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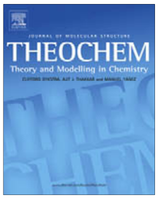

Prevalence of the adiabatic exchange-correlation potential approximation in time-dependent density functional theory

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ABSTRACT

Time-dependent (TD) density functional theory (TDDFT) promises a numerically tractable account of many-body electron dynamics provided good simple approximations are developed for the exchange-correlation (XC) potential functional (XCPF). The theory is usually applied within the adiabatic XCPF approximation, appropriate for slowly varying TD driving fields. As the frequency and strength of these fields grows, it is widely held that memory effects kick in and the eligibility of the adiabatic XCPF approximation deteriorates irreversibly. We point out, however, that when a finite system of electrons in its ground-state is gradually exposed to a very a high-frequency and eventually ultra-strong homogeneous electric field, the adiabatic XCPF approximation is in fact rigorously applicable. This result shows that adiabatic XCPF has a larger scope of applicability than previously suspected and in this sense is compliant with recent numerical findings by Thiele et al. [M. Thiele, E.K.U. Gross, S. Kümmel, Phys. Rev. Lett. 100 (2008) 153004] of negligible memory effects in strong-field double ionization.

Time-dependent density functional theory (TDDFT) is an in-principle exact approach to the quantum dynamics of electrons under time-dependent fields [1,2]. So far, the theory is very successful in many cases where the adiabatic-linear-response limit holds. These are small excitations over the ground state and the theory draws upon the ground-state density functional theory [3] and in particular the static exchange-correlation potential functional (XCPF) [4]. In strong fields and faster processes the time-dependent exchange-correlation potential at time t should depend also on the density at previous times $t' < t$, an effect referred to as "memory" [5]. It is then expected that "memory effects" must dominate or at least be important and cannot be neglected. Even in linear response memory effects may be important, especially when static correlation effects are dominant [6]. While several works have recently been published on the deployment of memory with TDDFT or time-dependent current-density functional theory (TDCDFT) [5,7–16] there is not yet available reliable and generally satisfying exchange-correlation potential functionals with memory. As part of the effort to develop new approaches, relatively simple model systems have been used to reveal some of the properties of the exact time-dependent XC potential [17–19]. A somewhat surprising result emerged from these studies: memory effects were seen to be small or even negligible in a certain range of fast and non-perturbative cases. Another surprising result, seen in many linear response calculations using the adiabatic local density approximation [20] is that the calculated high-frequency photo-absorption spectra is impressively accurate when compared to experiment, considerably more than in the visible and UV range (see for example results on different systems in Refs. [11,20,21]).

The purpose of this letter is to show that the adiabatic approximation is in fact of greater generality and has a broader range of applicability than previously suspected. We show that for electrons in finite (molecular) systems, evolving in time under the influence of a *high-frequency* homogeneous classical electric-field $\vec{E}(t)$ (which can also be strong) the adiabatic approximation is valid. The oscillating electric field takes the following form: $\vec{E}(t) = \omega^2 \frac{m_e}{e} X(t)(p_x \cos\omega t, p_y \sin\omega t, 0)$, where ω is the frequency, $\vec{p}$ is a polarization vector (assumed in the x–y plane for simplicity) and the ratio m_e/e between electron mass and charge is inserted for later convenience. We assume that the field is zero for negative times, so it is turned on slowly starting at $t = 0$, as described by the ramp envelop $\omega^2 X(t)$. The field $\vec{E}$ is usually applied as a strong laser pulse propagating in the z direction, in which case one must assume eligibility of the dipole approximation.

The electrons in the molecular system start from their ground state $\psi_{gs}(\{\vec{r}\})$, where $\{\vec{r}\} \equiv \{\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N\}$ is shorthand notation for the position $\vec{r}_i$ and spin σ_i coordinates of the N electrons in the system. The Schrödinger equation is $i\hbar\dot{\psi}(\{\vec{r}\}, t) = (\widehat{F} + \widehat{V}(t))\psi(\{\vec{r}\}, t)$ where $\widehat{F} = \sum_j \left(-\frac{\hbar^2}{2m_e}\nabla_j^2\right) + 1/2\sum_{k \neq j} \frac{\kappa}{|\vec{r}_j - \vec{r}_k|}$ is the sum of kinetic energy and the potential energy of electron–electron repulsion, $\kappa = e^2(4\pi\varepsilon_0)^{-1}$ and ε_0 is the vacuum permeability. The external potential can be written as: $\widehat{V}(t) = \int v(\vec{r}, t)\hat{n}(\vec{r})d^3r$, where $\hat{n}(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j)$ is the number-density operator and:

$$v(\vec{r}, t) = v_N(\vec{r}) - e\vec{E}(t) \cdot \vec{r}, \tag{1}$$

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with $v_N(\vec{r})$ the potential of the external force on the electrons (originating from the static nuclei, for example). The TD Kohn–Sham procedure replaces the interacting electron system by a "non-interacting" one, namely the wave function is replaced by a time-dependent Slater determinant that evolves in time starting from the Kohn–Sham ground-state determinant. The basic relation between the interacting and non-interacting systems is that both have the same density $n(\vec{r},t)$ for all times. This serves to define uniquely the potential exerted on the non-interacting system, written as [1]:

$$v_s(\vec{r},t) = v(\vec{r},t) + v_H[n(t)](\vec{r}) + v_{XC}[n](\vec{r},t), \tag{2}$$

where the $v_H[n(t)](\vec{r}) = \kappa \int n(\vec{r}',t)/|\vec{r}-\vec{r}'|d^3r$ is the Hartree potential and $v_{XC}[n](\vec{r},t)$ is the universal, exact yet forever elusive XCPF. The central issue in TDDFT is the developments of useful approximations for the XCPF. The adiabatic approximation is extremely popular and consists of plugging the instantaneous density into the ground-state XCPF (assuming v-representability):

$$v_{XC}^{ad}[n](\vec{r},t) = v_{XC}^{gs}[n(t)](\vec{r}) \tag{3}$$

Can the drastic approximation in Eq. (3) be expected to work exactly for high frequencies and strong fields? One case where it certainly does is that of electrons in a harmonic trap ("Hooke's atom"). This can be readily proved using the Harmonic potential theorem [22] and Galilean covariance of the exact exchange correlation potential functional [23]. But the harmonic potential is a very special case and the question lingers for more general circumstances.

In order to set the stage for our argument, we move from the laboratory frame to the acceleration-frame, the rest frame of an electron subject to the given electric field. The trajectory $\vec{x}(t)$ of such an electron in laboratory-frame adheres to $\ddot{\vec{x}}(t) = -\frac{e}{m_e}\vec{E}(t)$. The initial conditions of the trajectory are chosen so as to have the accelerated observer not move *on the average* (with respect to the rest frame). Furthermore, we may redefine the origin so as to have $\vec{x}(0) = 0$. In this so-called Kramers–Henneberger (KH) frame [24,25] the Schrödinger equation becomes:

$$i\hbar\dot{\psi}_{KH}(\{\vec{r}\},t) = [\hat{F} + \hat{V}_{KH}(t)]\psi_{KH}(\{\vec{r}\},t) \tag{4}$$

where $\hat{V}_{KH} = \int v_{KH}(\vec{r},t)\hat{n}(\vec{r})d^3r$ and $v_{KH}(\vec{r},t) = v_N(\vec{r}+\vec{x}(t))$. The wave functions in the rest- and accelerated-frames must relate through:

$$\psi(\{\vec{r}\},t) = e^{i\theta(\{\vec{r}\},t)}\psi_{KH}(\{(\vec{r}-\vec{x}(t))\},t) \tag{5}$$

where $\theta(\{\vec{r}\},t)$ is a space-time-dependent phase ensuring particle conservation in the acceleration frame. We may take $\psi_{KH}(\{\vec{r}\},0) = e^{i\theta(\{\vec{r}\},0)}\psi_{gs}(\{\vec{r}\})$ as an initial condition just as in the rest-frame. This entire procedure is exact as only a change of frame of reference was made. Note that the expectation value of the electron number-density in the rest-frame $n(\vec{r},t)$ is related to that seen in the accelerated-frame by:

$$n(\vec{r},t) = n_{KH}(\vec{r}-\vec{x}(t),t) \tag{6}$$

Let us now discuss the case of a high-frequency electric field. In particular, consider a finite ω and make an approximation which becomes exact as ω is increased to infinity. The field envelope $X(t)$ changes slowly on the time scale of $2\pi\omega^{-1}$, thus the Newtonian trajectory can be approximated by:

$$\vec{x}(t) = X(t)(p_x\cos\omega t, p_y\sin\omega t, 0) \tag{7}$$

(One may verify this by double differentiation, neglecting terms of order $\omega^{-1}\dot{X}/X$). This approximation becomes exact when $\omega\to\infty$ while $X(t)$ is left unchanged. It is clear that in this limit the electric field $\vec{E}$ which is proportional to ω^2X grows to infinity as well. Thus we are now looking at the *high-frequency strong-field limit*.

