Correlation in time-dependent density-functional theory

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The exact time-dependent correlation energy in time-dependent density-functional theory is shown to sometimes become positive, which is impossible with most present TDDFT approximations. Both the correlation potential and energy can be strongly nonlocal in time. A new inequality is derived for the time-dependent exchange-correlation energy. The correlation energy appears to scale to a constant function of scaled time in the high-density limit. In the linear response regime, the correlation energy is shown to become purely adiabatic, but the correlation potential is generally nonadiabatic. The usefulness of the virial theorem as a test of numerical accuracy is demonstrated. All results are found or inspired by exact numerical solution of a simple model system (Hooke's atom), and inversion of the corresponding Kohn–Sham equations. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1479349]

I. INTRODUCTION

Ground-state density functional theory (DFT) has become a useful alternative to traditional methods in quantum chemistry, because of its ability to treat large numbers of electrons with reasonable accuracy.[1] Time-dependent density-functional theory (TDDFT) is the generalization of ground-state DFT to include *time-dependent* external potentials on electrons, and its formal validity was established with the Runge–Gross theorem.[2] The one-to-one correspondence between time-dependent densities and time-dependent potentials for a given initial state leads to the time-dependent Kohn–Sham system, a set of noninteracting fictitious electrons moving in a time-dependent Kohn–Sham potential. TDDFT has now been applied to many problems in atomic, molecular and solid-state systems, including optical response, dynamic polarizabilities and hyperpolarizabilities, excitation energies, species in intense laser fields and highly energetic collisions.[3–34] Although most of these calculations take place in the linear response regime, TDDFT also applies to species in intense fields and is perhaps the only feasible method to study many-electron dynamics in this regime.[35–39]

The only unknown part of a TDDFT calculation (beginning in a nondegenerate ground state[40]) is the exchange-correlation potential $v_{XC}[n](\mathbf{r}t)$ as a functional of the entire history of the density, $n(\mathbf{r}t)$. In the special case of optical response, including electronic excitation energies, this is needed only in the vicinity of the ground-state density of the system, and this information is contained in the exchange-correlation kernel, $f_{XC}[n](\mathbf{r},\mathbf{r}',t-t')$. But relatively little is known about these functionals, partly because relatively few conditions that the exact functionals satisfy are known.

Exact conditions have been essential in ground-state DFT, both for guiding construction of universally applicable functionals,[41] and in explaining why some approximations work well while others do not.[42,43] Known exact conditions in TDDFT include Newton's third law,[44–46] the harmonic

potential theorem,[47] a viral theorem,[48] the relation between coupling constant and scaling,[48] and the memory formula.[40] For example, part of the motivation for developing the Vignale–Kohn approximation for the exchange-correlation kernel[49] was that the Gross–Kohn approximation[50] violated the harmonic potential theorem. The present work makes several new exact statements about correlation functionals in TDDFT, many of which are *not* satisfied by the present generation of approximate functionals.

A key focus in this work is on the limitations of adiabatic approximations to correlation functionals. Such an approximation ignores the temporal nonlocality of the correlation potential, i.e., its dependence on the history of the density. In the case of linear response, this leads to a real-valued, frequency-independent, exchange-correlation kernel. Most (if not all) chemical applications of TDDFT[51] employ an adiabatic approximation such as ALDA,[52–55] but little is known about its reliability or accuracy. Almost all our results demonstrate *failures* of this approximation; failures that likely must be addressed if ultimately TDDFT is to achieve the quantitative accuracy enjoyed by ground-state DFT today.

The errors made by the adiabatic approximation are called dynamical effects, due to history-dependence in the time-dependent functionals. A key technique of the present work is to study the time-dependent correlation *energy*, as opposed to the potential. This is primarily a technical device, designed to limit the amount of information presented. The time-dependent correlation energy is determined by integrals over the correlation potential, so that poor approximations to the energy imply poor approximations to the potential. Also, approximations that are poor for the potential point-wise in space may produce reasonable approximations for integrated quantities, as is true in the ground-state case. Lastly, the time-derivative of the correlation energy yields the correlation contribution to the power absorbed during the disturbance.

Our calculations are performed on a time-dependent Hooke's atom, two electrons in a harmonic well[56] with a

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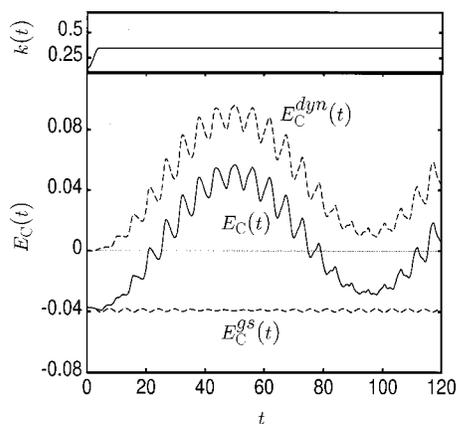   72   © 2002 American Institute of Physics

FIG. 1. Correlation energy components as a function of time when the force constant is changed as shown in the top panel (all in atomic units): Instantaneous ground-state correlation energy (bottom dashed line), true correlation energy (solid line), dynamical part of the correlation energy (top dashed line).

time-dependent force constant.[57] Because the system remains spherical, the time-dependent Schrödinger equation can easily be solved numerically, and the Kohn–Sham equation inverted. The model system is *not* intended to represent an atom or molecule under conditions in present-day experiments. But, Hooke's atom is a Coulomb-interacting fermion system and so its behavior is governed by the same functionals as for all electronic systems: Atoms, molecules, and solids. Until recently,[48,59] there have been no exact TDDFT calculations on any system. These two previous exact calculations[48,59] employ this system: In two-dimensions in Ref. 59 and in three-dimensions in Ref. 48.

