Violation of the ‘Zero-Force Theorem’ in the time-dependent Krieger-Li-Iafrate approximation

Michael Mundt and Stephan Kümmel
Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

Robert van Leeuwen
University of Groningen, Theoretical Chemistry, Zernike Institute for Advanced Materials, 9747AG, Nijenborgh 4, Groningen, The Netherlands

Paul-Gerhard Reinhard
Institut für Theoretische Physik II, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany

We demonstrate that the time-dependent Krieger-Li-Iafrate approximation in combination with the exchange-only functional violates the ‘Zero-Force Theorem’. By analyzing the time-dependent dipole moment of Na$_5$ and Na$_9$, we furthermore show that this can lead to an unphysical self-excitation of the system depending on the system properties and the excitation strength. Analytical aspects, especially the connection between the ‘Zero-Force Theorem’ and the ‘Generalized-Translation Invariance’ of the potential, are discussed.

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Since the pioneering work of Ando, Peuckert, Zangwill and Soven [1, 2, 3] and the rigorous foundation by Runge and Gross [4], time-dependent density functional theory (TDDFT) has become one of the most successful theories for the calculation of electronic properties. Based on the idea of describing a system only in terms of its time-dependent density, TDDFT offers the opportunity to access large systems which are out of reach for any wave-function based method. Additionally, it offers a tractable method to deal with strong, non-linear and non-perturbative excitations of atoms, molecules and clusters. High-harmonic generation and above-threshold ionization are just two examples for applications of TDDFT in this domain.

As in ground-state density functional theory, most TDDFT calculations are done in the Kohn-Sham (KS) scheme [5]. In this approach, the interacting many-particle system is replaced by a fictitious system of non-interacting particles moving in a local effective potential $v_{KS}$. This potential is chosen in such a way that it exactly reproduces the time-dependent density. As in the static case, the potential is split into the Hartree part $v_H$, containing the classical electrostatic interaction, the local external potential $v_{ext}$ from the ions and other external potentials, e.g., from a laser, and the exchange-correlation (xc) potential $v_{xc}$ containing all quantum-mechanical exchange-correlation effects. Since the exact xc potential is not known, it is crucial to have good approximations for it. The most well-known approximation is the time-dependent local-density approximation (TDLDA). It simply uses the static local-density approximation functional for $v_{xc}$ in combination with the time-dependent density. Although being based on the ground-state energy of the homogenous electron gas, this approximation works well in many situations [6, 7, 8, 9, 10]. Nevertheless it can also fail dramatically in some situations (see, e.g., [11, 12, 13]). One of its most prominent problems is the self-interaction error leading to a wrong asymptotic behavior of $v_{xc}$ and, as a consequence, wrong ionization dynamics. In addition, it lacks a derivative discontinuity [14, 15] and does not include any memory effects [16].

One possible way of overcoming these problems are orbital functionals [17]. These functionals depend explicitly on the KS orbitals and implicitly on the density. Thus, they are legitimate density functionals and provide many advantages over explicit functionals of the density. For instance, they include memory effects, show a derivative discontinuity, and using the exact-exchange functional (EXX) with the KS orbitals cures the Hartree self-interaction problem. Unfortunately, they also pose a severe problem: in order to find $v_{xc}$, it is necessary to solve the time-dependent optimized-effective potential (TDOEP) equation [18]. This is not an easy task [19]. To circumvent this problem, Ullrich et al., already in the first publication of the TDOEP equation, proposed an approximation to the exact potential, namely what they called the time-dependent Krieger-Li-Iafrate (TDKLI) approximation. TDKLI has been frequently used to carry out TDDFT calculations with orbital functionals, e.g., to calculate ionization processes and high-harmonic generation [18, 20, 21]. In fact, besides the time-dependent common energy denominator approximation (CEDA) [22, 23], this is the only practicable approximation to the exact TDOEP outside the linear domain at present. On first sight it might be surprising that although the EXX-TDKLI potential is not obtained as the functional derivative of the EXX orbital functional, it is nevertheless a legitimate density functional due to the one-to-one correspondence between the density and
the external potential applied to the non-interacting KS system.

