

On the Floquet formulation of time-dependent density functional theory

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Abstract

The time-periodic density of a Floquet state of a time-periodic potential does *not* uniquely determine that potential. A simple example demonstrates this, and the implications are discussed. © 2002 Published by Elsevier Science B.V.

Ground-state density functional theory (DFT) [1] has been tremendously successful in predicting the electronic structure of atoms, molecules and solids relatively inexpensively [2]. DFT hugely simplifies calculations by introducing a fictitious system of non-interacting electrons with exactly the same density as the interacting many-electron system, the Kohn–Sham system [3]. In 1984, Runge and Gross generalized ground-state density functional theory to time-dependent problems (TDDFT) [4]. TDDFT has become popular for studying atoms and molecules in laser fields, calculating excitation spectra, polarizabilities, optical response of solids, etc. [5,6]. Most applications are in the linear response regime, where weak fields are applied, using adiabatic local-density and generalized gradient approximations (see in [6] for many references). But it is especially for intense laser

fields that TDDFT would appear to be the only practical way of studying the dynamics of many-electron systems, where correlation effects are important. This would prove very useful in quantum control problems [7].

In wavefunction methods, Floquet theory is an attractive approach for studies of species in intense laser fields. A time-periodic potential, such as in the case of laser fields, allows for a complete set of ‘steady-state’, or Floquet solutions, in which the problem reduces to a matrix diagonalization, similar to the finding of Bloch states for spatially periodic problems [8–11]. The system is assumed to reach a Floquet state by some adiabatic ramping of the time-dependent part of the potential (see e.g. [11]). Floquet theory is particularly useful because it is not limited to weak time-dependent fields. Floquet theory has been successful in describing a variety of phenomena, including multiphoton ionization and detachment problems [12,13], two-colour ionization [14,15], analysing microwave ionization experiments [16], high harmonic generation [17], selective excitation of molecular

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vibrational states using short laser pulses [18]. Most applications consider a one-electron picture, although recently an *R*-matrix Floquet theory [19–21] has been developed to address multiphoton processes in many-electron systems.

Time-dependent density functional theory transforms an interacting many-electron system into a fictitious non-interacting Kohn–Sham system with the same time-dependent density. The basis of any density functional theory is a demonstration of a one-to-one correspondence, for a certain class of problems, between densities and potentials, for a given interparticle statistics and interaction. Ground-state DFT is founded on a one-to-one mapping between densities of ground-states and their potentials, whereas TDDFT is based on a one-to-one mapping between time-dependent densities and potentials for a specified initial state. Consider problems in which the external potential is time-periodic, and the interacting system has reached a Floquet state, so that its density is time-periodic. It is natural to ask if the time-periodic density of a Floquet state uniquely determines the time-periodic potential. If it does, then all properties of the system are functionals of that density, which was the basis of [22,23]. However, we demonstrate here that two different Floquet states can be found that evolve with the *same* periodic density in *different* periodic potentials, so the mapping is not unique.

Floquet states are steady-state solutions of the time-dependent Schrödinger equation when the Hamiltonian is time-periodic [8,9], $H(t+T) = H(t)$. There exists a complete set of Floquet solutions of the form [8,9]

$$\psi_n(t) = e^{-i\epsilon_n t} u_n(t), \quad u_n(t+T) = u_n(t). \quad (1)$$

The time-periodic functions $u_n(t)$ are termed quasi-energy eigenstates (QES), and ϵ_n is termed the quasi-energy. The QESs satisfy

$$\{H(t) - i\partial/\partial t\}u_n(t) = \epsilon_n u_n(t) \quad (2)$$

and play a role analogous to the stationary states of a time-independent Hamiltonian. We shall construct an example involving non-interacting electrons in the periodically driven one-dimensional harmonic oscillator

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega_0^2 x^2 + \lambda x \sin(\omega t). \quad (3)$$

The QESs are known analytically [24]:

$$u_n(xt) = \phi_n(\bar{x}(t)) \exp\{i(\omega A x \cos(\omega t) + \alpha(t))\}, \quad (4)$$

where ϕ_n are the eigenstates of the static harmonic oscillator ($\lambda = 0$ in Eq. (3)), $\bar{x}(t) = x - A \sin(\omega t)$, the amplitude of the periodic shift

$$A = \lambda/(\omega^2 - \omega_0^2), \quad (5)$$

and

$$\alpha(t) = \lambda^2 (\sin(2\omega t)/8 + \cos(\omega t) - 1 - \omega^2 \cos(\omega t) \times \sin(\omega t)/(\omega^2 - \omega_0^2))/(\omega(\omega^2 - \omega_0^2)).$$

The quasi-energy is $\epsilon_n = (n + 1/2)\omega_0 + \lambda^2/(4(\omega^2 - \omega_0^2))$ (modulo ω).

For our first Floquet state, Φ , we take two non-interacting electrons in a spin-singlet in this potential, occupying the $n = 0$ and $n = 1$ quasi-energy orbitals. The density is then

$$n(xt) = \sqrt{\frac{\omega_0}{\pi}} (1 + 2\omega_0 \bar{x}(t)^2) e^{-\omega_0 \bar{x}(t)^2}. \quad (6)$$

