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On the mapping of time-dependent densities onto potentials in quantum mechanics

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The mapping of time-dependent densities on potentials in systems of identical quantum mechanical particles is examined. This mapping is of significance ever since Runge and Gross [Phys. Rev. Lett. **52**, 997 (1984)] established its uniqueness, forming the theoretical basis for time-dependent density functional theory. Beyond uniqueness there are two important issues: existence, often called v-representability, and stability. We show that v-representability for localized densities in turn-on situations is not assured and we give a simple example of nonexistence. As for stability, we discuss an inversion procedure and by computing its Lyapunov exponents we demonstrate that the mapping is unstable with respect to fluctuations in the initial state. We argue that such instabilities will plague any inversion procedure. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2822124]

A fundamental conjecture lying at the very heart of quantum mechanical density functional theory (DFT) is the property of v-representability (VR) of a given density function, namely, the existence of a system of N identical particles that has this density in its quantum ground state.[1] This and a related issue, of "noninteracting" VR, have been explored in several important works.[1–8] The main result is that VR in DFT is not guaranteed in general even for reasonable looking densities in real-space. However, for discretized systems, such as systems on lattices, it was shown in a series of developments that all densities are noninteracting VR.[1,4] The same is true (but with uniqueness problems) for finite-dimensional spaces.[8,9]

A similar issue arises in time-dependent (TD) DFT when the "density on potential mapping" (DoPM) is considered. Runge and Gross[10] (RG) proved uniqueness, while Mearns and Kohn[11] found that VR cannot be guaranteed in temporal sinusoidal density fluctuations. This crack in TDVR was partially healed when van Leeuwen considered "switch-on densities"[12] showing that VR is assured in a variety of important cases. A third aspect of the DoPM, largely neglected up to now, is its chaotic nature. This issue is important in practical attempts to apply DoPM.[13] Recently the issue of stability of the DoPM has come up "through the back door" when it was realized that the optimized effective potential procedure suffers from instabilities.[14–17]

The present study explores VR, uniqueness, and stability in "switch-on" densities. First, we show by example that in finite lattice models TDVR is not guaranteed. Next, we consider a real-space system represented on a grid. We find that although VR is formally assured, it is impossible to carry out DoPM due to inherent instabilities which are coupled to near singularities.

Let us start by considering VR in general following Ref. 12. Suppose we are given a three-dimensional particle density $n(\mathbf{r},t)$, $t\geqslant 0$ of N_e particles and a compatible initial state ψ_0 such that the following two conditions hold:

$$n(\mathbf{r},0)=\langle\hat{n}(\mathbf{r})\rangle_{t=0},\quad \dot{n}(\mathbf{r},0)=\nabla\cdot\langle\hat{\mathbf{j}}(\mathbf{r})\rangle_{t=0}, \tag{1}$$

where $\hat{n}(\mathbf{r})$ and $\hat{\mathbf{j}}(\mathbf{r})$ are the operators of density and current density at $\mathbf{r}$ and $\langle\cdot\rangle_t\equiv\langle\psi(t)|\cdot|\psi(t)\rangle$. Denoting $\hat{F}=\hat{T}+\hat{U}$ as the sum of kinetic energy $\hat{T}$ and interaction energy $\hat{U}=\frac{1}{2}\Sigma_{i,j}v_{12}(|\mathbf{r}_i-\mathbf{r}_j|)$ of the particles we want to find the potential $v(\mathbf{r},t)$ for which the Schrödinger equation

$$i\dot{\psi}(t)=\left[\hat{F}+\int v(\mathbf{r},t)\hat{n}(\mathbf{r})d^3r\right]\psi(t),\quad \psi(0)=\psi_0 \tag{2}$$

yields a TD wave function $\psi(t)$ for which $n(\mathbf{r},t)=\langle\hat{n}(\mathbf{r})\rangle_t$. An implicit equation for v follows from Heisenberg's equations

