Adiabatic Approximation in Nonperturbative Time-Dependent Density-Functional Theory

M. Thiele,[1] E. K. U. Gross,[2] and S. Kümmel[1]

[1]*Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany*
[2]*Theoretische Physik, Freie Universität Berlin, D-14195 Berlin, Germany*

(Received 22 November 2007; published 18 April 2008)

We construct the exact exchange-correlation potential of time-dependent density-functional theory and the approximation to it that is adiabatic but exact otherwise. For the strong-field double ionization of the Helium atom these two potentials are virtually identical. Thus, memory effects play a negligible role in this paradigm process of nonlinear, nonperturbative electron dynamics. We identify the regime of high-frequency excitations where the adiabatic approximation breaks down and explicitly calculate the nonadiabatic contribution to the exchange-correlation potential.

DOI: 10.1103/PhysRevLett.100.153004 PACS numbers: 31.15.ee, 31.70.Hq, 32.80.Rm

Progress in laser technology has provided the experimental tools to study and manipulate electron dynamics on atomic scales [1]. On the theoretical side, this strong-field regime can in principle be accessed by solving the many-electron time-dependent Schrödinger equation (TDSE). In practice, however, a first-principles approach in this vein is ruled out by the tremendous computational cost of solving the TDSE for more than two electrons in three dimensions. Time-dependent density-functional theory (TDDFT) [2] offers a computationally attractive approach to strong-field electron dynamics [3,4] which is in principle exact, but in practice requires approximations for the time-dependent exchange-correlation (xc) potential $v_{\mathrm{xc}}(\mathbf{r}, t)$.

Up to now applications of TDDFT almost exclusively rely on ''adiabatic approximations'' [e.g., the adiabatic local density approximation (ALDA)], which are obtained by plugging the time-dependent density into one of the existing ground-state density functionals for v_{xc}. Approaches of this type have also been used to calculate the double ionization (DI) of the helium atom, one of the most prominent effects in the regime of strong-field electron dynamics. Its importance as a benchmark for theoretical many-body methods stems from the fact that DI yields in the low-intensity regime are found to be substantially increased due to pronounced electron correlation effects [5,6]. As a result of this ''nonsequential ionization'' (NSI), the famous ''knee'' structure appears in the double-ionization probability as a function of intensity. A combination of theoretical [7–12] and experimental [13–15] studies has by now established the recollision model as the mechanism responsible for NSI. But most attempts based on adiabatic TDDFT have failed completely to even qualitatively describe NSI [16–19]. It has been argued [20] that this failure may be due to a missing particle number discontinuity [21] in the commonly used ground-state functionals for v_{xc}.

A priori there is little reason to believe that any ground-state functional can yield reliable results for a process like DI, because it is known that nonadiabatic effects in v_{xc} can play an important role [22–28]. It is a natural and common assumption that these effects should be particularly important in nonlinear, nonperturbative processes that take a system far away from its ground-state, as, e.g., in strong-field ionization.

In this Letter we explore the adiabatic approximation beyond the linear response regime. For the hallmark example of a strong-field process, the helium DI, we compare the exact time-dependent xc potential to the xc potential (defined in detail below) that is an adiabatic approximation but is exact otherwise. This adiabatically exact approximation is local in time, i.e., shows no memory effects, but is fully nonlocal in space, i.e., the multiplicative potential $v_{\mathrm{xc}}(\mathbf{r})$ depends not only on the density n at $\mathbf{r}$, but also on n at all other points of space. Our calculations reveal that for the intensities and frequencies that are usually considered in the context of strong-field electron dynamics, and specifically for the helium DI, the adiabatic approximation works extremely well. Thus, an accurate description requires nonlocality in space more than nonlocality in time.