Our most dramatic result is to show that, due to dynamic correlation, the correlation energy can become positive. In Fig. 1, we plot the correlation energy of Hooke's atom as a function of time when the force constant is increased smoothly from 0.15 to 0.35 during $t=0-4$ and then held constant, as shown in the top panel. We also plot the (almost) exact correlation energy if the instantaneous density was the ground-state density of some system, i.e., $E_C^{gs}[n(\mathbf{r}t)]$, where $n(\mathbf{r}t)$ is the time-dependent density. (Precisely how this is done is given in Sec. III.) The difference between the two, which we call the dynamical contribution $E_C^{dyn}(t)$, is very significant, so much so that the correlation energy even becomes positive. Clearly, any adiabatic approximation, being local in time, can at best approximate $E_C^{gs}[n(\mathbf{r}t)]$, and will miss the dynamical contribution entirely. Such strong exchange-correlation effects *must* be present in any species perturbed by a laser field near a resonance. In the linear response formalism, exchange and correlation change ground-state Kohn–Sham transition frequencies and oscillator strengths into exact quantities of the true system. A perturbation tuned to a Kohn–Sham transition will cause the Kohn–Sham system to resonate, but exchange-correlation corrections stop the true system from doing so.

We prove rigorously an inequality relating the dynamic exchange-correlation energy and the dynamic noninteracting kinetic energy (see Sec. V A). We also demonstrate explicitly that the correlation potential and energy can have a strong

nonlocality in time, depending on the history of the density (see Sec. V B). Again, any adiabatic approximation fails to capture this effect. On the other hand, we argue that the exchange energy for N electrons, will typically depend only weakly on the history (for a two electron singlet, as in our model, it depends only on the instantaneous density).

Notwithstanding a previous study in two-dimensions,[59] we show in Sec. V C, that there *is* a finite dynamical contribution to the correlation potential in this limit. (Ironically, this does *not* show up in the correlation energy, which can be proven to be second-order in the strength of the perturbation in general.) Even in Hooke's atom, corrections to an adiabatic approximation can be important in linear response as well as in strong fields.

The behavior of functionals under uniform coordinate scaling has been an important guide to the construction of functionals in the ground-state theory. A key improvement of the PBE generalized gradient approximation[41] over the local density approximation (LDA)[60] and the Perdew–Wang exchange-correlation functional (PW91)[61] is that, for a finite system, it scales correctly to a constant in the high-density limit, while remaining exact for the uniform electron gas [unlike the Lee–Yang–Parr (LYP)[62] correlation functional]. In Ref. 48, the relation between coupling constant and scaling within TDDFT was deduced. We demonstrate here that, in the high-density limit, the correlation energy numerically scales to a constant function of scaled time (see Sec. V D) for Hooke's atom. If universally true, this plausible result would imply that the Görling–Levy second-order perturbation energy remains finite in TDDFT. In the same way that there has been much recent interest in orbital-dependent functionals for accurate ground-state calculations,[63–65] the time-dependent optimized effective potential (OEP) scheme[6] could be used (suitably modified to avoid asymptotic difficulties with the correlation potential[66]) to include correlation.

The paper begins with some formal theory and definitions. We introduce some terms with very precise meanings, including the idea of dynamical contributions to time-dependent quantities. In the third section, we discuss our numerical algorithm, and the various tests based on the equations of motion, which demonstrate the accuracy of our solutions. Section IV is a discussion of many effects that can be seen in the one-electron version of our system: A time-dependent three-dimensional harmonic oscillator. This is needed to illustrate the qualitative one-body features of our electronic system, to be contrasted with the next section, where two interacting electrons are introduced and the correlation effects summarized above are discussed in detail. Atomic units ($e^2=\hbar=m=1$) are used throughout, so that all energies are in Hartree, all distances are in Bohr radii, and all times are in units of 2.419×10^{-17} s.

II. THEORY

The Schrödinger equation for time-dependent systems is

$$\{\hat{T}+\hat{V}_{\text{ext}}+\hat{V}_{\text{ee}}\}\Psi(t)=i\dot{\Psi}(t), \tag{1}$$

where $\hat{T}$ is the kinetic-energy operator, $\hat{V}_{\text{ext}}$ is the external

7one-body potential, $\hat{V}_{ee}$ is the electron–electron repulsion operator, and a dot implies a derivative with respect to time. The Kohn–Sham equations are

$$\{-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r}t)\}\phi_i(t) = i\dot{\phi}_i(t),\tag{2}$$

where $v_s(\mathbf{r}t)$ is the Kohn–Sham potential, an effective (one-body) external potential chosen to make

$$n(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2\tag{3}$$

exactly equal the time-dependent density of the interacting wave function $\Psi(t)$ in Eq. (1). In general, the one-to-one mapping between densities and potentials depends on the initial state (both for the physical system and the Kohn–Sham system).[2,67] In this paper, we study the evolution of the system initially prepared in its nondegenerate ground state, so that the initial wave function is a functional of the ground-state density.

For two electrons in a spin-singlet, we decompose the Kohn–Sham orbital as

$$\phi(\mathbf{r}t) = A(\mathbf{r}t)\exp(i\alpha(\mathbf{r}t)),$$
$$n(\mathbf{r}t) = 2|\phi(\mathbf{r}t)|^2,\tag{4}$$

where A and α are real. Insertion of Eq. (4) into Eq. (2), and the requirement that the resulting potential be real leads to

$$v_s = \frac{1}{4}\frac{\nabla^2 n}{n} - \frac{1}{8}\frac{|\nabla n|^2}{n^2} - \frac{1}{2}|\nabla\alpha|^2 - \frac{\partial\alpha}{\partial t},\tag{5}$$

where

$$\nabla\cdot\nabla\alpha + \frac{1}{n}\nabla\alpha\cdot\nabla n + \frac{1}{n}\frac{\partial n}{\partial t} = 0.\tag{6}$$

In the special case of a spherical system

$$v_S = \frac{1}{2r}\left(\frac{n'}{n}\right) + \frac{n''}{4n} - \frac{1}{8}\left(\frac{n'}{n}\right)^2 - \frac{1}{2}\alpha'^2 - \dot{\alpha},\tag{7}$$

where

$$\alpha' = -\frac{1}{n(\mathbf{r}t)r^2}\int_0^r \dot{n}(r't)r'^2 dr',\tag{8}$$

and the prime denotes a derivative with respect to r.