The next step is to introduce a "slow" time variable t' in addition to the fast "time". The idea, based on the $t-t'$ formalism [26] and was raised in Ref. [27]. This leads to a $t-t'$ Hamiltonian in the KH frame of the form $\hat{H}(t') = \hat{F} + \hat{V}_2(t,t') - i\hbar\frac{\partial}{\partial t}$ where t is now considered a dynamical variable and $\hat{V}_2$ is a two-time potential: $\hat{V}_2(t,t') = \int v_2(\vec{r},t,t')\hat{n}(\vec{r})d^3r$ and:

$$v_2(\vec{r},t,t') = v_N(\vec{r}+X(t')(p_x\cos\omega t, p_y\sin\omega t, 0)) \tag{8}$$

It is possible to show that the $t-t'$ wave $\Psi(\{\vec{r}\},t,t')$ function starting at $\Psi(\{\vec{r}\},t,0) = \psi_{KH}(\{\vec{r}\},0)$ and evolving under the SE $i\hbar\partial_{t'}\Psi(t,t') = \hat{H}(t')\Psi(t,t')$ will produce the physical wave function through the relation $\psi_{KH}(\{\vec{r}\},t') = \Psi(\{\vec{r}\},t',t')$. The potential is periodic in t and therefore, can be expanded as a Fourier series: $v_2(\vec{r},t,t') = \sum_m \tilde{v}_m(\vec{r},t')e^{im\omega t}$ where:

$$\tilde{v}_m(\vec{r},t') = \frac{1}{2\pi}\int_0^{2\pi} e^{-im\theta} \times v_N(\vec{r}+X(t')(p_x\cos\theta, p_y\sin\theta, 0))d\theta. \tag{9}$$

Using a Floquet approach (in Ref. [27] a detailed derivation is given) it is possible to show that at high-frequency these potential terms with $m \neq 0$ have a negligible effect on the wave function and $\Psi(\{\vec{r}\},t,t')$ becomes independent of t (apart from a phase factor). As a consequence, we find a great simplification in that the high-frequency limit $\psi_{KH}(\{\vec{r}\},t')$ obeys the following SE:

$$i\hbar\frac{\partial}{\partial t'}\psi_{KH}(\{\vec{r}\},t') = (\hat{F} + \hat{V}_0(t'))\psi_{KH}(\{\vec{r}\},t'), \tag{10}$$

where $\hat{V}_0(t') = \int \tilde{v}_0(\vec{r},t')\hat{n}(\vec{r})d^3r$. This equation is a generalization of the adiabatic theory of ionization stabilization [28]. It is clear from Eq. (9), that $\tilde{v}_0(\vec{r},t')$ is an instantaneous fast-time-average of the KH potential.

We ended up with a Schrödinger equation (Eq. (10)) having a new "averaged" potential without *high-frequency*. Still, the rate of change of the potential can be large: $X(t)$ can change very fast relative to the electron motion in the KH frame while it changes slowly relative to the laser frequency.

We now discuss the applicability of the adiabatic XCPF of Eq. (3). Consider first the limit of very slowly varying envelop $X(t)$ (henceforth we replace t' by t for simpler notation). According to the adiabatic theorem applied to Eq. (10) $\psi_{KH}(\vec{r},t)$ is (up to a time-dependent phase) the instantaneous ground-state of the averaged KH Hamiltonian $\hat{H}_0(t) = \hat{F} + \hat{V}_0(t)$. The instantaneous ground-state density $n_{KH}(\vec{r},t)$ is thus uniquely mapped to the KH potential $v_0(\vec{r},t)$, in the Hohenberg–Kohn way (i.e. as a ground-state mapping) [3]. In parallel, the same density can be considered the ground-state density of non-interacting particles. These non-interacting electrons are subject to a unique slowly varying external potential:

$$v_{s,KH}(\vec{r},t) = v_0(\vec{r},t) + v_H[n_{KH}(t)](\vec{r}) + v_{XC}^{gs}[n_{KH}(t)](\vec{r}) \tag{11}$$

