Demonstration of initial-state dependence in time-dependent density-functional theory

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Time-dependent density functionals depend in principle on the initial state of a system, but this is ignored in functional approximations presently in use. For one electron, it is shown that there is no initial-state dependence: for any density, only one initial state produces a well-behaved potential. For two noninteracting electrons with the same spin in one dimension, an initial potential that makes an alternative initial wave function evolve with the same density and current as a ground state is calculated. This potential is well-behaved, and can be made arbitrarily different from the original potential.

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I. INTRODUCTION AND CONCLUSIONS

Ground-state density-functional theory [1,2] has had an enormous impact on solid-state physics since its invention, and on quantum chemistry in recent years [3]. Time-dependent density-functional theory allows the external potential acting on the electrons to be time dependent, and so opens the door to a wealth of interesting and important phenomena that are not easily accessible, if at all, within static theory. Important examples include atomic and molecular collisions [4], atoms and molecules in intense laser fields [5], electronic transition energies and oscillator strengths [6,7], frequency-dependent polarizabilities and hyperpolarizabilities, etc. [8], and there has been an explosion of time-dependent Kohn-Sham calculations in all these fields. In almost all these calculations, the ubiquitous adiabatic local-density approximation (ALDA) [9,10] is used to approximate the unknown time-dependent exchange-correlation potential, i.e., $v_{XC}^{\mathrm{ALDA}}[n](\mathbf{r}t)=v_{XC}^{\mathrm{unif}}(n(\mathbf{r}t))$, where $v_{XC}^{\mathrm{unif}}(n)$ is the *ground-state* exchange-correlation potential of a uniform electron gas of density n. While this seems adequate for many purposes [11], little is known about its accuracy under the myriad of circumstances in which it has been applied.

Runge and Gross [12] formally established the time-dependent density-functional theory (TDDFT), showing that, for a given initial state, the evolving density uniquely identifies the (time-dependent) potential. This established the correspondence of a unique noninteracting system to each interacting system and so a set of one-particle Kohn-Sham equations, much like in the static theory. This one-to-one mapping between densities and potentials is the time-dependent analog of the Hohenberg-Kohn theorem, but with a major difference: in the time-dependent case, the mapping is unique only for a specified initial state. The functionals in TDDFT depend not only on the time-dependent density but also on the initial state. This dependence is largely unexplored and indeed often neglected, for example in the ALDA for the exchange-correlation potential mentioned above.

What do we mean by an initial-state dependence? In ground-state theory, there is a simple one-to-one relation between ground-state densities and Kohn-Sham potentials v_S, assuming they exist. For example, for one electron in one dimension, we can easily invert the Schrödinger equation, to yield

$$v_S(x)=\frac{d^2\sqrt{n(x)}/dx^2}{2\sqrt{n(x)}}+\epsilon, \tag{1}$$

where $n(x)$ is the ground-state density. We use atomic units throughout ($\hbar=m=e^2=1$). For N electrons in three dimensions, one can easily imagine continuously altering $v_S(\mathbf{r})$, the Kohn-Sham potential, solving the Schrödinger equation, finding the orbitals and calculating their density, until the correct $v_S(\mathbf{r})$ is found to reproduce the desired density. By the Hohenberg-Kohn theorem, this potential is unique, and several clever schemes for implementing this idea have appeared in the literature [13–21]. This procedure could in principle be implemented for interacting electrons, if a sufficiently versatile and accurate interacting Schrödinger equation solver were available.

Now consider the one-dimensional one-electron density

$$n(x)=2x^2\exp(-x^2)/\sqrt{\pi}, \tag{2}$$

(actually the density of the first excited state of a harmonic oscillator). If we consider this as a ground-state density, we are in for an unpleasant surprise. Feeding it into Eq. (1), we find that the potential which generates this density is parabolic almost everywhere ($x^2/2$), but has a nasty unphysical spike at $x=0$, of the form $\delta(x)/|x|$. We usually exclude such potentials from consideration [22], and regard this density as not being v-representable.

But now imagine this density as being the density of a first excited state. In this case, the relation between density and potential is *different*, because the orbital changes sign at the node. The mapping becomes

$$v_S(x)=\frac{d^2[\mathrm{sgn}(x-x_0)\sqrt{n(x)}]/dx^2}{2[\mathrm{sgn}(x-x_0)\sqrt{n(x)}]}+\epsilon, \tag{3}$$

where $\mathrm{sgn}(x)=1$ for $x>0$ and -1 for $x<0$, and $n(x_0)=0$. If we use this mapping, we find a perfectly smooth parabolic well ($x^2/2$). This is a simple example of how the *mapping* between densities and potentials depends on the initial state.