$$\hat{D}v(\mathbf{r},t)=-\langle[\hat{F},[\hat{T},\hat{n}(\mathbf{r})]]\rangle_t-\ddot{n}(\mathbf{r},t), \tag{3}$$

where $\hat{D}$ is a linear "Hermitian" operator on potentials $\hat{D}v(\mathbf{r},t)=\int\langle[\hat{n}(\mathbf{r}'),[\hat{T},\hat{n}(\mathbf{r})]]\rangle_t v(\mathbf{r}',t)d^3r'$. van Leeuwen showed that in real space, under conditions that the density drops to zero at infinity, $\hat{D}_{\rm rs}v=-\nabla\cdot(n\nabla v)$. The integral form for $\hat{D}$ is useful in finite basis calculations. In real space and Fourier grid applications the operator is, in fact, essentially positive definite. Because of this latter property, VR is assured in TDDFT ($\hat{D}$ is invertible) and Eq. (3) combined with Eq. (2) gives the DoMP.[12]

Before we analyze more fully the real-space case, let us first consider a simple two-site system with wave function $\psi=(\psi_1\ \psi_2)^T$. We now show that this system is not VR. The Schrödinger equation is

$$i\dot{\psi}(t)=\hat{H}(t)\psi,\quad \hat{H}(t)=V(t)\hat{\sigma}_z+\hat{\sigma}_x, \tag{4}$$

where σ_i $(i=x,y,z)$ are the Pauli matrices:

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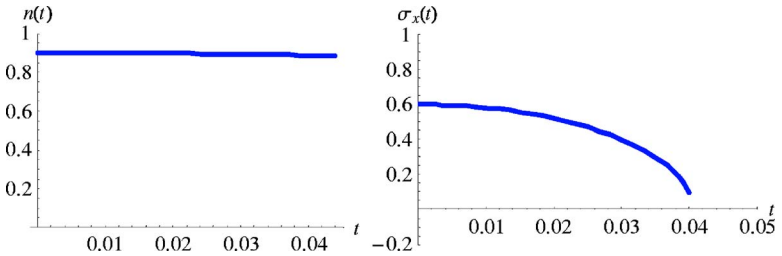

FIG. 1. (Color online) The density $n(t)$ (left) and $\sigma_x(t)$ for the two-level system case study.

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{5}$$

having the well-known cyclic commutation relations $2i\hat{\sigma}_x = [\hat{\sigma}_y, \hat{\sigma}_z]$. A term proportional to σ_y was not included in the Hamiltonian; it corresponds to the presence of magnetic vector potentials.

The density is $\hat{n} = (\hat{\sigma}_z + 1)/2$ (clearly, knowing the density at one site is sufficient). The analog of the RG theorem in this case states that given a density $n(t)$ and a compatible initial state $\psi(0)$ obeying conditions analogous to Eq. (1):

$$n(0) \equiv \langle n \rangle_{t=0}, \quad \dot{n}(0) \equiv \langle \sigma_y \rangle_{t=0}, \tag{6}$$

the potential $V(t)$ is uniquely determined. From Heisenberg's equations $\ddot{\hat{n}}(t) = 2(V\hat{\sigma}_x - \hat{\sigma}_z)$ so the potential $V(t)$ affects $\ddot{n}(t)$ and the analog of Eq. (3) for this system is

$$\sigma_x(t)V(t) = \ddot{n}(t)/2 + \sigma_z(t) \equiv f(t), \tag{7}$$

where $\sigma_x(t) = \langle \psi(t) | \hat{\sigma}_x | \psi(t) \rangle$. Clearly, $f(t) = \ddot{n}(t)/2 + 2n(t) - 1$ is determined solely by the given density. $V(t)$ is determined directly from Eqs. (7) and (4), obtaining the nonlinear Schrödinger equation

$$i\dot{\psi}(t) = \left(\frac{f(t)}{\sigma_x(t)} \hat{\sigma}_z + \hat{\sigma}_x \right) \psi(t). \tag{8}$$