On the fundamental side of TDDFT, many exact constraints which \( v_{\text{xc}} \) must fulfill have been revealed. Well-known examples are the ‘Harmonic-Potential theorem’ and the ‘Zero-Force theorem’ \( \text{[8, 23, 24]} \). The statement of the latter is that the force which the xc potential exerts on an electron cloud must vanish, i.e.,

\[
\int n(r, t) \nabla v_{\text{xc}}(r, t) \, d^3r = 0 .
\]

Since the force from the Hartree potential vanishes, this guarantees that

\[
\partial_t \mathbf{P}(t) = -\int n(r, t) \nabla v_{\text{ext}}(r, t) \, d^3r
\]

holds with \( \mathbf{P}(t) \) being the electronic momentum of the system. From earlier work it is known that the EXX functional is a ‘conserving approximation’ if the full TDOEP equation is solved. However, since this is a crucial requirement for the proof, the situation is less clear for the case of the EXX-TDKLI potential. It is the aim of this manuscript to explore whether the EXX-TDKLI nevertheless satisfies the ‘Zero-Force theorem’.

In order to answer this question, we have calculated the response of a Na\(_5\) cluster to a small dipole excitation. This cluster has planar geometry (oriented here in the \((x-y)\)-plane) and a rather “soft” electron cloud which provides a critical test case for our purposes. For the calculation we used a modified version of the PARSEC program in combination with a local pseudopotential for the Na cores. For the real-space grid a sphere of radius 20 \( a_0 \) and a grid spacing of 0.7 \( a_0 \) was used. The kinetic energy part of the KS Hamiltonian was approximated by a 12-point formula for the Laplacian. After the ground-state calculation, we applied a momentum boost \( \exp(i \mathbf{r} \cdot \mathbf{p}_{\text{boost}}/\hbar) \) with \( |\mathbf{p}_{\text{boost}}| = 3.834 \times 10^{-4} \hbar a_0^{-1} \), corresponding to a total excitation energy of the system of 1.0 \( \times 10^{-5} \) eV, to all KS orbitals. The boost had an equal strength in \( x-, y-, \) and \( z\)-direction. The resulting excited state was propagated in real time with fixed ions. The propagation was done with a fourth-order Taylor approximation to the propagator. We checked the convergence of our results with respect to the time step and found a value of \( \Delta t = 0.003 \) fs for the propagation sufficient.

Fig. 1 shows the resulting \( y\)-component of the dipole moment \( d_y(t) = e \int y n(r, t) \, d^3r \) (with \( e \) being the electron’s charge). For a while the amplitude shows reasonable oscillations in agreement with the initial boost. But after about 400 a.u., it increases rapidly and steadily. For comparison, the same quantity is plotted for a TDLDA calculation. There, no increasing amplitude is observed. Since the TDLDA satisfies the ‘Zero-Force theorem’, this is already a hint that the increasing amplitude in the TDKLI calculation is related to a violation of the ‘Zero-Force theorem’.

To demonstrate that this is indeed the case, we have monitored the expected time-derivative of the total momentum, i.e., we have calculated the right-hand side of Eq. (2) with the external potential or, respectively, the external and the exchange potential. The violation of the ‘Zero-Force theorem’ is visible in the difference between ‘\( v_{\text{ext}} + v_{\text{xc}} \)’ and ‘\( v_{\text{ext}} \)’.
cantly from the total force obtained from the sum of both equations. This clearly demonstrates that \( v_x \) violates the ‘Zero-Force theorem’ and contributes to the total force. Since the time-dependent dipole moment is connected to the total force \( \mathbf{F}(t) \) via (see, e.g., [23])

\[
\partial_t^2 \mathbf{d}(t) = e \partial_t \mathbf{P}(t) = e \mathbf{F}(t),
\]

it follows that the violation of the ‘Zero-Force theorem’ leads to a wrong time-dependent dipole moment and to a self-excitation of the system. Finally, we have checked that Eq. (3) holds for the KS system. For this we calculated the force from the total KS potential, i.e.,

\[
\mathbf{F}(t) := -\int n(r, t) \nabla v_{KS}(r, t) \, d^3r,
\]

and compared it to the time-derivative of the KS current

\[
\mathbf{j}_{KS}(r, t) = \frac{\hbar^2}{2m} \sum_{k=1}^N (\varphi_k^*(r, t) \nabla \varphi_k(r, t) - \text{c.c.})
\]

from our calculation. The current is connected to the total momentum via \( \mathbf{P}(t) = m \int \mathbf{j}_{KS}(r, t) \, d^3r \). By explicitly calculating the second time-derivative of the monitored dipole signal, we confirmed that Eq. (3) holds in our calculation as it should be.