Once $v_S(\mathbf{r}t)$ has been found, we define energies in the same fashion as for the ground state: The Kohn–Sham non-interacting kinetic energy is

$$T_S[n](t) = \int d^3r |\nabla\phi(\mathbf{r}t)|^2,\tag{9}$$

the Hartree energy is

$$U[n](t) = \frac{1}{2}d^3r\int d^3r'\frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|},\tag{10}$$

and the external potential is

$$V_{ext}[n](t) = \int d^3r\, v_{ext}(\mathbf{r}t)n(\mathbf{r}t).\tag{11}$$

The exchange and correlation contributions are given as differences between quantities evaluated on the interacting and

noninteracting system. Exchange is trivial for two electrons, $E_x(t) = -U(t)/2$. Correlation contains both kinetic and potential contributions

$$E_C(t) = T_C(t) + U_C(t),\tag{12}$$

where

$$T_C(t) = T(t) - T_S(t),$$
$$U_C(t) = V_{ee}(t) - U(t)/2.\tag{13}$$

This paper will focus almost exclusively on the time-dependent energy components. However, most approximations for time-dependent density functional theory have been given directly in terms of the exchange-correlation *potential*,[49,68,69] defined as

$$v_{XC}(\mathbf{r}t) = v_S(\mathbf{r}t) - v_{ext}(\mathbf{r}t) - v_H(\mathbf{r}t),\tag{14}$$

where $v_H(\mathbf{r}t)$ is the time-dependent Hartree potential

$$v_H(\mathbf{r}t) = \int d^3r'\frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|}.\tag{15}$$

We can extract time-dependent energy components from any approximation to the potential, via two results proved using equations of motion in Ref. 48: The time-dependence of the energy

$$E_{XC}(t) = E_{XC}(0) + \int_0^t dt'\int d^3r\, v_{XC}(\mathbf{r}t')\dot{n}(\mathbf{r}t'),\tag{16}$$

and the virial theorem

$$T_C(t) = -E_{XC}(t) - \int d^3r\, n(\mathbf{r}t)\mathbf{r}\cdot\nabla v_{XC}(\mathbf{r}t).\tag{17}$$

Thus time-dependent energy components encapsulate global information about potentials.

A very useful formal device is to consider, at some instant in time, the density $n(\mathbf{r}t)$ as the *ground-state* density of some system, even though the wave function at this time is typically not the ground state of *any* potential. For any energy component, e.g., the correlation energy, we then define the *dynamical* contribution as

$$E_C^{dyn}[n](t) = E_C[n](t) - E_C^{gs}[n(\mathbf{r}t)],\tag{18}$$

where $E_C^{gs}[n(\mathbf{r}t)]$ is the ground-state correlation energy functional evaluated on the time-dependent density. For an approximate functional, $E_C^{dyn}[n](t) = E_C^{approx}[n](t) - E_C^{approx,gs}[n(\mathbf{r}t)]$, where $E_C^{approx,gs}[n]$ is the approximate ground-state energy of density, n, evaluated from $E_C^{approx}[n]$. Any adiabatic approximation, e.g., ALDA, has $E_C^{dyn} = 0$. Such dynamical effects appear as memory effects: The energies have a nonlocal dependence in time on the density. Note, however, that the dynamical component as defined here may exist even for static densities if the underlying wave function is an excited state. Provided we begin in the ground-state of some potential, the dynamical contribution vanishes if the external potential is static, or for any problem in which it is varied infinitely slowly.

Functionals that are truly local in time, such as the Hartree energy, have no dynamical component. We know this dynamical component for one nontrivial case. From Eq. (9),

for the noninteracting kinetic-energy functional for one electron (or two paramagnetic electrons in the same spatial state)

$$T_S[n](t) = \int d^3r \frac{|\nabla n(\mathbf{r}t)|^2}{8n(\mathbf{r}t)} + \int d^3r \frac{|\mathbf{j}_s(\mathbf{r}t)|^2}{n(\mathbf{r}t)} \qquad (19)$$

where $\mathbf{j}_s(\mathbf{r}t) = \nabla \alpha(\mathbf{r}t)$ is the Kohn–Sham current density

$$\mathbf{j}_S(\mathbf{r}t) = \frac{1}{i}\{\phi^*(\mathbf{r}t)\nabla \phi(\mathbf{r}t) - \phi(\mathbf{r}t)\nabla \phi^*(\mathbf{r}t)\}. \qquad (20)$$

The first term in Eq. (19) is the ground-state contribution to the noninteracting kinetic energy density, $T_S^{gs}[n]$. The second term is therefore $T_S^{dyn}[n]$, and is semilocal in time, since the continuity equation

$$\dot{n}(\mathbf{r}t) = -\nabla \cdot \mathbf{j}(\mathbf{r}t), \qquad (21)$$

implies that (for spherical systems at least) $\dot{n}$ uniquely determines the current

$$j(rt) = \mathbf{j} \cdot \hat{\mathbf{r}} = \int_r^\infty dr' \dot{n}(r't). \qquad (22)$$

Thus T_S^{dyn} is a functional of the density which is semilocal in time, but highly nonlocal in space. However, as a functional of both the density and current, it is local in both space and time. The local approximation for T_S would be to ignore T_S^{dyn} and to approximate T_S^{gs} by the Thomas–Fermi contribution.

III. ALGORITHM

The time-dependent Schrödinger equation was solved in Ref. 48 by expanding the wave function in a basis set and solving the partial differential equation in time using the Runge–Kutta method. In Fig. 4 of Ref. 48 the virial of the correlation potential (right-hand-side of Eq. (17) excluding the exchange contribution) deviates from $E_C(t) + T_C(t)$ around $t = 1.6$. If the virial and $E_C(t) + T_C(t)$ do not agree, the wave function generated by the algorithm is inaccurate beyond this point in time. This illustrates the usefulness of Eq. (17) as a stringent test of the numerical accuracy of a solution of the time-dependent Kohn–Sham equations. Note that a standard test of accuracy in the ground-state problem, that of making small changes in densities and checking that the corresponding change in an energy is accurately reproduced by integrating its potential (functional derivative) times the density change is not available for time-dependent problems. The time-dependent potentials are not typically functional derivatives of the time-dependent energies.[70] Possible sources of error in Ref. 48 are the fourth-order Runge–Kutta method or an insufficient number of levels in the basis set to accurately construct the wave function after the wave function was sufficiently excited by the perturbation. In the present paper, the Crank–Nicolson method is used to solve the Schrödinger equation. For this method, we first construct the ground-state wave function for a given external potential. The wave function is transformed onto a grid and propagated forward in time. The normality of the wave function is guaranteed at each time step because Crank–Nicolson employs a unitary operator (unlike Runge–Kutta). For all calculations with this algorithm, we have found that we can satisfy the virial theorem of Eq. (17) to arbitrary accuracy once suffi-
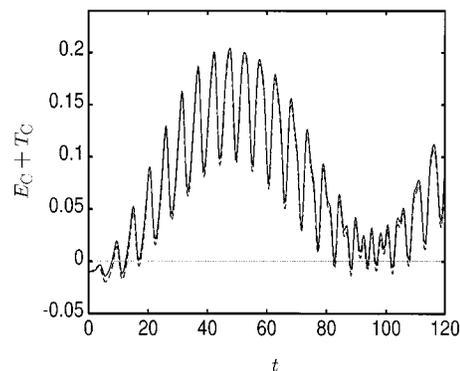