This is a direct analogy to the combination of Eqs. (3) and (2) in the real-space system. Solving this equation yields the mapped potential $V(t) = f(t)/\sigma_x(t)$. Indeed this potential is unique. Existence, however, is not assured because $\sigma_x(t)$ is not a positive definite. Thus at some t_c the denominator may vanish while the numerator does not. This happens whenever the system localizes on one site. It also happens when $\mathrm{Re}\, \psi_1^* \psi_2$ vanishes, as seen in the following example. Consider the given density:

$$n(t) = (1 + \mu \cos \omega t)/2, \tag{9}$$

with $\mu = 0.8$ and $\omega = 2\pi$. The density has the property that $n(0) = 9/10$ and $\dot{n}(0) = 0$; thus a compatible initial state is the real state $\psi(0) = (3\ 1)^T/\sqrt{10}$. It is periodic with period of $T = 1$ but we will only consider a small fraction of the first period, $t \in [0, 0.04]$. The density in this time interval is given in Fig. 1 (left), smooth and almost constant. The value of $f(t)$ is almost constant as well, equal to ~ -0.7. Still, looking at σ_x, one sees that it quickly drops from an initial value of 0.6 to zero at $t_c \approx 0.04$. At this time the SE blows up and the potential becomes undefined. In conclusion, here is a case where a naïve time-dependent density on a (two-site) lattice is non-v-representable.

What about circumventing this, forcing an approximate solution in Eq. (7)? A standard approach due to Tikhonov[18] is to replace f/σ_x by $V = \sigma_x f/(\sigma_x^2 + \alpha)$, where $\alpha > 0$ is small, leading to the regularized Schrödinger equation

$$i\dot{\psi}(t) = \left(\frac{f(t)\sigma_x(t)}{\sigma_x(t)^2 + \alpha} \hat{\sigma}_z + \hat{\sigma}_x \right) \psi(t). \tag{10}$$

This gives an approximate density $\tilde{n}(t)$. If the difference $\Delta n(t) = n(t) - \tilde{n}(t)$ is small, we can be satisfied with $\tilde{n}$ as an approximation. Sometimes this works. But it can also fail. In our case, a small value of α (10^{-8}) leads to insurmountable numerical instabilities even when stiff solvers for Eq. (10) are used. Lowering the value of α to 10^{-4} leads to large divergence in precision as $t > t_c$ [Fig. 2 (left)].

The reason for the large deviances near and after $t > t_c$ is a result of instability of Eq. (8), as shown by a Lyapunov analysis,[19] whose details will be described in a later publication. The wave function at time t $\psi(t) = \xi + i\eta$ is decomposed into its real and imaginary parts. If a fluctuation $\delta\psi = \delta\xi + i\delta\eta$ is formed at this time it will evolve under the linearized equation $(|\delta\dot{\xi}\rangle\ |\delta\dot{\eta}\rangle)^T = \hat{L}(|\delta\xi\rangle\ |\delta\eta\rangle)^T$, where

$$\hat{L} = \begin{pmatrix} 0 & \hat{H} \\ -\hat{H} & 0 \end{pmatrix} - \frac{f}{\sigma_x^2} \begin{pmatrix} \hat{\sigma}_z |\eta\rangle\langle\xi| \hat{\sigma}_x & \hat{\sigma}_z |\eta\rangle\langle\eta| \hat{\sigma}_x \\ -\hat{\sigma}_z |\xi\rangle\langle\xi| \hat{\sigma}_x & -\hat{\sigma}_z |\xi\rangle\langle\eta| \hat{\sigma}_x \end{pmatrix}. \tag{11}$$

The stability of Eq. (8) is determined by the eigenvalue of $\hat{L}$ having the largest real part $\lambda(t) = \lambda' + i\lambda''$. If $\lambda' > 0$ then there will be fluctuations that grow in proportion to $e^{+\int_0^t \lambda'(t')dt'}$. $\lambda'(t)$ is called the local Lyapunov exponent.[19] Denoting the local Lyapunov exponent for Eq. (8) by $\lambda(t) = -\Lambda(t) f(t)/\sigma_x^2$ we calculated numerically $\Lambda(t)$. This quantity, shown in