More generally, for any given time-dependent density $n(\mathbf{r}t)$, we ask how the potential $v(\mathbf{r}t)$, whose wave function yields that density, depends on the choice of initial wave function Ψ_0, i.e., in general $v[\Psi_0,n](\mathbf{r}t)$. Our aim in this

paper is to explicitly calculate two different potentials giving rise to the same time-dependent density by having two different initial states. Note that even finding such a case is nontrivial. The choice of wave functions is greatly restricted by the time-dependent density. As van Leeuwen pointed out [23], the continuity equation $\dot{n} = -\nabla \cdot \mathbf{j}$ implies that only wave functions that have the correct initial current are candidates for generating a given time-dependent density. van Leeuwen also showed how to explicitly construct the potential generating a given density from an allowed initial wave function using equations of motion.

Why is this important? The exchange-correlation potential, $v_{XC}(\mathbf{r}t)$, of TDDFT is the difference between a Kohn-Sham potential and the sum of the external and Hartree potentials. Since both the interacting and noninteracting mappings can depend on the choice of initial state, this potential is a functional of both initial states and the density, i.e., $v_{XC}[n,\Psi_0,\Phi_0](\mathbf{r}t)$. But in common practice, only the dependence on the density is approximated. We show below that this misses significant dependences on the initial state (which can in turn be related to memory effects, i.e., dependences on the density at prior times).

In the special case of one electron, we prove in Sec. II A that only one initial state has a physically well-behaved potential. Any attempt to find another initial state which evolves in a different potential with the same evolving density results in a ''pathological'' potential. The potential either has the strong features at nodes mentioned above, or rapidly plunges to minus infinity at large distances where the density decays. (How such a potential can support a localized density is discussed in Sec. III.) Such nonphysical states and potentials are excluded from consideration (as indeed they are in the Runge-Gross theorem). Thus there is no initial-state dependence for one electron.

We might then reasonably ask whether we can ever find a well-behaved potential for more than one allowed initial wave function. The answer is yes, which we demonstrate with a specific example. Consider two noninteracting electrons of the same spin in a harmonic well. In the ground state of this two-electron system, the first electron occupies the oscillator ground state, and the second occupies the first excited state, as shown in Fig. 1. If we keep the potential constant, the density will not change. By multiplying each orbital by a spatially varying phase, and choosing these phases to make the current vanish, we find an allowed alternative initial state (see Sec. III for details). van Leeuwen's prescription then yields a unique potential which makes this wave function evolve with the same density. The difference is perfectly well-behaved, and can be made arbitrarily large by adjusting a constant in the phases of the alternative orbitals. To our knowledge, this is the first explicit construction of two different potentials that yield the same time-dependent density. Other examples are given in Sec. III.

Now imagine that the density of Fig. 1 is the ground-state density of some *interacting* two-electron system, in some external potential $v_{\text{ext}}(x)$. Then both potentials shown in lower panels of Fig. 1 are possible Kohn-Sham potentials $v_S(x)$ for this system. Since the Hartree potential is uniquely determined by the density, we have two very different

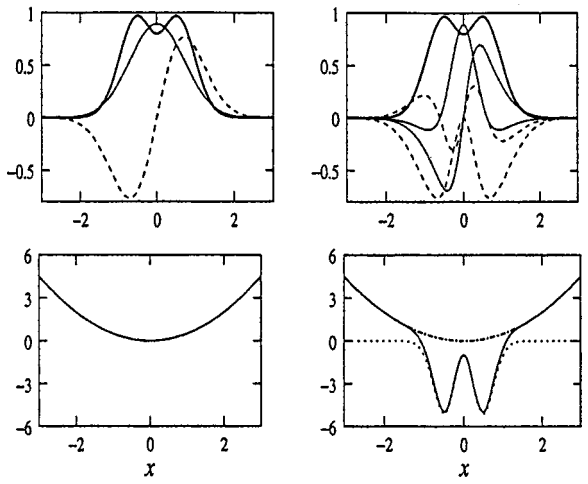

FIG. 1. The top left-hand plot shows the ground-state orbitals ϕ_1 (solid) and ϕ_2 (dashed) and their density n (thick solid line) for the harmonic potential in the lower-left-hand plot (atomic units). The top right-hand plot contains the real and imaginary parts of alternative orbitals $\tilde{\phi}_1$ (solid line) and $\tilde{\phi}_2$ (dashed line), and their density n (thick solid line), while below is the unique initial potential $\tilde{v}$ (solid line) that keeps the density constant.

exchange-correlation potentials, differing by the amount shown. In fact, different choices of the initial wave function allow us to make the two dips arbitrarily deep or small. Any purely density-functional approximation misses this effect entirely, and will produce the same exchange-correlation potential for all cases.

So, even in the simplest case of nondegenerate interacting and Kohn-Sham ground states, one can choose an alternative Kohn-Sham initial state, whose potential will look very different from that which evolves from the initial ground state. In practice, the majority of applications of TDDFT presently involve response properties of the ground state of a system, and one naturally chooses to start the Kohn-Sham system in its ground state. This choice is also dictated by the common use of adiabatic approximations for exchange-correlation potentials, which are approximate *ground-state* potentials evaluated on the instantaneous density. Such models will clearly be inaccurate even at $t=0$ if we start our Kohn-Sham calculation in any state other than its ground state.