FIG. 2. A test of accuracy of the solution of the time-dependent system for the truncated run (T) (see Table I). $k(t)$ is shown in the top panel. $E_C + T_C$ and the virial of the correlation potential are plotted. The virial (dashed line) lies about on top of $E_C + T_C$ indicating a highly accurate solution.

ciently fine grids in space and time are used. Figure 2 gives an example of this, showing that the virial theorem for correlation is satisfied at each time step. Note the magnitude of energies involved. The spatial grid used for the Crank–Nicolson algorithm was typically steps of 0.0025 and the time grid was 0.0001 (both in atomic units).

Considering the time-evolving two-electron density at time t as the ground-state density of some static potential is very useful in analyzing the interacting system. For our choice of time-dependent potential, the density closely retains its Gaussian-type shape throughout the modulation of the external frequency. This suggests that the time-independent potential which has a ground-state density matching our instantaneous density, is very close to that of a static Hooke's atom of a certain effective force constant which we shall denote k_{eff}. Comparisons to this instantaneous ground state will be made throughout this paper.

The ground-state quantities that were used for this comparison were produced by matching the Hartree energy from the exact Kohn–Sham calculation to one in a table of ground-state values for Hooke's atom.[71] The energies for that ground-state Hooke's atom with force constant k_{eff}, were taken as approximations to E_C^{gs}, T_C^{gs}, etc. This process was repeated by matching values of $\langle r^2 \rangle$, and again by matching values of T_S. All three matching procedures produced essentially identical ground-state results and the Hartree energy was chosen as the matching parameter for all runs.

IV. ONE ELECTRON

Before studying correlation effects, it is necessary to understand the noninteracting system, a nontrivial task for most time-dependent systems. Much about the dynamics of the interacting two-electron density can be understood from the dynamics of one electron in the same time-dependent potential, $V(t) = k(t)r^2/2$.

The quantum time evolution in the 3dHO is generally related to the 1dHO when we begin in the ground state of each at $t = 0$ because of the separability of the time-dependent Schrödinger equation in Cartesian coordinates. Expectation values of observables are then simply related to the one-dimensional (1D) case, e.g., $\langle r^2 \rangle_{3d} = 3\langle x^2 \rangle_{1d}$.

TABLE I. Table of figures and their run parameters.

	Run parameters and figures				
Type	$\bar{k}$	ω	ϵ	Duration	Figures
Nonresonant (NR)	0.25	0.75	0.1	entire run	6 and 7
Nonresonant (WNR)	0.25	0.75	0.05	entire run	3 and 9
Linear response (LR)	0.25	0.75	≤ 0.025	entire run	8
Resonant (R)	0.25	1.0	0.05	entire run	4 and 5
Truncated (T)	0.25	0.75	0.1	$\frac{1}{2}$ oscillation	1, 2, and 10

The time-dependent force constant used in all our calculations is

$$k(t) = \bar{k} - \epsilon \cos \omega t. \tag{23}$$

The values of the control parameters $\bar{k}$, ϵ, ω for each figure are given in Table I. In the one-electron case, this is the Mathieu oscillator (see, for example, Ref. 72).

A. A measure of system response

The dynamics of the density are reflected in the time-evolution of the spread of the density $\langle r^2(t) \rangle$. In Fig. 3 we plot the root-mean-square (rms) variance, $r_{\text{rms}}(t) = \sqrt{\langle r^2(t) \rangle}$, for two noninteracting electrons in the Mathieu oscillator (dashed line in lower panel) and compare this with its value had the system remained in the instantaneous ground-state of the external potential (upper panel).

We see how the wave function is initially unchanged, and then compresses far more than an instantaneous ground-state wave function would. After the slow initial response during the first half-oscillation, during the second half-oscillation, the potential broadens again, but the density continues to compress at first, because the response of the wave function continues to lag behind the changes in the perturbation.

In thinking of the time-dependent response of an oscillator, two extreme limits come to mind. In the first, adiabatic, the potential is turned on infinitely slowly, and the wave function is always in its instantaneous ground-state. In this case, the response to any external potential is immediate. At the opposite extreme is "sudden switching," in which the force constant is instantly changed from one value to another. The wave function is not an eigenstate of the new potential, and evolves accordingly. In such cases, the change in the wave function is quadratic in t for small t. The time scale of our perturbation is in between these two extremes.

In fact, the quantum dynamics follows directly from the classical dynamics due to the harmonic nature of the potential. Classically evolving an initial ensemble, distributed in phase-space according to the initial quantum ground-state (quasi-classical evolution), results in phase-space distributions close to that of the quantum state at later times.

The solid line in Fig. 3 is the rms variance for the evolving density of the interacting two-electron system (see Sec. V). We observe how it also displays the response time lag and the overshooting–undershooting pattern present in the one-electron case. In fact it resembles twice the one-electron value closely in both its amplitude and frequency patterns; the differences are due to the interaction of the two electrons. Consequently, the kinetic and potential energies of the interacting system, follow similar trends (see Sec. V).