For the definition of the ''adiabatically exact approximation'' one should recall that, for the initial state being the ground state, the exact xc potential shows ''memory'' as at any given time t it is a nonlocal functional of the exact time-dependent density n at all previous times, i.e., $v_{\mathrm{xc}}^{\mathrm{ex}}(\mathbf{r}, t) = v_{\mathrm{xc}}^{\mathrm{ex}}[n(\mathbf{r}', t')](\mathbf{r}, t)$ where $t' \leq t$. By definition it is related to the exact Kohn-Sham (KS) potential $v_s^{\mathrm{ex}}[n(\mathbf{r}', t')](\mathbf{r}, t)$ by

$$v_{\mathrm{xc}}^{\mathrm{ex}}(\mathbf{r}, t) = v_s^{\mathrm{ex}}(\mathbf{r}, t) - v_h(\mathbf{r}, t) - v_{\mathrm{ext}}(\mathbf{r}, t), \qquad (1)$$

where v_{ext} is the external potential and v_h is the Hartree potential, which is a functional of the density only at $t' = t$. By virtue of the Runge-Gross theorem, the potential v_s^{ex} corresponding to the exact time-dependent density is unique, and it can be shown to exist [29].

The adiabatic approximation is defined by treating the time-dependent density at a fixed time $t = t_0$ as a ground-state density, i.e., $n_0(\mathbf{r}) = n(\mathbf{r}, t_0)$. Consequently, the adiabatically exact KS potential $v_s^{\mathrm{adia,ex}}(\mathbf{r})$ is the local potential which yields $n_0(\mathbf{r})$ as the solution of the *noninteracting*,

single-particle Schrödinger equation. The correspondence between n_0 and $v_s^{\mathrm{adia,ex}}$ is unique according to Hohenberg and Kohn [30]. Following standard ground-state DFT, the xc contribution to $v_s^{\mathrm{adia,ex}}(\mathbf{r})$ is given by

$$v_{\mathrm{xc}}^{\mathrm{adia,ex}}(\mathbf{r}) = v_s^{\mathrm{adia,ex}}(\mathbf{r}) - v_h(\mathbf{r}, t_0) - v_{\mathrm{ext},0}(\mathbf{r}), \quad (2)$$

i.e., this defines the adiabatically exact xc potential at $t = t_0$. Here, v_h is again the Hartree potential corresponding to the given density n_0 and $v_{\mathrm{ext},0}(\mathbf{r})$ is the local external potential which yields n_0 as the solution of the *interacting* many-particle Schrödinger equation. Also the mapping between n_0 and $v_{\mathrm{ext},0}(\mathbf{r})$ is unique according to Hohenberg and Kohn. Therefore, $v_{\mathrm{xc}}^{\mathrm{adia,ex}}(\mathbf{r})$ is uniquely defined by Eq. (2) and is a numerical representation of the unknown exact ground-state xc potential functional. The existence of the ground-state potentials is also guaranteed [31]. Comparing $v_{\mathrm{xc}}^{\mathrm{ex}}$ and $v_{\mathrm{xc}}^{\mathrm{adia,ex}}$ will directly reveal the nonadiabatic effects.

Using these definitions in practice requires the exact time-dependent density as an input. For the helium atom the latter can be calculated at bearable computational cost from the solution of the TDSE by using a one-dimensional model which reproduces the essential features of the DI process [10,11,16,17,32]. In this model, the helium atom in a time-dependent external potential $v_{\mathrm{ext}}(z, t)$ is described by the Hamiltonian

$$H = \sum_{j=1,2}\left(\frac{p_j^2}{2m} + v_{\mathrm{ext}}(z_j, t)\right) + W(z_1 - z_2) \quad (3)$$