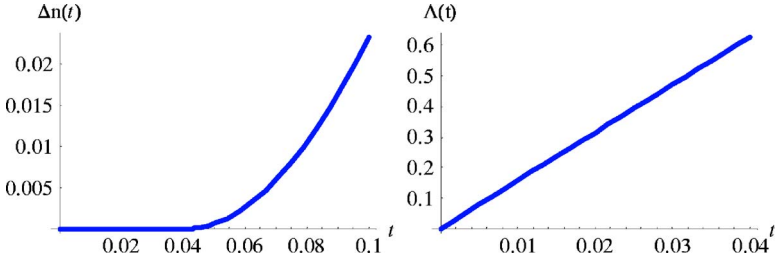

FIG. 2. (Color online) (Left) The error in density when $\alpha = 10^{-4}$. (Right) The nonexplosive coefficient of the maximal local Lyapunov exponent.

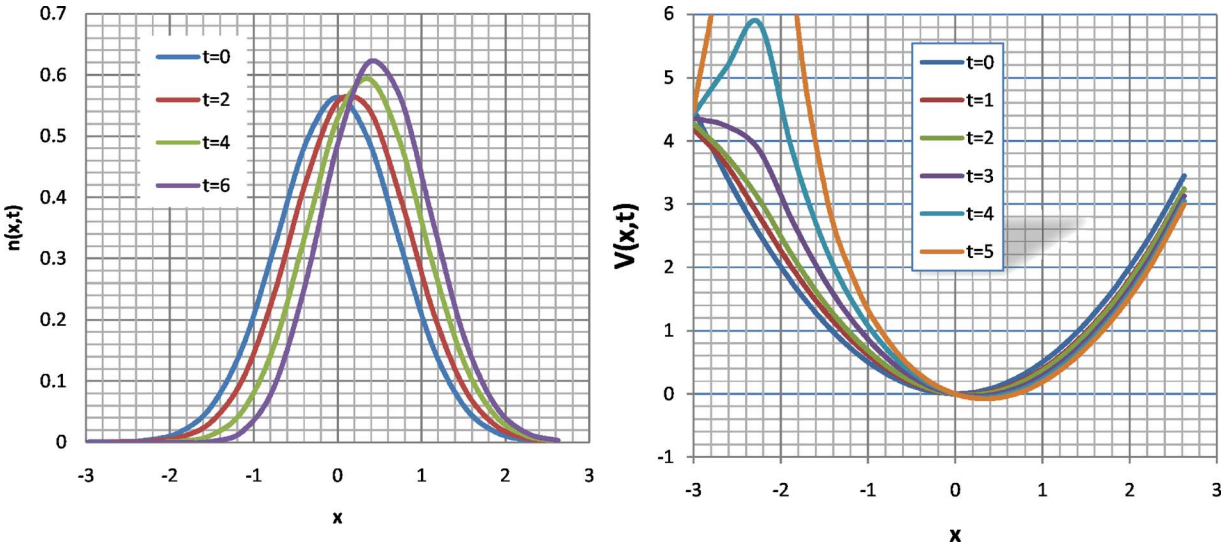

FIG. 3. (Color online) (Left) The density as a function of time for the model problem. (Right) The calculated mapped potential.

Fig. 2 (right), is positive and grows more or less linearly with t. Since $f(t)$ is almost constant, with a value near −0.7, we find that in the vicinity of t_c, where $\sigma_x(t)$ drops near zero the Lyapunov exponent $\lambda'(t)$ becomes huge and positive, rendering Eq. (8) highly chaotic near t_c: any small fluctuation in the wave function will cause a large change in the density which in turn causes the wave function to change even more and thus will build itself into a large density fluctuation growing exponentially with time, as indeed seen in Fig. 2.