Figure 4 shows the same quantities for a different (resonant) choice of external spring constant; the response of the system is rather dramatic. The overshooting–undershooting behavior is present again, as it is in all our runs; and is particularly striking in this case. Note especially the increasingly extreme compression of the density near $t = 17$ and periodically thereafter. Again, the classical result is a very good approximation and again, the interacting two-electron
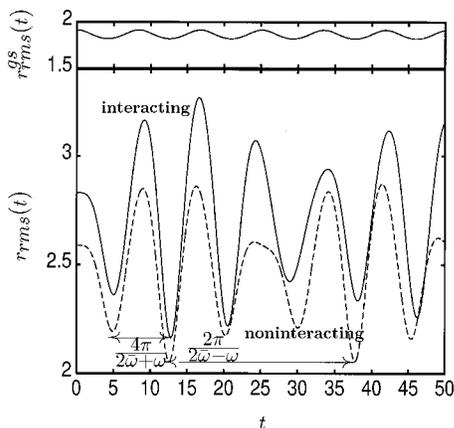
FIG. 3. Spread of parabolic well in linear response regime as a function of time for the weak nonresonant run (WNR) (see Table I). The solid line is for two interacting electrons and the dashed is for two noninteracting electrons. The top panel shows the rms variance had the system remained in the noninteracting instantaneous ground-state of the potential.
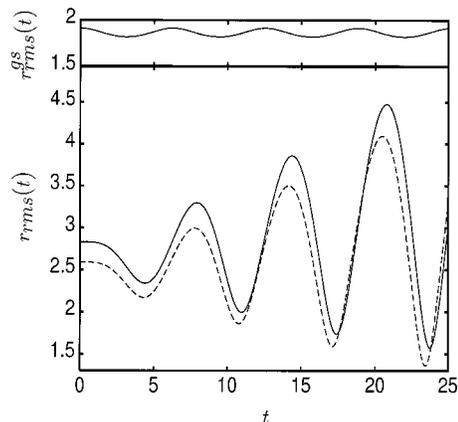
FIG. 4. Spread of parabolic well for Hooke's atom in resonance (R) as a function of time. The solid line is for two interacting electrons, the dashed line is for two noninteracting electrons. The top panel shows the rms variance had the system remained in the noninteracting instantaneous ground-state of the potential.
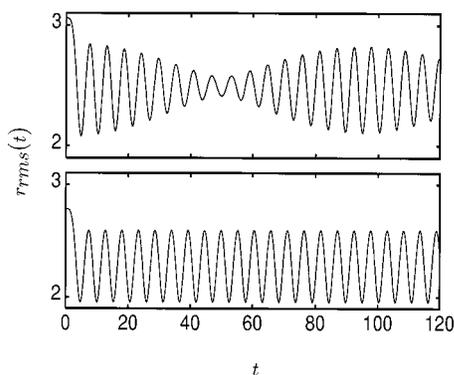
FIG. 5. Top graph: Oscillations in an envelope of a slow beating period for time-dependent Hooke's atom where the perturbation is turned off after one half-oscillation for $\bar{k}=0.25$, $\omega=0.75$, $\epsilon=0.1$. Bottom graph: 3DHO with same perturbation. $\omega_f=0.591$ for all runs.
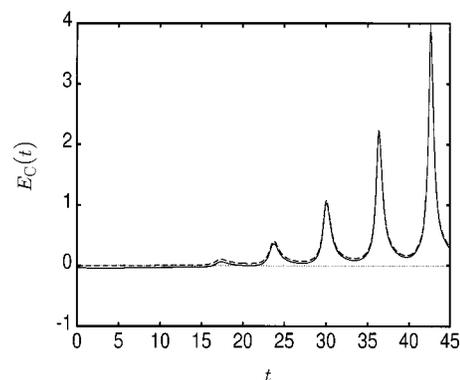

FIG. 6. Hooke's atom in resonance (R): $E_C(t)$ (solid line) and $E_C^{\mathrm{dyn}}(t)$ (dashed line) match almost exactly demonstrating the importance of the dynamical component in resonance.

case closely resembles twice the one-electron case. How we can understand the behavior of the one-electron system under the various spring constants is explained in the next subsection.

B. Time-dependent perturbation theory and linear response

For small enough ϵ, perturbation theory can predict the dynamics of the Mathieu oscillator. (The discussion in the previous subsection suggests that classical perturbation theory on the 1D case can capture most of the behavior of the fully quantum three-dimensional (3D) case, provided Gaussian averaging over initial conditions is performed. It is simpler to do quantum time-dependent perturbation theory.) For the variance in position, we obtain

$$\langle r^2(t)\rangle = \frac{3}{2\bar{\omega}} + \frac{3\epsilon}{4\bar{k}}\left[\frac{\cos(2\bar{\omega}t)}{\bar{\omega}} + 2\sin\left(\frac{(2\bar{\omega}-\omega)t}{2}\right)\right.$$
$$\left.\times\sin\left(\frac{(2\bar{\omega}+\omega)t}{2}\right)\left(\frac{1}{2\bar{\omega}-\omega} + \frac{1}{2\bar{\omega}+\omega}\right)\right],$$
(24)

where $\bar{\omega}=\sqrt{k}$. This is a good approximation to the dynamics, with the term involving the product of the sines giving the essential dynamical behavior: Beating at frequency $(2\bar{\omega}-\omega)/2$ superposed on the faster oscillations of frequency $(2\bar{\omega}+\omega)/2$ (see Fig. 3). The beating amplitude is approximately $3\epsilon/(2\bar{k}(2\bar{\omega}-\omega))$ when ω and $\bar{\omega}$ are of the same order, as in our calculations.

On resonance, $\omega=2\bar{\omega}$, the oscillator becomes unstable and we obtain

$$\langle r^2(t)\rangle = \frac{3}{2\bar{\omega}} + \frac{3\epsilon}{4\bar{k}}\left[\frac{\cos(2\bar{\omega}t)}{\bar{\omega}} + t\sin(2\bar{\omega}t)\right.$$
$$\left. + \frac{2\sin((2\bar{\omega}-\omega)t/2)\sin((2\bar{\omega}+\omega)t/2)}{2\bar{\omega}+\omega}\right]. \quad (25)$$

The middle term in the brackets describes a secular growth, evident in Fig. 4 (see also Fig. 5). Note that the factor of 2

multiplying $\bar{\omega}$ in the resonance condition and in the beat frequency off-resonance, is a consequence of the perturbation being quadratic and only connecting states of quantum number differing by 2.

For larger ϵ a full nonlinear analysis needs to be done. Much has been studied about the parameter regimes of stability and instability in the Mathieu oscillator.[72] In the limit that $\epsilon\to0$, it can be shown[72] that the seeds of the unstable regions are at $\omega=2\sqrt{k}$, $\sqrt{k}$ and $2\sqrt{k}/3$. Only the first emerges as unstable in our linear response analysis, because the instability of the other cases only occurs at larger ϵ.