with electron coordinates z_1, z_2, momenta p_1, p_2, electron mass m and the soft-core interaction $W(z) = e^2/\sqrt{z^2 + 1}$. The external potential $v_{\mathrm{ext}}(z, t) = -2W(z) - ezE(t)$ contains the electron-nucleus interaction and the potential of the time-dependent electrical field $E(t)$. Taking the spatial wave function to be be symmetric under exchange of electrons, the time-dependent Schrödinger equation $i\hbar\partial_t\psi = H\psi$ is solved numerically. The two-electron wave function obtained in this way allows to calculate the exact time-dependent density $n(z, t) = 2\int|\psi(z, z', t)|^2 dz'$ and, via the inversion of the time-dependent KS equation (TDKS) [20,33], the exact time-dependent KS potential v_s^{ex}. From the latter, the exact correlation potential $v_c^{\mathrm{ex}} = v_{\mathrm{xc}}^{\mathrm{ex}} - v_x$ follows by Eq. (1), as for a two-electron singlet system $v_{\mathrm{hx}} := v_h + v_x = 1/2 v_h$ with $v_h(z, t) = \int n(z', t)W(z - z')dz'$.

Thus, $v_{\mathrm{xc}}^{\mathrm{ex}}$ can readily be calculated. However, obtaining $v_{\mathrm{xc}}^{\mathrm{adia,ex}}$ is a formidable task even in the one-dimensional model. Calculating the adiabatically exact total KS potential is still easy: Making the above described identification $n_0(z) = n(z, t_0)$, the adiabatically exact total KS potential follows from the inversion of the static KS equation,

$$v_s^{\mathrm{adia,ex}}(z) = \frac{\hbar^2}{m}\frac{1}{2\varphi(z)}\frac{d^2\varphi(z)}{dz^2} + \mathrm{const.}, \quad (4)$$

where $\varphi(z) = \sqrt{n_0(z)/2}$. The challenge is posed by the exact xc part according to Eq. (2): finding $v_{\mathrm{ext},0}(\mathbf{r})$ requires the inversion of the *interacting* static Schrödinger equation $H_0\psi_0 = E_0\psi_0$ (SE) for the ground state ψ_0 which satisfies the constraint $n_0(z) = 2\int|\psi_0(z, z')|^2 dz'$. Here,

$$H_0 = \sum_{j=1,2}\left(\frac{p_j^2}{2m} + v_{\mathrm{ext},0}(z_j)\right) + W(z_1 - z_2). \quad (5)$$

To find $v_{\mathrm{ext},0}$ for a given n_0 we implemented a generalization of an iterative scheme [34]. Starting with an initial guess $v_{\mathrm{ext},0}^{(1)}$ for $v_{\mathrm{ext},0}$ we calculate [33] the corresponding ground-state wave function, which in turn yields the density $n_0^{(1)}$ corresponding to $v_{\mathrm{ext},0}^{(1)}$. Then a new potential is constructed according to the rule

$$v_{\mathrm{ext},0}^{(i)}(z) = v_{\mathrm{ext},0}^{(i-1)}(z) + w(z)[n_0^{(i-1)}(z) - n_0(z)], \quad (6)$$

where $i = 2$ for the first step. $w(z) = \alpha|z|^\beta$ (with parameters α, $\beta > 0$) is a weight function allowing to increase the contribution of the density-fall-off region. The thus obtained $v_{\mathrm{ext},0}^{(2)}$ in turn leads to a $n_0^{(2)}$ via solution of the SE. These steps are iterated until the density $n_0^{(i)}$ has converged to n_0 according to the criterion

$$\int|n_0^{(i)}(z) - n_0(z)|dz \le \Delta, \quad (7)$$

where Δ is a measure for the desired accuracy. Once we have obtained $v_{\mathrm{ext},0}(z)$, the adiabatically exact correlation potential $v_c^{\mathrm{adia,ex}}(z)$ follows from Eq. (2) with v_{hx} being identical for the time-dependent and static case.

In order to assess the validity of the adiabatic approximation, we solve the two-electron TDSE for given potentials $v_{\mathrm{ext}}(z, t)$ representing paradigm cases of strong-field electron dynamics (discussed in detail below). At every time step t we then construct v_c^{ex} and $v_c^{\mathrm{adia,ex}}$ according to the procedure described above.

