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Comment

# Comment on "Analysis of Floquet formulation of time-dependent density-functional theory" [Chem. Phys. Lett. 433 (2006) 204]

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**Abstract**

We discuss the relationship between modern time-dependent density-functional theory and earlier time-periodic versions, and why the criticisms in a recent Letter [Chem. Phys. Lett. 433 (2006) 204] of our earlier analysis [Chem. Phys. Lett. 359 (2002) 237] are incorrect.


The idea of a formulation of density-functional theory (DFT) applied directly to Floquet states has attracted much attention over recent years (see e.g. Refs. [1–3]). Such a method would benefit from the favorable system-size scaling of density-functional approaches as well as the natural treatment of time-periodic intense field processes that Floquet approaches provide. Underlying any DFT is a one-to-one mapping between densities and applied potentials, which depends on both the particle statistics and the particle interaction. In static DFT, this mapping exists only for the ground-state density [4]. In time-dependent DFT (TDDFT), established by Runge and Gross [5], this mapping depends on the initial state.

However, the Floquet density-functional theory (Floquet DFT) proposed in earlier work [1,3] is based on a one-to-one mapping between densities and potentials, without initial-state dependence. In a recent Letter [6] (henceforth MB), we showed that this mapping does not exist, so that the time-periodic density of an arbitrary many-electron Floquet state does not uniquely determine the potential in which it evolves. If analyzed within the framework of TDDFT, one can construct a one-to-one mapping, but it depends on the initial state of the system [6]. This proof does not exclude the possibility that a mapping might exist for some specified state, a hope on which some of the original works were based.

A recent Letter [7] (henceforth SH), incorrectly claims that MB overlooked important points and that in fact Floquet DFT is well-founded and valid. There are at least four simple errors in SH:

(1) The concept of a 'ground Floquet state' used in SH implies the existence of an adiabatic theorem for Floquet states. This is known *not* to exist in general [12–19]. But, even if it did, the subject of MB was TDDFT applied to any Floquet state, under periodic fields of any field strength, weak or strong, as formulated and applied in Ref. [3]. SH considers only 'ground Floquet states', and implicitly their work applies only to weak fields (see also point (2)).
(2) The minimal principle for the quasi-energy that SH use holds only for weak, off-resonant driving. In particular, it does not hold for strong-fields.
(3) Time-dependent DFT (TDDFT), as formulated by Runge and Gross [5], can be applied to Floquet states, in contrast to what is claimed in SH.
(4) The example in MB is valid, and SH's criticism of it is incorrect.

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Points (1) and (2) are errors that stem back to the original Letter of Deb and Ghosh [1] where, although the limitations of the proposed Floquet DFT are acknowledged in their footnotes and references, they not explicitly discussed. Ref. [1] was the basis of the Floquet DFT of Telnov and Chu [3], where it was however used for strong-field applications, and for general Floquet states, i.e. far beyond its regime of validity.

Before explaining the points in detail, we first remark on a fundamental problem when attempting to connect Floquet theory with (TD)DFT [8–10]. Floquet states are only guaranteed to exist [9] in systems with a discrete spectrum (which may be infinite or finite), yet the theorems of density-functional theory are based on the full Hilbert space, including any continuum. Therefore, adapting any kind of variational theorem in Floquet theory to density-functional theory requires careful inspection, and is likely invalid for systems which do not have a purely discrete spectrum, i.e. the vast majority of systems to which DFT is applied. Our Letter MB showed that even when Floquet states do exist, there is no one-to-one mapping between their densities and the potentials, as was assumed in the Floquet DFT's in the earlier literature [3,1].

We now explain points (1)–(4) above in detail.

(1) The most important conceptual error is that a 'ground Floquet state' can be uniquely defined by adiabatically tracking the unperturbed (field-free) ground-state as the time-periodic field is turned on. But there are significant, and well-recognized, problems with defining such a state. First, there is no adiabatic limit when a complete infinite set of basis states is included [18,16,17,12,15,19]. For example, in Ref. [12], it is stated 'Demonstration of the existance of a set of quasiperiodic solutions for an adiabatically switched harmonic potential is somewhat problematic in general', going on to cite Refs. [16,13,14]. In Ref. [17], the need for conditions on the 'ineffectiveness of resonances' is discussed.
Essentially the problem stems from having an increasingly dense spectrum [15,17,20,18], as eigenvalues are squeezed into a zone of width $\omega$, the driving frequency. There is a weakly avoided crossing near every point in the zone as a function of the strength of the applied periodic potential, $\lambda$. Quoting from Ref. [18], 'the structure of the exact states and quasienergy spectrum is remarkably irregular....the familiar quasienergy 'dispersion' curves as functions of $\lambda$...become discontinuous everywhere. One consequence...is the absence of a true adiabatic limit; there is no unique final state to which the system tends as the periodic perturbation is switched on arbitrarily slowly'. In summary, there is in general no adiabatic limit for Floquet states within a complete infinite Hilbert space.
Several works have nevertheless derived types of modified adiabatic theorems for Floquet states, but each require some further assumption or approximation [20,18,16,19]. Often truncation to a finite basis and studies of convergence of Floquet states with respect to basis size are made. Ref. [18] argue that the effects of interactions with the environment are likely to restore an adiabatic theorem for open systems. For these reasons, the usual Floquet methods apply in many physical situations.
Finally, there is ambiguity in SH regarding how their 'ground Floquet state' is defined: for example, shortly after Eq. (7) in SH, is the statement that 'Here the 'ground-state' refers to a steady-state having the lowest quasienergy'. But the 'lowest' depends on the choice of zone; in this definition, any state may be chosen as the 'ground-state' by simply shifting the zone boundary. The quasi-energies are defined modulo $\omega$, the driving frequency, so may be chosen to lie in the zone $[x-\omega/2, x+\omega/2)$, where $x$ is any real number [11]. In other parts of SH, however, the ground Floquet state is defined as that obtained by adiabatically ramping up the field, beginning in the unperturbed static ground-state.