To study the influence of the ‘Zero-Force theorem’ violation in more detail, we have carried out the same calculation as it should be. The current is connected to the total momentum via \( \mathbf{P}(t) = m \int \mathbf{j}_{KS}(r, t) \, d^3r \). By explicitly calculating the second time-derivative of the monitored dipole signal, we confirmed that Eq. (3) holds for the KS system. For this we calculated the force from the total KS potential, i.e.,

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To study the influence of the ‘Zero-Force theorem’ violation in more detail, we have carried out the same calculation for a Na\(_9^+\) cluster. In contrast to Na\(_8\), this cluster can be considered as one of the most ‘forgiving’ systems because of its spherical shape and the positive charge leading to a stable ‘plasmon’-like oscillation when excited. Fig. 3 shows the resulting violation of Eq. (1). A close look reveals that the ‘Zero-Force theorem’ is slightly violated again. But, in contrast to Na\(_8\), the violation does not increase in time. Checking the time-dependent dipole moment shows that it is also stable. Beside the stronger binding forces a possible explanation for this observation could be that the higher inversion symmetry of the almost spherical Na\(_9^+\) leads to an error cancellation in the course of one density oscillation and thus to a strongly reduced increase of the violation. In any case, the result clearly corroborates the intuitive expectation that the system properties have a strong influence on the degree of the violation of the ‘Zero-Force theorem’.

In addition to the system properties, one can also expect an influence of the excitation energy on the ‘Zero-Force’ violation. And indeed, this can be found. Fig. 4 shows the results for Na\(_8\) excited with three different boost strengths of 3.834 \( \times \) 10\(^{-4}\) \( \hbar a_0^{-1}\), 6.062 \( \times \) 10\(^{-4}\) \( \hbar a_0^{-1}\), and 8.573 \( \times \) 10\(^{-4}\) \( \hbar a_0^{-1}\). Obviously, the deviation from zero varies with the boost strength. The importance of the excitation energy can also be demonstrated by considering the extreme situation of no excitation at all. In this case, the time-dependent KS orbitals are given by the ground-state orbitals multiplied by a time-dependent phase factor \( \exp(-i \epsilon_k t / \hbar) \) containing the KS eigenvalue \( \epsilon_k \). But since this phase factor does not influence the potential, the whole system remains in a stationary state and the violation of the ‘Zero-Force theorem’ remains constant. This constant violation does not lead to a non-stationary state since \( \int n(r, t) \nabla v_{KS}(r, t) \, d^3r \) vanishes due to the ground-state iteration. In other words, for the ground-state density the total force from the external and the xc potential are in equilibrium leading to a stationary state.

Beside the just discussed aspects, there are three other conditions under which a violation of the ‘Zero-Force
theorem’ in a TDKLI calculation may not be observed. First, for short time scales the accumulation of the violation can be too small to show up significantly. Certainly, this time scale depends on the two aspects discussed above: the excitation strength and the system properties. The second situation occurs when a strong, ionizing external field is applied to the system. This can hide the error in the xc potential completely. Finally, for spin-saturated two-particle systems the TDKLI and the TDOEP potential coincide and, as a consequence, the ‘Zero-Force theorem’ is rigorously satisfied if the TDKLI potential comes from a ‘conserving approximation’ \cite{26,32}. Since, to the best of our knowledge, one of these three conditions can be found in all applications of the TDKLI potential to date, it is not surprising that the violation of the ‘Zero-Force theorem’ was not reported earlier.

After the numerical results we now focus on analytical considerations. As Vignale has shown, any potential obtained from a ‘generalized-translation invariant’ xc action functional satisfies the ‘Zero-Force theorem’ \cite{24,29}. In addition, the potential also satisfies ‘Generalized-Translation invariance’, i.e., $v_{xc}$ rigidly follows a rigidly translated density, and, as a consequence, the ‘Harmonic-Potential theorem’. Actually, the same arguments show that if $v_{xc}$ satisfies ‘Generalized-Translation invariance’ and is the functional derivative of some xc action functional, it must also satisfy the ‘Zero-Force theorem’. Since the EXX-TDKLI satisfies the ‘Harmonic-Potential theorem’ \cite{34}, we conclude from our numerical results that the EXX-TDKLI potential in general cannot be obtained as the functional derivative of some xc action functional with respect to the density. This result is in line with earlier results for the static Slater potential \cite{34}. The missing action functional for the EXX-TDKLI potential, in combination with the observation that the TDKLI potential is nevertheless used as part of a legitimate density functional procedure, makes any rigorous approximation for the xc potential which satisfy the ‘Zero-Force theorem’, our findings clearly demonstrate the urgent need for a working TDOEP scheme in order to make orbital functionals accessible for real-time TDDFT.