C. Perturbation of finite duration

In some of our runs, we turn off the perturbation after half a cycle. After this time in the harmonic oscillator, $\langle r^2\rangle$ oscillates at frequency $2\omega_f$ where ω_f is the frequency in which the harmonic oscillator is left (see Fig. 5). This can be explained by expanding the wave function in eigenstates of the final oscillator and noting that matrix elements of x^2 are only nonzero between quantum states differing in quantum number by 2 or 0. In the case of Hooke's atom, one observes a slow beating on top of the fast oscillation in Fig. 5. Unlike the harmonic oscillator, the eigenenergies of Hooke's atom are not quite equally spaced so that the terms in the wave function expansion no longer all oscillate at the same frequency. The slight difference between the frequencies gives rise to a fast oscillation close to that of the harmonic oscillator but contained within a slow envelope.

V. TWO ELECTRONS

In this section, we present results for the time-dependent Hooke's atom. The overall trends of the dominant contributions are guided by the shape of the density which is similar to that in the one-electron case as shown in Figs. 3, 4, and 5. Now, however, we have correlation effects.

We shall be comparing the exact energies to those obtained from an almost exact ground-state approximation, as described in Sec. II and III. Dynamical contributions to the energy components [Eq. (18)] can be significant even when the potential becomes static, as shown in Fig. 1 for the cor-
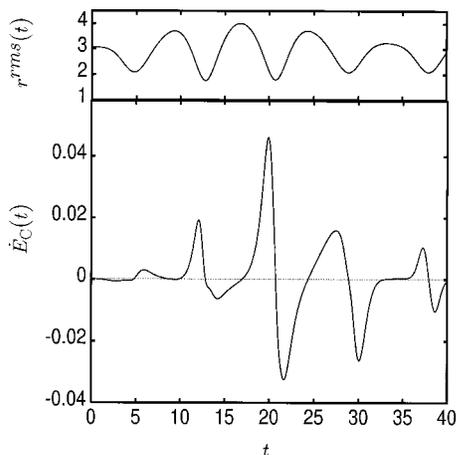
FIG. 7. A measure of the nonlocality of $\dot{E}_C$ with respect to time for the nonresonant run (NR): Contrast the very similar density profiles implied in the top panel near times $t = 4.8$ and 28.9 with the very different values of $\dot{E}c$ there in the graph above. Similar comparisons may be made near $t = 9.35$ and $t = 24.3$.

relation energy, because the time-evolving density is not static. Because the evolving wave function is not generally a ground-state of any potential (except at $t = 0$), any calculation of its correlation energy based on a ground-state functional will be erroneous. This is demonstrated by the qualitatively different behavior of the time-dependent correlation energy (see next section).

A. Positive correlation energies

In ground-state DFT calculations, it has always been found that $E_C + T_C < 0$. The unusual positive behavior of $E_C + T_C$ of this time-dependent system was first reported in Ref. 48. Here we show that $E_C(t)$ can itself be positive. This differs dramatically from the ground-state problem where E_C is a negative quantity as a consequence of the variational principle. Thus, any *adiabatic* approximate ground-state correlation energy functional will fail to capture this behavior (as can be seen in Figs. 1, 5, and 8) because they are constructed from ground-state functionals evaluated on the time-dependent density.

A striking example of how the exact correlation energy can differ significantly from any approximation that assumes the system is in its instantaneous ground state, e.g., ALDA, is provided by our Hooke's atom at resonance. Figure 6 plots $E_C(t)$ and $E_C^{dyn}(t)$ for the resonance case $\omega = 2\sqrt{k}$. On this scale, $E_C^{gs}(t) [= E_C(t) - E_C^{dyn}(t)]$ would be a relatively flat line. For most of the run, the full correlation energy and its dynamical component lie on top of each other, showing that $E_C(t)$ is almost completely dynamical. $E_C^{gs}(t) \approx -0.04$ while $E_C^{dyn}(t)$ can reach ≈ 4, causing an error of two orders of magnitude if a ground-state approximation is made for the correlation energy. This error is much greater than desired chemical accuracy.

In all runs we found $E_C^{dyn}(t)$ to be greater or equal to zero. Because the instantaneous ground-state minimizes the energy over all wave functions of that instantaneous density, $E^{gs}(t) \leq E(t)$. Here $E(t)$ is the energy of the evolving wave function at time t, $E(t) = T_S(t) + V_{ext}(t) + U(t) + E_{XC}(t)$,

and $E^{gs}(t)$ is the energy of the ground-state whose density is the instantaneous density at time t. Then it follows that $E^{dyn}(t) \geq 0$, and hence

$$E_C^{dyn}(t) \geq -T_S^{dyn}(t). \tag{26}$$

We have used the fact that for two electrons in the same spatial state, $E_X(t) = -U(t)/2$ has no dynamical component. In the general N-electron case, the relation is

$$E_{XC}^{dyn}(t) \geq -T_S^{dyn}(t). \tag{27}$$

Note that the right-hand-side of these inequalities is always less than or equal to zero by the ground-state variational principle for the Kohn–Sham kinetic energy. Thus we have proved that $E_C^{dyn}(t)$ is always greater than a negative number $-T_S^{dyn}(t)$. Whether the stronger statement of positivity of $E_C^{dyn}(t)$ is generally true remains an open question.

We also found in all our runs that $T_C(t) > 0$, i.e., $T(t) > T_S(t)$, much like in the ground-state case. Whether this is true in general also has yet to be proved.

B. Nonlocality in time

Little is known about the importance of nonlocal effects in time in TDDFT. These are completely lost by any adiabatic approximation which considers only the density at the present time. The dynamical effects can be very large as seen above. To what degree does our system remember the past? How far back in time do we need to know the density in order to evaluate the various energy components?

