapid non-time-analytic phase. Similarly, it is s^4 order for a particle in a delta well with an applied electric field, and the leading short-time behavior in ψ is

$$- \frac{(4+4i)\epsilon Z^{3/2}\exp[ix^2/(2t)]}{\sqrt{\pi}x^5}t^{9/2}, \qquad |x| \gg \sqrt{t}, \quad (25)$$

consistent with the known polarizability and its high-frequency limit [26].

Our results are proven only for single electrons. However, the nuclear potential dominates over the electron-electron repulsion in the region of the nucleus, so that the cusp condition on the time-dependent density near a nucleus remains valid regardless of the interelectron repulsion. Thus we expect the qualitative features (i.e., half-powers of t in the short-time behavior) to remain true even in the presence of interaction.

We conclude by discussing the relevance of our results for TDDFT, whose theorems certainly apply (or not) for $N = 1$. The proof of a one-to-one correspondence [5] shows that, for two t-analytic potentials whose Taylor expansions first differ in the kth order, the difference in the $(k + 2)$th-order t derivative of the densities is nonzero. Thus the two densities differ, the Runge-Gross proof applies, and the potential is a functional of the density under the conditions stated [5]. Whether or not the TE density matches the true density is irrelevant.

On the other hand, the KS potential of Ref. [24] produces a density whose t derivatives equal those of the interacting density. If we assume that the density is v representable by a t-analytic potential (e.g., if the KS and interacting wave functions themselves are t analytic), then that potential will yield this density. But the wave functions are not t analytic in the examples given here, and typically are not when an initial wave function with a cusp undergoes a nontrivial evolution. In general, a more sophisticated procedure is needed to ensure the constructed potential generates the desired density, and some progress has been made [21–23]. This is important as the constructive procedure has been invoked or applied *as is* to a variety of situations [31–33].

One might argue that real atoms have finite nuclei, or that real molecules and solids have nuclear wave functions that smear the cusps due to nuclei, as well as that most of the practical TDDFT calculations are done on cusp-free Gaussian basis sets. But such arguments miss the basic point. Just as in ground-state DFT, time-dependent DFT is an exact mapping of the quantum mechanics of electrons, for which there are no difficulties within BO or need for finite nuclei.

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