After considering the two-level system, let us return to real space using the combination of Eqs. (3) and (2). The first problem one encounters is that in any typical quantum mechanical system there are regions where the density is very small (the asymptotes, for example) and this causes near singularities in $\hat{D}$ [$\hat{D}$ is positive definite except for a trivial singularity in that $\hat{D}v=0$ whenever $v(\mathbf{r})=$const, but this is easy to handle]. These near singularities lead to an ill-posed Eq. (3). Thus some sort of regularization is needed. We can use Tikhonov's regularization for the inverse of $\hat{D}=\Sigma_n d_n|w_n\rangle\langle w_n|$ (written in terms of its eigenvalues d_n and eigenvectors $|w_n\rangle$) replacing $\hat{D}^{-1}$ by

$$\hat{D}^{-1} \to \sum_n i(d_n)|w_n\rangle\langle w_n|, \tag{12}$$

where $i(d_n)=[d_n/(d_n^2+\alpha)]$ $\alpha>0$ is the small regularization parameter. In any application the value of α must be chosen carefully as a compromise between two Platonic ideals: precision and stability.

As in the two-level system, the problem one encounters is that small errors (incurred by Tikhonov regularization) are sometimes amplified by the unstable nature of the nonlinear time propagation. We performed a stability analysis of the Lyapunov type here as well. A fluctuation in the wave function will grow in time approximately as $e^{\int_0^t \lambda'_n(\tau)d\tau}$, where λ'_n is the Lyapunov exponent. If the $1/t\int_0^t \lambda'_n(\tau)d\tau$ is positive, the solution is unstable, i.e., fluctuations will grow exponentially. We give now an explicit example where this happens (such an example was not difficult to find: practically any attempt to map a potential for a given density failed in a similar manner). Consider a one-dimensional particle of unit mass in a Harmonic potential well $V(x)=\frac{1}{2}x^2$ with time-dependent density:

$$n(x,t) = (\cos \omega\tau(t)\psi_0(x) + \sin \omega\tau(t)\psi_1(x))^2, \tag{13}$$

where $\psi_0(x)$ and $\psi_1(x)$ are the ground and first excited states of this potential. We choose the function $\tau(t)=t^4/(1+t^3)$. Since $\dot{\tau}(0)=0$, $\psi_0(x)$ can be taken as the initial state. We took $\omega=2\pi/100$ and considered only short times relative to the period (i.e., $t\ll 100$) so here too only relatively gentle perturbations of the density are considered. The density as a function of x and t is shown in Fig. 3 (left).

We solve the inversion equations, Eqs. (2) and (3), on a grid, spanning the range $x\in[-3,3]$ and using $N=16$ points. The representation is based on the Fourier grid approach, employing periodic boundary conditions.[20] The nonlinear time propagation was implemented using two different methods, which gave almost identical results, namely, the explicit fifth order adaptive step size Runge-Kutta (ERK) and a third order implicit Runge-Kutta (IRK) method. The latter is suited for stiff problems. We took $\alpha=10^{-12}$ for regularization: eigenvalues of $\hat{D}$ much larger than 10^{-5} are treated almost exactly while those much smaller than 10^{-6} are almost completely neglected. This means that $\hat{D}$ has a condition number of about 10^6 and therefore is not too susceptible to roundoff errors (which are of the order of 10^{-13}). The deviance between the given densities $n(x,t)$ and $|\psi(x,t)|^2$, $\Delta n \equiv \max_{i\in \text{grid}}|n_i(t)-|\psi_i(t)|^2|$ is shown in Fig. 4. In the ERK calculation a moderate monotonic increase in the error is abruptly broken and a catastrophic increase is seen at $t_c=5.5$. This is accompanied by huge increase in calculation time since the time step of the adaptive algorithm quickly drops to a minute value due to the instability. In the IRK the algorithm does not explode but halts at time $t=5.6$ where it becomes impossible to converge the self-consistent IRK iterations. We have computed the eigenvalues of the Lyapunov operator $\hat{L}$ for this problem. These are given in Fig. 4 (right),