The initial-state dependence of functionals is deeply connected to the issue of memory effects which are ignored in most TDDFT functional approximations used today. Yet these can often play a large role in exchange-correlation energies in fully time-dependent (i.e., nonperturbative) calculations [24], as well as giving rise to frequency dependence of the exchange-correlation kernel $[f_{XC}(\omega)]$ in linear response theory [25]. Functionals in general depend not only on the density at the present time, but also on its history. They may have a very nonlocal (in time) dependence on the density. But still more about the past is required: the functional is also haunted by the initial wave function. The initial state dependence is inextricably linked to the history of the density, and in fact can often be absorbed into density-dependence along a pseudoprehistory [26]. The results of this current paper shed some light on the importance of

memory effects arising from the initial wave function. To summarize, we have shown that there is no initial-state dependence for one electron, and that there can be arbitrarily large initial-state dependence for two electrons.

II. THEORY

Consider a many-electron density $n(\mathbf{r}t)$ evolving in time under an external (time-dependent) potential $v(\mathbf{r}t)$. Can we obtain the same evolving density $n(\mathbf{r}t)$ by propagating some different initial state in a different potential $\tilde{v}(\mathbf{r}t)$? This was answered in the affirmative in Ref. [23] under the condition that the two initial states have the same initial density and initial first time derivative of the density. Here we shall show that additional restrictions are required on the initial state for this statement to hold. In the one-electron case, the additional restrictions are so strong that there is *no* other initial state that evolves with the same density, as another does in a different potential.

A. One electron

Any two one-electron wave functions $\phi(\mathbf{r}t)$ and $\tilde{\phi}(\mathbf{r}t)$, with the same density $n(\mathbf{r}t)=|\phi(\mathbf{r}t)|^2=|\tilde{\phi}(\mathbf{r}t)|^2$, are related by a space- and time-dependent phase factor,

$$\tilde{\phi}(\mathbf{r}t)=\phi(\mathbf{r}t)\exp[i\alpha(\mathbf{r}t)], \tag{4}$$

where the phase $\alpha(\mathbf{r}t)$ is real. The evolution of each wave function is determined by the time-dependent Schrödinger equation with its potential (dot implies a time derivative):

$$[-\boldsymbol{\nabla}^2/2+v(\mathbf{r}t)]\phi(\mathbf{r}t)=i\dot{\phi}(\mathbf{r}t). \tag{5}$$

Both will satisfy the continuity equation

$$\dot{n}(\mathbf{r}t)=-\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}t), \tag{6}$$

where the current density of a wave function ϕ is

$$\mathbf{j}(\mathbf{r}t)=i[\phi(\mathbf{r}t)\boldsymbol{\nabla}\phi^*(\mathbf{r}t)-\phi^*(\mathbf{r}t)\boldsymbol{\nabla}\phi(\mathbf{r}t)]/2. \tag{7}$$

Substituting $\tilde{\phi}(\mathbf{r}t)$ from Eq. (4) into Eq. (7), we obtain

$$\Delta\mathbf{j}(\mathbf{r}t)=n(\mathbf{r}t)\boldsymbol{\nabla}\alpha(\mathbf{r}t). \tag{8}$$

(We use the notation Δa to denote $\tilde{a}-a$.) Because the densities are the same for all times, $\Delta\dot{n}(\mathbf{r}t)=0$, so, by Eq. (6),

$$\boldsymbol{\nabla}\cdot[n(\mathbf{r}t)\boldsymbol{\nabla}\alpha(\mathbf{r}t)]=0. \tag{9}$$

Integrating Eq. (9) with $\alpha(\mathbf{r}t)$, and performing the integral by parts, we find

$$\int d^3r\, n(\mathbf{r}t)|\boldsymbol{\nabla}\alpha(\mathbf{r}t)|^2=0. \tag{10}$$

We have taken the surface term $\int d^2\mathbf{S}\cdot(\alpha n\boldsymbol{\nabla}\alpha)$, evaluated on a closed surface at infinity, to be zero: this arises from the physical requirement that at infinity, where the electron density decays, any physical potential remains finite. (In fact this condition is required in the proof of the Runge-Gross theorem [12]). If the surface term did not vanish, then $\alpha\boldsymbol{\nabla}\alpha$ must grow at least as fast as $[r^2n(\mathbf{r})]^{-1}$ as r approaches infinity. This would lead to a potential that slides down to $-\infty$, which can be seen by inversion of the time-dependent Schrödinger equation in the limit of large distances. The state would oscillate infinitely wildly at large distances in the tails of the density, but the decay of the density is not enough to compensate for the energy that the wild oscillations impart: this state would have an infinite kinetic energy, momentum, and potential energy. (We shall see this explicitly in Sec. III A). So for physical situations, the surface term vanishes.