(2) SH argue that a one-to-one density-potential mapping holds, based on an energy minimum principle [12,1]. However, use of a minimum principle implies existence of a complete set of Floquet states but, as discussed above point (1), their existence is called into question when the spectrum of the system possesses a continuum component. Even if there is no continuum, the proofs of the minimum principle [12] depend on adiabatic turn-on, and so hold only for a basis truncated to a finite number of dimensions. Yet, even if we now restrict to systems with a purely discrete finite spectrum, the minimum principle holds only when the driving frequency $\omega$ 'is chosen to insure transitions to excited states cannot occur' [12]. For linear response, this means that $\omega$ must not be one of the resonant frequencies of the system. For increasingly intense fields, this means that the minimum principle holds only for an increasingly small frequency-region (as explained in footnote 80 of Ref. [12]). A one-to-one density-potential mapping for Floquet states adiabatically ramped from the unperturbed ground-state has been argued to exist [1] only under the following approximations: (a) truncation of the problem to a finite basis, and (b) only for weak, off-resonant driving. Point (b) appears to be recognized in some places in SH for linear response, but on the other hand, SH do not discuss the severe restriction that this imposes for strong-fields, making it inapplicable to Ref. [3].
One may ask whether the problems of adiabatic ramping may be bypassed by simply choosing a zone for the quasi-energies and considering a minimal principle based on the lowest quasi-energy in that zone. But this approach would require a 'zone-dependence' in any functional; if the zone is shifted even

slightly, the state with the lowest quasi-energy may be completely different. Moreover, if the field strength is altered even slightly, the 'minimal' state may hop from the bottom of the chosen zone to the top, and another completely different state be minimal.

(3) None of these problems occur within the full TDDFT framework of Runge–Gross (RG) [5], as used in MB. There the one-to-one mapping depends on the initial-state of the system. The initial time may be chosen to be any time, in particular, once the time-periodic Floquet state is established. SH correctly point out adiabatic turn-on is excluded from the RG theorem, but incorrectly deduce that this invalidates the use of TDDFT for Floquet phenomena. SH incorrectly state that 'the steady-state solutions are obtained by an adiabatic switching of the periodic potential'. This is not true: Floquet states are defined as quasi-periodic solutions to the Schrödinger equation for time-periodic potentials [11], independent of any adiabatic switching. This is particularly important in light of point (1). When one applies RG TDDFT to a Floquet state, one assumes the system is already in the Floquet state. As in TDDFT applied to a general problem, the initial time and initial-state may be chosen to be any time at which the interacting and Kohn–Sham wavefunctions are known [5,23]. But the initial-state dependence of RG implies that the density-functionals are different from those that are almost always used in TDDFT applications today, i.e. when the system starts from a ground-state.

(4) We now turn to the discussion in SH of the example of MB. The authors claim that '...Maitra and Burke are incorrect on two counts. First, they consider a system in steady-state solution that is supposed to have been obtained by an adiabatic switching'. We never state this and, as discussed above, one cannot assume adiabatic switching in the general case without further assumptions. SH concludes then that RG is not applicable to this system, but this is incorrect as explained in point (3). SH devote a long discussion to the similarity of Floquet states with excited states in time-independent problems, and the problems with uniqueness of mappings for excited states, claiming MB 'fail to make' this connection. This is however well-recognized in several works (e.g. [4,22,23,21]) containing explicit examples. Indeed one of the examples discussed in detail in SH is, up to a trivial change in parameter, identical to that of the uncited Ref. [23]!

We close by noting that the example of the periodically driven harmonic oscillator in MB is an exceptional case from the point of view of adiabatic turn-on, since the quasi-energies monotonically increase as a function of the driving strength, but with discontinuities arising solely from each quasi-energy being knocked down from the top to the bottom of the chosen quasi-energy-zone. For this special case, it may be argued that the state without spatial nodes could be called a 'ground-Floquet state'. This example is nevertheless used correctly in MB to simply show the non-uniqueness property, i.e. that one may find different Floquet states that evolve with the same time-periodic density in different time-periodic potentials. It is clear that examples may be constructed in the same way for more generic potentials whose quasi-energy spectra display the more typical discontinuities discussed in Ref. [18]. e.g., 'kicked rotor' (driven free-particle in a box).

Finally, we note that within the approximate finite-basis methods implicit in the numerical treatment of many linear response approaches, as in Refs. [25,24] a Floquet approach is redeemed, as the problems discussed above are bypassed.

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