In Ref. 48 equations of motion for various energy components were derived. For example, $\dot{T}_S = -\int d^3 r \dot{n}(\mathbf{r}t) \times v_S(\mathbf{r}t)$ and $\dot{E}_{XC} = \int d^3 r \dot{n}(\mathbf{r}t) v_{XC}(\mathbf{r}t)$. Integrating the right-hand-side of these from 0 to t gives $T_S(t)$ and $E_{XC}(t)$, respectively, but these do not imply that the density along the entire history from 0 to t is required to evaluate the energy component at time t. Certainly it is not if the integrand is the exact time-derivative of some function. This is the case for $\dot{T}_S$, at least for two electrons in the same spatial state where $\mathbf{j} = \mathbf{j}_S$. Consequently, $T_S(t)$ is semilocal in time: It depends only on $n(\mathbf{r}t)$ and $\dot{n}(\mathbf{r}t)$ [see Eq. (19)].

The exchange energy E_X for this case is completely local, since it is simply minus half the Hartree energy. We suspect that even in general it is not strongly nonlocal in time for the following reasons. E_X may be expressed as the classical Coulomb energy between the charge density and its exchange hole $n_X(\mathbf{r},\mathbf{r}',t)$,[73] $E_X = \int\int d^3 r d^3 r' n(\mathbf{r},t) \times n_X(\mathbf{r},\mathbf{r}',t)/|\mathbf{r} - \mathbf{r}'|$. The exchange hole satisfies two fundamental constraints at each instant in time: (i) Its on-top value is a local function of the spin-densities $n_X(\mathbf{r},\mathbf{r},t) = -(n_\alpha^2(\mathbf{r},t) + n_\beta^2(\mathbf{r},t))/n(\mathbf{r},t)$, and (ii) it satisfies the sum-rule $\int d^3 r n_X(\mathbf{r},\mathbf{r}',t) = -1$.[73] These two conditions, which depend only on the value of the density at the present time, determine much about the shape of the exchange hole. Consequently we may expect that a good approximation to the exact exchange energy can be obtained using only the density at the present time. Indeed, a recent calculation of the exchange kernel in linear response for the uniform electron gas[74] was dominated by the frequency-independent contribution.

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In contrast, the correlation energy $E_C(t)$ and the correlation potential $v_C(\mathbf{r}t)$ appear to have a very nonlocal component, depending on the entire history of the density. Consider the plot of $\dot{E}_C$ in Fig. 7 together with its density profile implied by the rms variance shown above. The figure suggests that $\dot{E}_C$ is a very nonlocal functional of the density: The density profile for a time range centered at time $t=4.8$ and that centered near $t=28.9$ are very similar, yet the values of $\dot{E}_C(t)$ near those times are significantly different. Similarly one may contrast the very similar densities in a time range centered near $t=9.35$ and near $t=24.3$ with the very different shape of $\dot{E}_C(t)$ in that time range. Then Eq. (16) directly implies that $v_C(\mathbf{r}t)$ is a highly nonlocal functional of the density.

Nonlocality of $\dot{E}_C$ implies nonlocality of the correlation energy $E_C(t)$. This is clearly evident in our runs. Consider the $E_C(t)$ of Fig. 7 corresponding to the run discussed above. Again, we contrast the very similar density profiles centered at time $t=4.8$ (or $t=9.35$) and $t=28.9$ (or $t=24.3$, respectively) with the significantly different values of $E_C(t)$ centered there. This implies that local (in time) information is not adequate for a reasonable estimate of $E_C(t)$. The highly nonlocal-in-time nature of correlation must be captured by the correlation energy and potential functionals for accurate results.

C. Linear response regime

The most well-studied regime of TDDFT is the linear response regime, in which the time-dependence of the external potential is weak relative to the static potential. Electronic excitation energies (and oscillator strengths) can be extracted from analysis of this linear response regime. The first TDDFT calculations were in this regime.[54]

We present only one basic result in this regime, but one which explains qualitative trends in our data. Writing[3]

$$n(\mathbf{r}t) = n_0(\mathbf{r}) + \epsilon n_1(\mathbf{r}t) + \cdots, \tag{28}$$

where ϵ is a small parameter to be taken to zero at the end of the derivation, we first note that, by construction, dynamical quantities are at least first-order in ϵ. Secondly, we note that $\dot{n}$ also has no zero-order component. Clearly then, from Eq. (16), the dynamical contribution to the correlation energy is at least *second*-order in ϵ. This means that, in the limit of weak time-dependent potentials, $T_C^{\text{dyn}} \approx -U_C^{\text{dyn}}$. This effect can be seen at the start of most runs where the system has not yet responded to the full strength of the perturbation. In Fig. 9, we plot the dynamical contribution to the kinetic-correlation and total correlation energies for two values of small ϵ, differing by a factor of 2. We see that the kinetic contribution scales linearly, while the dynamical correlation energy scales quadratically with ϵ.

These results shed more light on those of Ref. 59, who argue that the dynamic contribution to the exchange-correlation potential vanishes in linear response. This is clearly true for exchange, which dominates weakly interacting systems. While we find it to be true for the correlation energy, our results show this not to be the case for the po-
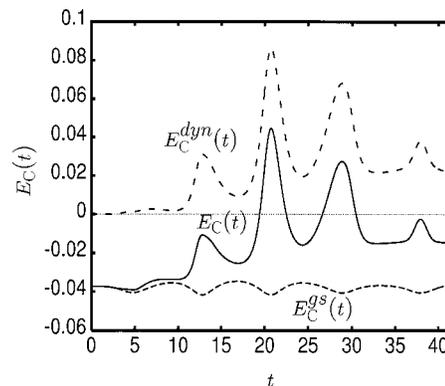

FIG. 8. Correlation energy as a function of time for time-dependent Hooke's atom for the nonresonant run (NR): Exact quantity (solid line), the ground-state approximation (bottom dashed line), and the dynamical component (top dashed line).

tential, or the kinetic contribution would also vanish. In fact, from the virial theorem and the vanishing of the total correlation energy, we find

$$T_C^{\text{dyn}} = -\int d^3r\, n_0(\mathbf{r}t)\mathbf{r}\cdot\nabla v_C^{\text{dyn}}(\mathbf{r}t) \tag{29}$$

to leading order in ϵ. Thus a linear term in T_C^{dyn} implies a linear term in v_C^{dyn}. However, if the dynamical correlation in TDDFT scales the same way as the ground-state case in the low density limit, where T_C^{gs} vanishes relative to E_C^{gs}, then T_C^{dyn} would vanish also.