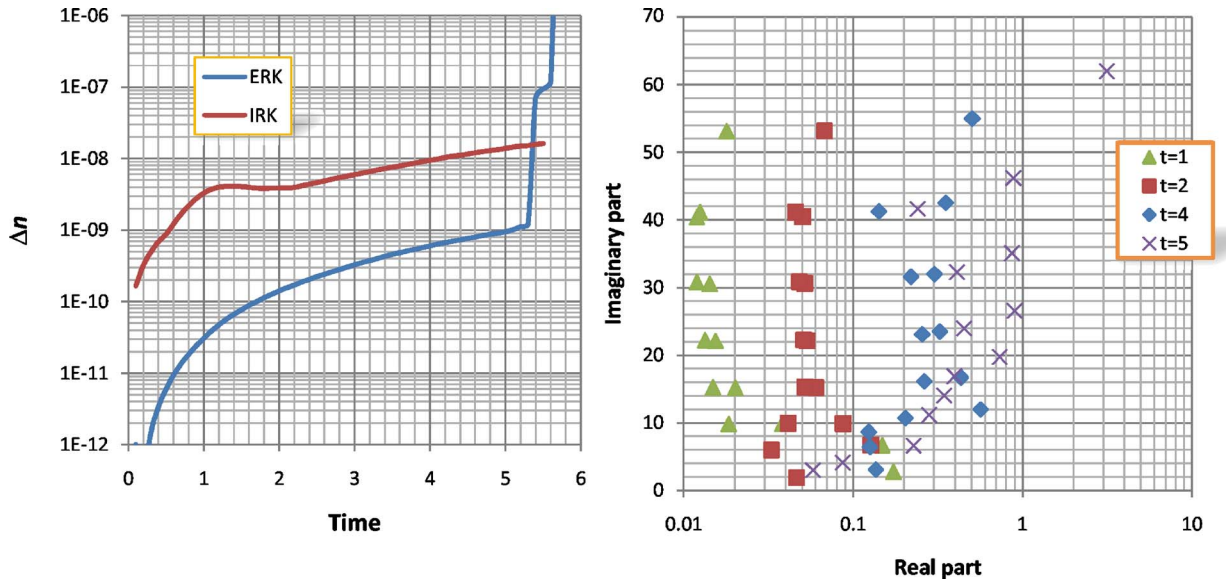

FIG. 4. (Color online) (Left) The density deviance $\Delta n(t)$ using two numerical propagators: IRK and ERK. (Right) The local Lyapunov exponents (positive real parts) for several times.

where the Lyapunov exponents are seen to be positive and fast growing as t approaches $t=5.6$.

In summary, we have considered two issues of the DoPM. First, the issue of v-representability on a lattice, where we showed by an example that it is not guaranteed. It is noteworthy that in DFT, v-representability is assured on lattices but not in real space while in TDDFT we find the situation is exact opposite.[12] Then, we considered the issue of stability by computing Lyapunov exponents. We gave two cases where the mapping of densities on potentials is highly unstable even in cases of "innocent looking" densities. The physical meaning of the instability is that the potential at time $t \gg 0$ is unstable with respect to errors in the initial state. Thus, any inversion procedure is amenable to instabilities. For TDDFT, the broader consequence here is that XC potentials $v_{XC}[n](\mathbf{r},t)$ are likely to be extremely sensitive functionals of the density n especially in strongly time-dependent problems.

Finally, we point out that these two issues, namely, the stability and existence (VR), are most likely intimately connected. Indeed, we find in our two-site lattice example that the instability is greatly amplified near the instant where the inversion procedure becomes singular. In non-time-dependent DFT it can be argued that instabilities in the DoPM are related to the existence of non-VR densities. The latter correspond to external potentials that are generalized functions[4] and thus there exist sequences of (ensemble) VR densities that converge to a non-VR density, while the associated sequence of potentials will not converge. Furthermore, the ill conditioning of the DoPM in DFT can also be seen as following from the fact that the linear response spectrum has an accumulation point at zero and thus the inverse linear response (density to potential mapping) is infinitely ill conditioned.

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