And a time-dependent determinantal wave function can be determined from the TD Schrödinger equation for orbitals:

$$i\hbar\dot{\varphi}_j(\vec{r},t) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{s,KH}[n_{KH}(t)](\vec{r},t)\right]\varphi_j(\vec{r},t). \tag{12}$$

But these are just the TDKS equations in the KH frame, provided we make the identification:

$$v_{XC}[n_{KH}](\vec{r},t) = v_{XC}^{gs}[n_{KH}(t)](\vec{r}). \tag{13}$$

According to the Runge–Gross theorem, this identification is unique (up to a purely time dependent function). Furthermore, due to static [29] and dynamic [23] Galilean covariance:

$$\begin{aligned} v_{XC}[n](\vec{r}+\vec{x}(t),t) &= v_{XC}[n_{KH}](\vec{r},t) \\ v_{XC}^{gs}[n(t)](\vec{r}+\vec{x}(t)) &= v_{XC}^{gs}[n_{KH}(t)](\vec{r}) \end{aligned} \tag{14}$$

Eq. (13) will hold also when $n_{KH}(t)$ is replaced by $n(t)$ thus we obtain finally:

$$v_{XC}[n](\vec{r},t) = v_{XC}^{gs}[n(t)](\vec{r},t) \tag{15}$$

This shows that when using the TDKS method, with a infinitely-slowly ramp, at high frequency, one can safely use $v_{XC}^{gs}[n(t)](\vec{r})$ instead of the general $v_{XC}[n](\vec{r},t)$ and get the exact result.

Now, let us consider what this result means for developing approximations to TDDFT. First, in the infinitely slow ramp limit the result may indicate that approximate DFT XCPFs can be based on the adiabatic XCPFs. For example, the local density approximation potential $v_{XC}^{LDA}(n(\vec{r}))$ could be a reasonable approximation to exact $v_{XC}^{gs}[n](\vec{r})$ in Eq. (11) and so may yield a good approximation to the high frequency response of the system. Indeed, as indicated above there are many numerical examples showing that adiabatic LDA linear response calculations provide excellent photoabsorption cross sections when compared to experiments in the high frequency limit, often a much better approximation than in the visible and ultraviolet frequency range [11,20,21]. The present development explains this rather surprising result.

Summarizing, we have shown that the adiabatic XCPF approximation is valid not only in the static limit but also on the opposite extreme, when a highly oscillatory (and not necessarily weak) electric-field is operative. This result shows that adiabatic XCPF has a larger scope of applicability than previously suspected and in this sense is compliant with recent numerical findings by Thiele et al. [19] who found negligible memory effects in strong-field double ionization of a 1-dimensional 2-electron system interacting with a linearly polarized short laser pulse [19].

When an infinitely long ramp is used our results are in compliance with those of Tokatly and Ullrich [30,31] who found negligible non-adiabatic effects for high-frequency perturbations of the homogeneous electron gas and related systems.

Our method involved Floquet states which do not by themselves conform to a Hohenberg–Kohn [3] principle [32]. This is not a problem in our case since our approach relies on the Hohenberg–Kohn theorem only at $t = 0$, where the interacting and non-interacting systems are in their respective ground-states. At $t > 0$ the Runge–Gross theorem [1] is invoked guaranteeing a unique time-dependent potential.

An interesting question remains unanswered: does this conclusion hold for other types of high frequency perturbations? One case, of physical significance, is in high-frequency laser pulses, for which the dipole-approximation may cease to be justified, since the wave length drops when the frequency increases (however, pretty high frequencies can be reached before the dipole approximation ceases to be eligible).

While we are not able to answer all questions at present, it is very comforting to find that the adiabatic XCPF approximation has an exact high-frequency strong-field limit. This fact may assist in developing new approaches, based on the adiabatic approximation for strong laser fields and intermediate frequencies. Furthermore, we find that improvement of approximate ground state XCPFs is an important step towards improved TDXCPFs.

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