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\begin{thebibliography}{100}
\bibitem[1]{1} T. Ando, Z. Phys. B \textbf{26}, 263 (1977).
\bibitem[2]{2} V. Peuckert, J. Phys. C \textbf{11}, 4945 (1978).
\bibitem[3]{3} A. Zangwill and P. Soven, Phys. Rev. A \textbf{21}, 1561 (1980).
\bibitem[4]{4} E. Runge and E. K. U. Gross, Phys. Rev. Lett. \textbf{52}, 997 (1984).
\bibitem[5]{5} W. Kohn and L. J. Sham, Phys. Rev. \textbf{140}, A1133 (1965).
\bibitem[6]{6} W. Ekardt, Phys. Rev. Lett. \textbf{52}, 1925 (1984).
\bibitem[7]{7} K. Yabana and G. F. Bertsch, Z. Phys. D \textbf{42}, 219 (1997).
\bibitem[8]{8} E. K. U. Gross, J. F. Dobson, and M. Petersilka, in \textit{Density Functional Theory}, edited by R. F. Nalewajski, Topics in Current Chemistry, Vol. 181, (Springer, Berlin 1996).
\bibitem[9]{9} P.-G. Reinhard \textit{et al.}, Eur. Phys. J. D \textbf{9}, 111 (1999).
\bibitem[10]{10} A. Castro \textit{et al.}, Eur. Phys. J. D \textbf{28}, 211 (2004).
\bibitem[11]{11} M. Petersilka and E. K. U. Gross, Laser Phys. \textbf{9}, 105 (1999).
\bibitem[12]{12} O. V. Gritsenko \textit{et al.}, J. Chem. Phys. \textbf{113}, 8478 (2000).
\bibitem[13]{13} S. J. A. van Gisbergen \textit{et al.}, Phys. Rev. Lett. \textbf{83}, 694 (1999); S. Kümmel, L. Kronik, and J. P. Perdew, Phys. Rev. Lett. \textbf{93}, 213002 (2004).
\bibitem[14]{14} J. P. Perdew \textit{et al.}, Phys. Rev. Lett. \textbf{49}, 1691 (1982).
\bibitem[15]{15} M. Mundt and S. Kümmel, Phys. Rev. Lett. \textbf{95}, 203004 (2005).
\bibitem[16]{16} N. T. Maitra, K. Burke and, C. Woodward, Phys. Rev. Lett. \textbf{89}, 023002 (2002).
\bibitem[17]{17} T. Grabo \textit{et al.}, in \textit{Strong Coulomb Correlation in Electronic Structure}, edited by V. Anisimov, (Gordon & Breach, Tokyo, 2000).
\bibitem[18]{18} C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Ber. Bunsenges. Phys. Chem. \textbf{99}, 488 (1995); Phys. Rev. Lett. \textbf{74}, 872 (1995).
\bibitem[19]{19} M. Mundt and S. Kümmel, Phys. Rev. A \textbf{74}, 022511 (2006).
\bibitem[20]{20} C. A. Ullrich, P.-G. Reinhard, and E. Suraud, J. Phys. B \textbf{31}, 1871 (1998).
\bibitem[21]{21} X.-M. Tong and Shih-I Chu, Phys. Rev. A \textbf{57}, 452 (1998).
\bibitem[22]{22} O. V. Gritsenko and E. J. Baerends, Phys. Rev. A \textbf{64},
\end{thebibliography}
As a consequence, the EXX-TDKLI potential does not lead to self-excitation in the case of systems confined by a harmonic external potential and a perturbing spatially homogeneous time-dependent force. In order to test our numerical implementation we have checked this and can confirm that the left-hand side of Eq. (1) remains constant.