We now find a different Floquet state that evolves with this density in a different periodic potential. Consider the spin-singlet with one doubly occupied spatial state

$$\tilde{\Phi}(x_1, x_2, t) = \tilde{u}(x_1, t) \tilde{u}(x_2, t) e^{2i\tilde{\epsilon}t}, \quad (7)$$

where

$$\tilde{u}(xt) = \sqrt{n(xt)/2} e^{if(xt)}, \quad (8)$$

where $f(xt)$ is a real, time-periodic function, $f(x, t+T) = f(x, t)$. $\tilde{\Phi}(x_1, x_2, t)$ has the same periodic density (Eq. (6)) as Φ , for all times. We now find the potential \tilde{v} that it evolves in. From inverting the time-dependent Schrödinger's equation, we have

$$\tilde{v}(xt) = \frac{1}{2} \frac{\tilde{u}''(xt)}{\tilde{u}(xt)} + i \frac{\dot{\tilde{u}}(xt)}{\tilde{u}(xt)} + \tilde{\epsilon}, \quad (9)$$

where $\tilde{\epsilon}$ is the orbital quasi-energy (see Eq. (7)). The function $f(xt)$ is determined by ensuring \tilde{v} is real, and, together with the quasi-energy, by requiring that $\tilde{v} - v \rightarrow 0$ at large x . We find

$$\begin{aligned} \tilde{v}(xt) = & \frac{1}{2} \omega_0^2 \bar{x}(t)^2 \left(1 - \frac{4}{(1 + 2\omega_0 \bar{x}(t))^2} \right. \\ & \left. - \frac{4}{1 + 2\omega_0 \bar{x}(t)^2} \right) + \frac{\omega_0}{1 + 2\omega_0 \bar{x}(t)^2} \\ & + A\omega^2 x \sin(\omega t) + \omega_0 - \omega_0^2 A^2 \sin^2(\omega t)/2. \end{aligned} \quad (10)$$

The phase,

$$\begin{aligned} f(xt) = & A\omega \cos(\omega t)x - A^2(\omega^2 - \omega_0^2)/2 \\ & \times \sin(2\omega t)/4\omega, \end{aligned} \quad (11)$$

is uniquely defined up to a purely time-dependent function. At large x , $\tilde{v}(xt) \rightarrow \omega_0^2 x^2/2 + \lambda x \sin(\omega t)$; this has the same form as the original potential $v(xt)$. The quasi-energy of $\tilde{u}(xt)$ is $\tilde{\epsilon} = 3\omega_0/2 + A^2(\omega^2 - \omega_0^2/2)/2$, (modulo ω). We notice how $\tilde{u}(xt)$ just sloshes back and forth in its well in a similar way that the original orbitals ϕ_0 and ϕ_1 do; the magnitude shifted by the same factor $A \sin(\omega t)$ and with the spatially dependent phase being the same.

Fig. 1 illustrates the periodic density, the two different pairs of orbitals and their potentials.

Let us assume that we can find a two-electron interacting system with this same density $n(xt)$. Then the wavefunctions Φ and $\tilde{\Phi}$ and potentials v and \tilde{v} are possible Kohn–Sham wavefunctions and potentials, respectively. The difference in the two Kohn–Sham potentials is then the difference in the exchange–correlation potential $v_{xc}(xt)$ for the two choices (see also [25]). Thus, despite several claims in the literature [22,26], the exchange–correlation potential is not a pure density functional: $n(xt)$ is the same in each case but $v_{xc}(xt)$ is not. (Note also that, except in the case of very weak, off-resonant driving [27], one cannot define a ‘ground Floquet state’ [26] by its quasi-energy, since this is only defined modulo ω .)

This phenomenon is explained in the theorem of Runge and Gross, where the functionals depend on the initial-state of the system as well as on the time-evolving density [4,25,28,29]. One can show that for one electron, there is no initial-state dependence [25]; here, this means that for Floquet states of one electron the mapping between den-

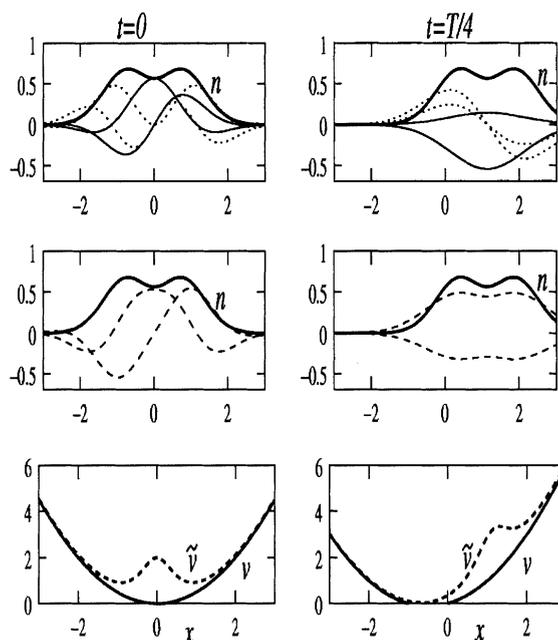


Fig. 1. Top LH panel: the real and imaginary parts of the original Floquet orbitals $\phi_0(x,0)$ (solid) and $\phi_1(x,0)$ (dotted) at time=0, together with their density (thick line). Middle LH panel: The real and imaginary parts of the alternative doubly occupied Floquet orbital $\tilde{\phi}(x,0)$ (dashed), which has the same density shown (thick line). Bottom LH panel: the two potentials, v is the solid, and \tilde{v} is dashed. The right-hand side shows the same quantities at $t = T/4$. The parameters were: $\omega_0 = 1$, $\lambda = 0.5$, $\omega = 1.2$.

sities and potentials is unique. This is not true for more than one electron. If we consider $t = 0$ as the initial time in our example, we have given the first explicit demonstration of this effect for Floquet states in time-periodic potentials. One cannot escape this initial-state dependence in the case of periodic dynamics. The Floquet TDDFT of [22] must be modified to account for this effect.

The situation here closely resembles that of excited states in time-independent problems: there may be a number of different excited states of different potentials that all share the same density. The functional for each of them must be different (see [30]).

Finally we note that, as in the general time-dependent case [25], any adiabatic approximation, that lacks initial-state dependence, would incor-

rectly predict the same potential for both the cases in our example.

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