D. High-density limit

In the case of the ground state, the behavior of various functionals under uniform scaling of the density, in which $n(\mathbf{r})$ becomes

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \tag{30}$$

has proven useful in the construction and analysis of approximate functionals. In particular, the ground-state correlation energy follows no simple rule when scaled, but is known to scale to a finite negative constant in the high-density limit:[75]

$$E_C[n_\gamma] \to E_C^{(2)}[n], \quad \gamma \to \infty. \tag{31}$$

This property is *not* satisfied by LDA, but is built in to most modern generalized gradient approximations.[41]

As shown in Ref. 48, the relevant density scaling for the time-dependent theory is

$$n_{\gamma\gamma^2}(\mathbf{r}t) = \gamma^3 n(\gamma\mathbf{r}, \gamma^2 t), \tag{32}$$

and so the expected analog of Eq. (31) would be

$$E_C[n_{\gamma,\gamma^2}](t) \to E_C^{(2)}[n](\gamma^2 t), \quad \gamma \to \infty. \tag{33}$$

However, the proof from the ground-state case does not easily generalize, as there is no minimum principle for the time-dependent theory. We therefore numerically implement this scaling, to see if Eq. (33) appears to be satisfied. Just as earlier in the paper, it is technically difficult to scale the density, as the potential becomes nonharmonic. Instead, we simply scaled the force constant, writing $k_\gamma = \gamma^4 k$, which
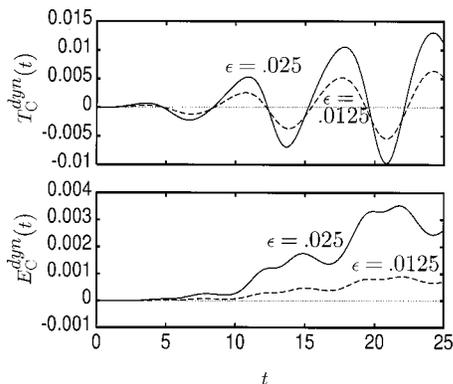
FIG. 9. E_C^{dyn} scales quadratically with respect to ϵ in the linear response regime while T_C^{dyn} scales linearly (LR) (see Table I).

causes the density to scale approximately, and (for some quantities) becomes equivalent to density-scaling in the high-density (i.e., noninteracting) limit. The energies $V_{\text{ext}}(\gamma^2 t)$ and $T(\gamma^2 t)$ of the system approach twice those of the time-dependent 3dHO with the same time-dependent external potential, as they should. Figure 10 indicates that the correlation energy $E_C(\gamma^2 t)$ becomes independent of γ as the system is scaled to high densities.

To see this in detail, note that the value at $t=0$ is the ground-state correlation energy for each system, and its variation with γ is a measure of both how close the $k=1/4$ Hooke's atom is to the high-density limit and (to a lesser extent) the error in our approximate scaling procedure. Thus the fact that, out to about $\gamma^2 t=36$, the differences between curves become no larger than at $t=0$, while undergoing significant changes as a function of $\gamma^2 t$, shows that (numerically), Eq. (33) is satisfied.

This will only hold for a finite amount of time, not the entire run. As the system is scaled to higher densities, the effective electron–electron interaction becomes weaker.[48] For large but finite γ, the difference in the time evolution of the interacting and Kohn–Sham systems eventually becomes significant. For the conditions of the run shown above, this appears to occur at about $\gamma^2 t = t_o$, where t_o is about 24.
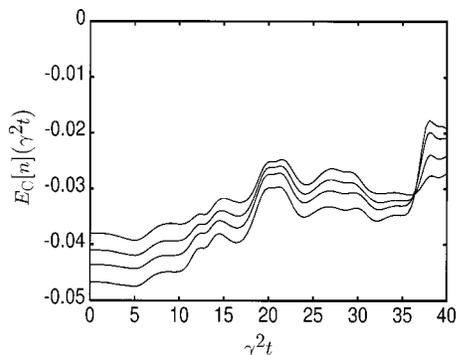

FIG. 10. Scaling of the system changes the values only slightly as they go to the 3dHO limit. E_C is plotted for scaling factors of $\gamma=1, 2, 4, 8$ for the weak nonresonant run (WNR).

VI. CONCLUSIONS

In all the data presented in this paper, comparisons between the exact correlation energy and a ground-state approximation are made. In a truly adiabatic system where the system has time to adjust to the external perturbation, a ground-state approximation will work well. But in any nonadiabatic case there are important dynamical effects present in the exact correlation energy that must be captured by any approximate functional.

We found that the dynamical effects can be very large and lead to qualitatively different behavior of the functionals than that predicted by any ground-state approximation. The most striking example of this is the correlation energy, $E_C(t)$, which can become positive unlike any ground-state approximation. It has been seen in all runs that E_C^{dyn} was always a positive quantity so the adjustment from the ground-state values have *raised* the value of the correlation energy. We proved that $E_C^{\text{dyn}}(t)$ is always bounded below by a negative number, $-T_S^{\text{dyn}}$, but whether the stronger statement of positivity is always true remains to be proved. We found that $E_C(t)$ and $v_C(\mathbf{r}t)$ are very nonlocal functionals of the density in time, and cannot be accurately predicted from only the density at recent times.

In the ground-state case T_C is always positive, which follows from a ground-state variational principle. In the time-dependent case, $T_C(t)$ was also found to be positive in all our runs, but we found no proof that this is true generally.

We proved in the linear response regime, that although the dynamical correlation energy $E_C^{\text{dyn}}(t)$ vanishes, the correlation potential $v_C(\mathbf{r}t)$, and therefore, the exchange-correlation kernel $f_{\text{XC}}(\mathbf{r},\mathbf{r}',t-t')$, has a nonzero dynamical piece. This piece is completely missed by the commonly used adiabatic approximation for f_{XC} [e.g., the adibatic local density approximation (ALDA), or any adiabatic generalized gradient approximation (GGA)].

Future work remains in many areas. Our runs were mostly in the moderate to high density regime. The low-density properties of our system remain to be investigated. The study of the dynamics when the initial state is other than the ground-state of the system must be explored. These results must be compared to approximate calculations made at the present time with adiabatic approximations. An approximate functional which includes the nonlocal effects discussed in Sec. V must be constructed and tested. We believe that ensuring the satisfaction of the exact statements shown in this paper will lead to the development of more accurate functionals.

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