Because the integrand above cannot be negative, yet it integrates to zero, the integrand itself must be zero everywhere. Thus $\boldsymbol{\nabla}\alpha(\mathbf{r}t)=0$ everywhere except perhaps at nodes of the wave function where $n(\mathbf{r}_0t)=0$. In fact, even at the nodes, $\boldsymbol{\nabla}\alpha(\mathbf{r}_0t)=0$ to avoid highly singular potentials: if $\boldsymbol{\nabla}\alpha$ was finite at the nodes and zero everywhere else, then, as a distribution, it is equivalent to being zero everywhere; for example, its integral α is constant. There remains the possibility that $\boldsymbol{\nabla}\alpha$ is a sum of delta functions centered at the nodes; however, this leads to potentials which are highly singular at the nodes, as in Sec. I. Such unphysical potentials are excluded from consideration, so that $\boldsymbol{\nabla}\alpha(\mathbf{r}t)=0$, i.e., $\alpha(\mathbf{r}t)=c(t)$. The wave functions $\phi(\mathbf{r}t)$ and $\tilde{\phi}(\mathbf{r}t)$ can therefore differ only by an irrelevant time-dependent phase. In particular, this means that only one initial state and one potential can give rise to a particular density, i.e., the evolving density is enough to completely determine the potential and initial states.

The one-electron case is a simple counterexample to the conclusions in Ref. [23], which rely on the existence of a solution to

$$\boldsymbol{\nabla}\cdot[n\boldsymbol{\nabla}\Delta v]=\eta(\mathbf{r}t), \tag{11}$$

where $\eta(\mathbf{r}t)$ involves expectation values of derivatives of the momentum-stress tensor and derivatives of the interaction (see Sec. II B). This is to be solved for the potential subject to the requirements that the two initial states have the same $n(\mathbf{r}0)$ and $\dot{n}(\mathbf{r}0)$, and that $\boldsymbol{\nabla}\Delta v\to 0$ as $r\to\infty$. The two initial wave functions in the one-electron case have the same initial $n(\mathbf{r}0)$ [Eq. (4)] and $\dot{n}(\mathbf{r}0)$ [Eq. (9)], but no two physical potentials exist under which they would evolve with the same density, because there is no solution to Eq. (11) subject to the boundary condition that $\boldsymbol{\nabla}\Delta v=0$. (For an explicit demonstration of this in one-dimension, see Sec. III A.)

Note that although the density and the first time derivative of the density are the same for the two candidate initial wave functions, their momenta are different. The momentum of one of the states in fact is infinite. Requiring the initial momenta to be the same would be an additional restriction on the wave function. We shall come back to a closely related point at the end of Sec. II B.

B. Many-electron case

In this section we follow van Leeuwen's prescription to find the potential needed to make a given initial state evolve

with the same density as that of another. However we simplify the equations there somewhat to make the search for the solution of the potential easier. Given an initial state Ψ_0 which evolves with density $n(\mathbf{r}t)$ in a potential $v(\mathbf{r}t)$, we solve for the potential $\tilde{v}(\mathbf{r}t)$ in which a state $\tilde{\Psi}$ evolves with the same density $n(\mathbf{r}t)$. If we require $\tilde{\Psi}$ to have the same initial density and initial first time derivative of the density, then a solution for $\tilde{v}$ may be obtained from equating the equations for the second derivatives of the density for each wave function, subject to an appropriate boundary condition like $\Delta v \to 0$ at large distances. We are not guaranteed that such a solution exists: the wave function must have the additional restriction that the initial potential computed in this way is bounded at infinity.

The equation of motion for $\dot{n}$ yields [Eq. (15) of Ref. [23]]

$$\ddot{n}(\mathbf{r}t) = \nabla \cdot [n(\mathbf{r}t)\nabla v(\mathbf{r}t) + \mathbf{t}(\mathbf{r}t) + \mathbf{f}_{ee}(\mathbf{r}t)], \tag{12}$$

where

$$\mathbf{t}(\mathbf{r}t) = (\nabla' - \nabla)(\nabla^2 - \nabla'^2)\rho_1(\mathbf{r}'\mathbf{r}t)\big|_{\mathbf{r}'=\mathbf{r}}/4 \tag{13}$$

and

$$\mathbf{f}_{ee}(\mathbf{r}t) = \int d^3r' P(\mathbf{r}'\mathbf{r}t)\nabla v_{ee}(|\mathbf{r}' - \mathbf{r}|)/2, \tag{14}$$

where $\rho_1(\mathbf{r}'\mathbf{r}t)$ is the (off-diagonal) one-electron reduced density matrix, $P(\mathbf{r}'\mathbf{r}t)$ is the pair density (diagonal two-electron reduced density matrix) and $v_{ee}(u)$ is the two-particle interaction, e.g., $1/u$. Here and in what follows, ∇ and ∇' indicate the partial gradient operators with respect to $\mathbf{r}$ and $\mathbf{r}'$, respectively. In Eq. (13) and similar following equations, $\mathbf{r}'$ is set equal to $\mathbf{r}$ after the derivatives are taken.

