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## On the Floquet formulation of time-dependent density functional theory

Neepa T. Maitra <sup>\*</sup>, Kieron Burke

*Department of Chemistry and Chemical Biology and Department of Physics, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, USA*

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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

<sup>\*</sup> Corresponding author. Fax: +732-445-5312.

E-mail address: [nmaitra@rutchem.rutgers.edu](mailto:nmaitra@rutchem.rutgers.edu) (N.T. Maitra).

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  $\epsilon_n$  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  $\phi_n$  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  $\omega$ ).

For our first Floquet state,  $\Phi$ , 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  $\Phi$ , 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  $\omega$ ). We notice how  $\tilde{u}(xt)$  just sloshes back and forth in its well in a similar way that the original orbitals  $\phi_0$  and  $\phi_1$  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  $\Phi$  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  $\omega$ .)

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-

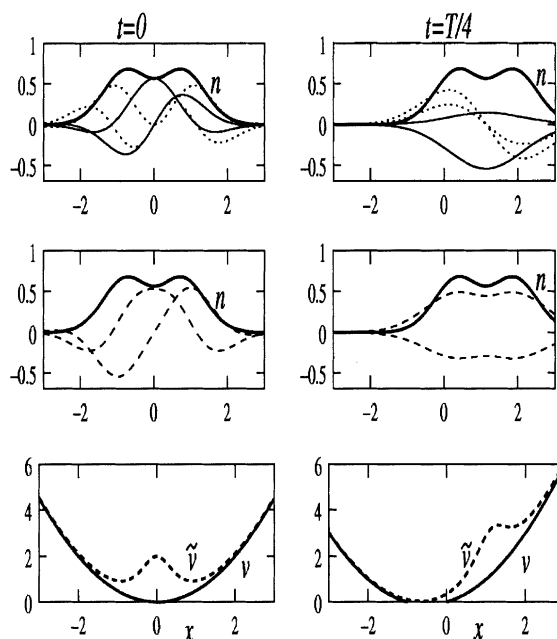


Fig. 1. Top LH panel: the real and imaginary parts of the original Floquet orbitals  $\phi_0(x, 0)$  (solid) and  $\phi_1(x, 0)$  (dotted) at time=0, together with their density (thick line). Middle LH panel: The real and imaginary parts of the alternative doubly occupied Floquet orbital  $\tilde{\phi}(x, 0)$  (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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### References

- [1] P. Hohenberg, W. Kohn, *Phys. Rev.* 136 (1964) B864.
- [2] W. Kohn, *Rev. Mod. Phys.* 71 (1999) 1253.
- [3] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133.
- [4] E. Runge, E.K.U. Gross, *Phys. Rev. Lett.* 52 (1984) 997.
- [5] K. Burke, E.K.U. Gross, in: D. Joubert (Ed.), *Density Functionals: Theory and Applications*, Springer, Berlin, 1998.
- [6] N.T. Maitra, K. Burke, H. Appel, E.K.U. Gross, R. van Leeuwen, in: K.D. Sen (Ed.), *Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R.G. Parr*, World Scientific, 2002.
- [7] H. Rabitz, *Science* 292 (2001) 709.
- [8] J.H. Shirley, *Phys. Rev.* 138 (1965) B979.
- [9] H. Sambé, *Phys. Rev. A* 7 (1973) 2203.
- [10] S.-I. Chu, *Adv. At. Mol. Phys.* 21 (1985) 197.
- [11] S.-I. Chu, *Adv. Chem. Phys.* 73 (1989) 739.
- [12] S.-I. Chu, W.P. Reinhardt, *Phys. Rev. Lett.* 39 (1977) 1195.
- [13] M.S. Pindzola, M. Dörr, *Phys. Rev. A* 43 (1991) 439.
- [14] T.-S. Ho, S.-I. Chu, J.V. Tietz, *Chem. Phys. Lett.* 96 (1983) 464.
- [15] M. Dörr, R.M. Potvliege, D. Proulx, R. Shakeshaft, *Phys. Rev. A* 44 (1991) 574.
- [16] H.P. Breuer, K. Dietz, M. Holthaus, *J. Phys. B* 22 (1989) 3187.
- [17] J.Z. Kaminski, *Phys. Lett. A* 151 (1990) 308.
- [18] H.P. Breuer, K. Dietz, M. Holthaus, *J. Phys. B* 24 (1991) 1343.
- [19] P.G. Burke, P. Francken, C.J. Joachain, *Europhys. Lett.* 13 (1990) 617.
- [20] M. Dörr, M. Terao-Dunseath, J. Purvis, C.J. Noble, P.G. Burke, C.J. Joachain, *J. Phys. B* 25 (1992) 2809.
- [21] J. Purvis, M. Dörr, M. Terao-Dunseath, C.J. Joachain, P.G. Burke, C.J. Noble, *Phys. Rev. Lett.* 71 (1993) 3943.
- [22] D.A. Telnov, S.I. Chu, *Chem. Phys. Lett.* 264 (1997) 466.
- [23] D.A. Telnov, S.I. Chu, *Phys. Rev. A* 63 (2001) 12514.
- [24] H.P. Breuer, M. Holthaus, *Ann. Phys.* 214 (1991) 249; *Z. Phys. D* 11 (1989) 1.
- [25] N.T. Maitra, K. Burke, *Phys. Rev. A* 63 (2001) 042501; 64 (2001) 039901 (E).
- [26] B.M. Deb, S.K. Ghosh, *J. Chem. Phys.* 77 (1982) 342.
- [27] P.W. Langhoff, S.T. Epstein, M. Karplus, *Rev. Mod. Phys.* 44 (1972) 602.
- [28] R. van Leeuwen, *Phys. Rev. Lett.* 82 (1999) 3863.
- [29] N.T. Maitra, K. Burke, C. Woodward, *Phys. Rev. Lett.* (in press).
- [30] A. Görling, *Phys. Rev. A* 59 (1999) 3359.