The idea [23] is to subtract Eq. (12) for wave function Ψ from that for wavefunction $\tilde{\Psi}$, and require that $\ddot{n}$ is the same for each. First we simplify the kinetic-type term $\mathbf{t}$. Differentiating the continuity equation [Eq. (6)] implies

$$(\nabla + \nabla')(\nabla^2 - \nabla'^2)\Delta\rho_1(\mathbf{r}'\mathbf{r}t)\big|_{\mathbf{r}'=\mathbf{r}} = 0. \tag{15}$$

This equality enables us to incorporate the satisfaction of the equation of continuity in Eq. (12) (when we subtract the equation for Ψ from that for $\tilde{\Psi}$), and it also simplifies the kinetic-type term:

$$\Delta\mathbf{t}(\mathbf{r}t) = -\nabla(\nabla^2 - \nabla'^2)\Delta\rho_1(\mathbf{r}'\mathbf{r}t)\big|_{\mathbf{r}'=\mathbf{r}}/2. \tag{16}$$

(We note that although this is no longer explicitly real, it is in fact real for states with the same density and first time derivative.) So our simplified equation to solve becomes

$$\nabla \cdot [n\nabla\Delta v + \Delta\mathbf{t} + \Delta\mathbf{f}_{ee}] = 0, \tag{17}$$

where $\Delta\mathbf{t}$ is given by Eq. (16) and $\Delta\mathbf{f}_{ee}$ is given by Eq. (14), applied to the pair density difference.

To calculate the derivatives in the kinetic-type term, we define

$$\gamma(\mathbf{r}\mathbf{r}'t) = \Delta \log \rho_1(\mathbf{r}'\mathbf{r}t). \tag{18}$$

Note that γ vanishes at $\mathbf{r} = \mathbf{r}'$, and since $\rho_1(\mathbf{r}'\mathbf{r}t) = \rho_1^*(\mathbf{r}\mathbf{r}'t)$, $\gamma(\mathbf{r}'\mathbf{r}t) = \gamma^*(\mathbf{r}\mathbf{r}'t)$. These relations also imply that $\nabla^m\gamma(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}} = \nabla^m\gamma^*(\mathbf{r}\mathbf{r}'t)|_{\mathbf{r}'=\mathbf{r}}$. Writing

$$\gamma(\mathbf{r}\mathbf{r}'t) = \beta(\mathbf{r}\mathbf{r}'t) + i\alpha(\mathbf{r}\mathbf{r}'t), \tag{19}$$

where α and β are real functions, we also find $\nabla\beta(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}} = 0$, since $\nabla[\beta(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}}] = 0$. Also, $\nabla \cdot \nabla'\alpha(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}} = 0$, which follows from the antisymmetry of α. The generalization of Eq. (8) is

$$\Delta\mathbf{j}(\mathbf{r}t) = n(\mathbf{r}t)\nabla\alpha(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}}. \tag{20}$$

Continuity [Eq. (6)] then gives us a condition on the near-diagonal elements of α:

$$\nabla \cdot [n(\mathbf{r}t)\nabla\alpha(\mathbf{r}'\mathbf{r}t)|_{\mathbf{r}'=\mathbf{r}}] = 0. \tag{21}$$

Using all these results in Eq. (17), we find

$$\begin{aligned}\nabla\Delta v(\mathbf{r}t) = {} & (\dot{n}\nabla\alpha - \nabla^2\alpha\nabla\,\mathrm{Im}\,\rho_1 + \nabla\times\mathbf{B})/n \\ & + \nabla\,\mathrm{Re}(\nabla\gamma\cdot\nabla\rho_1 - \nabla'\gamma\cdot\nabla'\rho_1)/n \\ & + \frac{1}{2}\nabla\,\mathrm{Re}[(\nabla\gamma)^2 - (\nabla'\gamma)^2] \\ & + \frac{1}{2}\nabla(\nabla^2 - \nabla'^2)\beta \\ & - \frac{1}{2n(\mathbf{r}t)}\int d^3r'\Delta P(\mathbf{r}\mathbf{r}'t)\nabla v_{ee}(|\mathbf{r}' - \mathbf{r}|),\end{aligned} \tag{22}$$

where in the first three lines we have omitted the arguments, and it is understood that $\mathbf{r}'$ and $\mathbf{r}$ are set equal after all the derivatives are taken. $\mathbf{B}(\mathbf{r}t)$ is an undetermined vector whose role, together with an additional constant $C(t)$, is to ensure satisfaction of a boundary condition on the potential.

Now the prescription is to pick an initial state which has the same initial density and initial first time derivative of the density as the state Ψ; that is, require $\gamma(\mathbf{r}\mathbf{r}0) = 0$, and Eq. (21) is taken at $t = 0$. Then one can evaluate Eq. (22) at $t = 0$ and so find $\tilde{v}(\mathbf{r}0)$. The procedure for $t > 0$ is described in detail in Ref. [23]. In order for this procedure to yield a well-behaved physical potential, one needs to first check that the initial potential is not divergent at infinity. Equivalently, we may require that the elements of the momentum-stress tensor appearing in Eq. (11) do not diverge at infinity. This gives an additional restriction on the initial state. In the one-electron case, this restriction rules out *any* other candidate for an initial wave function which evolves with the same density as another wave function does in another potential: there is no way to pick $\mathbf{B}(\mathbf{r}0)$ or the constant $C(0)$ to satisfy any physical boundary condition discussed above. In the many-electron case, our additional condition restricts the allowable wave functions, but does not render the question of initial-state dependence moot as in the one-electron case.

III. EXAMPLES

A. One electron in one dimension

By studying the time-dependent Schrödinger equation for one electron in one dimension, it is simple to find explicitly the potential $\tilde{v}(xt)$ which cajoles $\tilde{\phi}(xt)$ into evolving with the same density as that of $\phi(xt)$, which evolves in a different potential $v(xt)$. Consistent with the conclusions above, this potential diverges to $-\infty$ at large x, which is unphysical. The initial state is pathological in the sense that its expectation value of momentum, kinetic energy and potential energy all diverge. A phase-space picture helps us to see how such a potential can hold a localized density.

Inserting Eq. (4) into the time-dependent Schrödinger equation (5), and calculating the derivatives, we obtain

$$\Delta v = i\alpha''/2 + i\alpha'\phi'/\phi - \alpha'^2/2 - \dot{\alpha} = 0. \tag{23}$$

where primes denote spatial derivatives. We now write ϕ in terms of an amplitude and phase

$$\phi(xt) = \sqrt{n(xt)}\exp[i\theta(xt)]. \tag{24}$$

Substituting into Eq. (23), and setting the real and imaginary terms separately to zero, yields

$$\Delta v = -\dot{\alpha} - \alpha'\theta' - \alpha'^2/2, \quad \alpha'' + \alpha' n'/n = 0. \tag{25}$$

For α' we find:

$$\alpha' = c(t)/n(xt). \tag{26}$$

We observe that this is also obtained when Eq. (9) (which arose from setting the time-derivatives of the densities to be equal) is considered in one dimension. Integrating once more gives

$$\alpha(xt) = c(t)\int^x \frac{dx'}{n(x't)} + d(t). \tag{27}$$

Plugging this solution into Eq. (25) gives

$$\Delta v(xt) = -\frac{c(t)\theta'(xt)}{n(xt)} - \frac{1}{2}\frac{c^2(t)}{n^2(xt)} - \dot{c}(t)\int^x \frac{dx'}{n(x't)} + c(t)\int^x \frac{\dot{n}(x't)}{n^2(x't)}dx' - \dot{d}(t). \tag{28}$$

We see immediately the divergence of this potential [for nonzero $c(t)$] where the density decays at large x. This demonstrates by explicit solution of the time-dependent Schrödinger equation that the only potentials in which a density can be made to evolve as the density in some other potential are unphysical, consistent with the conclusions of Sec. II A.

The state $\tilde{\phi}$ oscillates more and more wildly as x becomes larger in the tails of the wave function. Although the decay of the density at large distances unweights the rapidly oscillating phase, it is not enough to cancel the infinite energy that the wild oscillations contribute. Calculating the expectation value of momentum or kinetic energy in the state [Eq. (4)] with α given by Eq. (27), for a typical density and state ϕ (e.g., one which decays exponentially at large x), we find that they blow up.

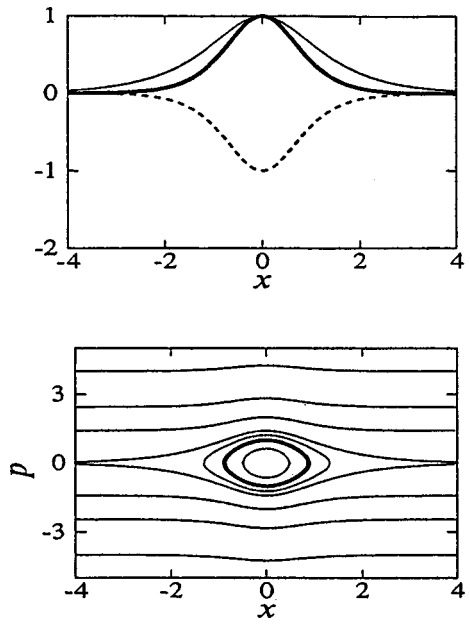

FIG. 2. The lower figure shows classical phase-space contours for the sech^2 well. The top figure shows the potential (dashed line), the wave function (solid line) corresponding to the heavily drawn contour in the phase-space below, and its density (thick solid line).

At first glance it may be striking that a potential which plunges to minus infinity at large distances can hold a wave function which is localized in a finite region in space. Consider the special case in that $\phi(xt)$ is an eigenstate of a time-independent potential $v(x)$. Let us also choose $c(t) = c$ to be time independent, so that $\tilde{v}(x)$ is also time independent and $\tilde{\phi}(xt)$ is an eigenstate of it. Let the density $n(x) = |\phi(xt)|^2 = |\tilde{\phi}(xt)|^2$ be localized at the origin. For example, v might be a potential well with flat asymptotes. Then we have the interesting situation where the eigenstate $\tilde{\phi}(x)$ is localized at the origin of its potential $\tilde{v}$ which plummets to $-\infty$ at large x. In Figs. 2 and 3 we have plotted the potentials, densities, and (real part of the) wave functions for the two cases; note the steep cliffs of $\tilde{v}$ and the rapid oscillations of $\tilde{\phi}$ as x becomes large, as we predicted. We chose the potential $v = -\text{sech}^2(x)$, and the state ϕ as its ground state. In the lower half of each figure are the classical phase space pictures (the classical energy contours) for the two potentials; to a good approximation the quantum eigenstates lie on those contours which have the correctly quantized energy (semiclassical approximation [27]). In Fig. 2 we show the situation for potential v; ϕ lies on the heavily drawn contour shown, which is a bound state oscillating inside the well. In Fig. 3 we show the situation for $\tilde{v}$; the heavy contour that $\tilde{\phi}$ lies on is of a different nature, not bound in any region in space. However, its two branches fall away from the origin very sharply, so that although they eventually extend out to large x, the projection on the x plane is much

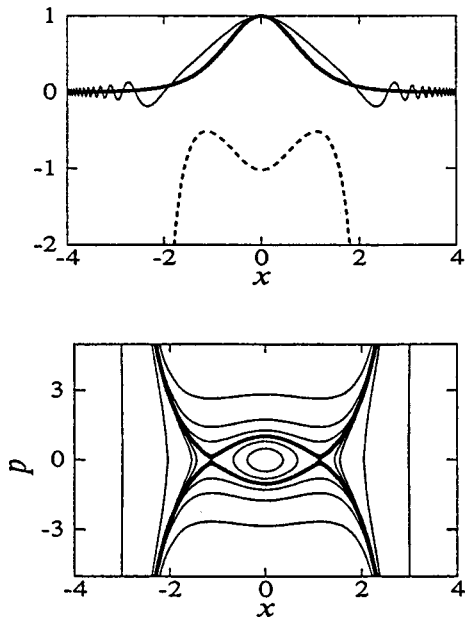

FIG. 3. As for Fig. 2, but for the pathological potential described in the text with $c=0.2$. The thinner solid line in the top figure is the real part of $\tilde{\phi}$.

denser near the origin than further away. This is how such a potential can support a localized density near the origin. The phase of the wave function in a semiclassical view is given by the action integral $\int p(x)dx$ along the contour, and the large step in p that is made in a short step in x thus implies that the phase oscillates rapidly. The tails of the density, which is the same in both cases, arise from fundamentally different processes: in the case of the simple sech^2 well (Fig. 2) the tails arise from classically forbidden tunneling, whereas in the case of the divergent potential (Fig. 3) they are classically allowed but have an exponentially small amplitude.

Finally, we relate the result for $\tilde{v}$ [Eq. (28)] to that obtained from the approach in Ref. [23] (and outlined in Sec. II B). Observe that for one electron, the initial conditions on $\tilde{\phi}$ required in Ref. [23] are the same as our Eqs. (4) and (9) [or, equivalently Eq. (26)], each evaluated at $t=0$. In one dimension it is then a straightforward exercise to calculate the terms of Eq. (22) at $t=0$, and, if we disregard the boundary condition, we can thus obtain an equation for the slope of the potential. This potential gradient is consistent with Eq. (28) evaluated at $t=0$ that we obtained by the time-dependent Schrödinger's equation above; here we obtain

$$\Delta v' = (c^2 n' + 2cn\dot{n} + 2cj + n^2 f)/n^3, \tag{29}$$

where $n=n(x0), j=j(x0), v=v(x0), c=c(0)$, and f is a constant to be determined by the boundary condition $\Delta v \rightarrow 0$ at ∞. However, in the present one-electron case such a boundary condition cannot be satisfied.

B. Two noninteracting electrons in one dimension

Here we explicitly construct the potential at the initial time under which two initial noninteracting wave functions evolve with the same density. Let ϕ_1 and ϕ_2 represent the initial orbitals for an initial state Φ, and $\tilde{\phi}_1$ and $\tilde{\phi}_2$ represent those for another initial state $\tilde{\Phi}$. We choose

$$\tilde{\phi}_i(x) = \phi_i(x)\exp[i\theta_i(x)], \tag{30}$$

where $\theta_i(x)$ are real functions. This form guarantees that the densities are the same initially. The difference of initial current between $\tilde{\Phi}$ and Φ is

$$\Delta j = \theta_1'(x)|\phi_1(x)|^2 + \theta_2'(x)|\phi_2(x)|^2, \tag{31}$$

where the prime indicates differentiation, and so the condition of equal initial $\dot{n}$ becomes

$$\frac{\partial}{\partial x}[\theta_1'(x)|\phi_1(x)|^2 + \theta_2'(x)|\phi_2(x)|^2] = 0. \tag{32}$$

The choices

$$\theta_1'(x) = c|\phi_2(x)|^2 \quad \text{and} \quad \theta_2'(x) = -c|\phi_1(x)|^2, \tag{33}$$

where c is some constant, ensures that Eq. (32) is satisfied.

To simplify the calculation of the potential gradient in Eq. (22) further, we take the orbitals ϕ_1 and ϕ_2 to be real, and take the density to be time independent. After straightforward calculations we arrive at

$$\Delta v' = -c^2[n'\phi_1^2\phi_2^2/n + 2\phi_1\phi_2(\phi_2\phi_1' + \phi_1\phi_2')]. \tag{34}$$

This gives the initial gradient of the potential in which $\tilde{\Phi}$ will evolve with the same density as that of Φ at $t=0$.

These equations were used to formulate Fig. 1, for which $c=4$. The orbitals $\phi_i(x)$ are just the lowest and first excited states of the harmonic oscillator of force constant $k=1$, and so their density remains constant in this potential. Although this kind of potential is not strictly allowed because it does not remain finite at ∞, we expect that the results still hold for well-behaved initial states: the difference between the potentials for Φ and $\tilde{\Phi}$ vanishes at ∞. Moreover, it, or rather, the interacting three-dimensional version (Hooke's atom) is instructive for studying properties of density functionals (see, e.g., Ref. [28]) because an exact solution is known. We can make the dips on the right of the figure arbitrarily large, simply by increasing c. Note that the alternative orbitals probably do not yield an eigenstate of this potential. In the next instant, this alternative potential will change, in order to keep the density constant. This change can be calculated using van Leeuwen's prescription.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[4] K. Yabana and G. F. Bertsch, e-print cond-mat/0005512.
[5] X.-M. Tong and S.-I. Chu, Phys. Rev. A **57**, 452 (1998).
[6] K. Yabana and G. F. Bertsch, Phys. Rev. A **60**, 3809 (1999).
[7] K. Yabana and G. F. Bertsch, Phys. Rev. A **60**, 1271 (1999).
[8] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **103**, 9347 (1995).
[9] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[10] E. K. U. Gross, J. F. Dobson, and M. Petersilka, Top. Curr. Chem. **181**, 81 (1996).
[11] G. D. Mahan and K. R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum Press, New York, 1990).
[12] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[13] J. Chen and M. J. Stott, Phys. Rev. A **44**, 2816 (1991).
[14] Q. Zhao and R. G. Parr, Phys. Rev. A **46**, 2337 (1992).
[15] Q. Zhao and R. Parr, Phys. Rev. A **46**, R5320 (1992).
[16] A. Görling, Phys. Rev. A **46**, 3753 (1992).
[17] Á. Nagy, J. Phys. B **26**, 43 (1993).
[18] Y. Wang and R. G. Parr, Phys. Rev. A **47**, R1591 (1993).
[19] C. J. Umrigar and X. Gonze, in *High Performance Computing and its Application to the Physical Sciences*, Proceedings of the Mardi Gras 1993 Conference, edited by D. A. Browne *et al.* (World Scientific, Singapore, 1993).
[20] E. V. Ludeña, R. Lopez-Boada, J. Maldonado, T. Koga, and E. S. Kryachko, Phys. Rev. A **48**, 1937 (1993).
[21] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[22] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
[23] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).
[24] P. Hessler, N. T. Maitra, and K. Burke (unpublished).
[25] M. Lein, E. K. U. Gross, and J. P. Perdew, Phys. Rev. B **61**, 13 431 (2000).
[26] N. T. Maitra and K. Burke (unpublished).
[27] E. J. Heller, J. Chem. Phys. **67**, 3339 (1977); and in *1989 NATO Les Houches Lectures, Summer School on Chaos and Quantum Physics*, edited by M-J. Giannoni, A. Voros, and J. Zinn-Justin (Elsevier, Amsterdam, 1991), p. 547.
[28] P. Hessler, J. Park, and K. Burke, Phys. Rev. Lett. **82**, 378 (1999); **83**, 5184(E) (1999).