In our first study we take $E(t)$ to be a dc electric field that is ramped up during 27 a.u. (0.65 fs) to a maximum value $E_0 = 0.141$ a.u. and held constant afterwards. Starting from the two-electron ground state this leads to field-induced ionization of the system with the electrons escaping to $z \to \infty$. To avoid numerical problems caused by strongly accelerated electrons, the interaction with the field is truncated at a distance of 35 a.u. from the nucleus [20]. The resulting time-evolution of the density and the potentials is shown in Fig. 1. v_s^{ex} and v_c^{ex} are defined only up to an additive time-dependent constant, which has been adjusted so that the boundary condition $v_c^{\mathrm{ex}}(z, t) \to 0$ for $z \to \infty$ is fulfilled. The free additive constant in $v_s^{\mathrm{adia,ex}}$ and $v_{\mathrm{ext},0}$ cannot be fixed, thus all adiabatically exact potentials are shifted to match the exact ones at $z = 0$. As with other known density-inversion schemes, our procedures work accurately only in regions of space where a sufficient amount of density is located. As a rule of thumb, regions where $n(z) > 10^{-2}$ a.u. can safely be considered.

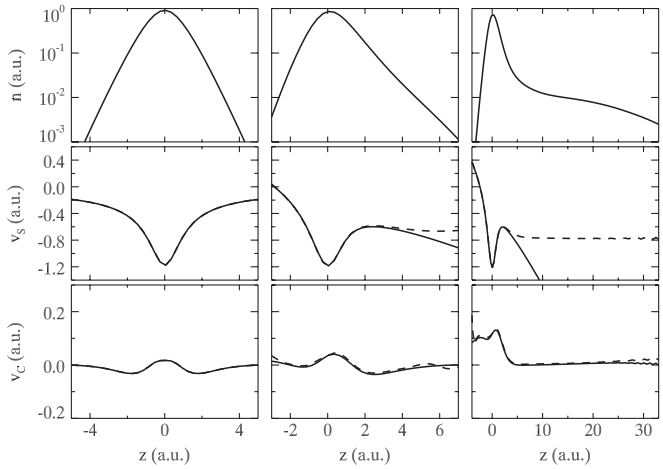

FIG. 1. Density, total KS potential, and correlation potential (from top to bottom) at the 3 times $t = 0$, 21.5, 43.0 a.u. (from left to right) during the interaction of the two-electron atom with a dc electric field. Solid curves: exact time-dependent v_s^{ex} and v_c^{ex}; dashed curves: adiabatically exact $v_s^{\mathrm{adia,ex}}$ and $v_c^{\mathrm{adia,ex}}$ (Hartree units). Note the different scales in the plots and that v_c^{ex} and $v_c^{\mathrm{adia,ex}}$ are very close, with deviations at the boundaries being a numerical consequence of low density; see text.

Restricting the analysis to regions of space where the density obtained with the iterative scheme also reproduces the one from the TDSE with high accuracy acts as a further safeguard against numerical artefacts.

Figure 1 shows that the exact and adiabatically exact versions of the total KS potential v_s differ substantially and qualitatively. This reflects the fact that the former corresponds to an excited density in the presence of the linear laser potential, and the latter to a bound ground state in a global potential minimum. However, the surprising result is that the lowest line of panels in Fig. 1 undoubtedly reveals that the correlation contributions to the potentials, i.e., $v_c^{\mathrm{ex}}(z)$ and $v_c^{\mathrm{adia,ex}}(z)$, agree extremely well at all times (also for times much longer than what is shown in Fig. 1). This indicates that memory effects in the correlation potential are practically negligible for this process. Also the buildup of a steplike structure in v_c at later times as identified in [20] is well reproduced by the adiabatically exact approximation.

To probe the regime where nonadiabatic effects manifest themselves in the correlation potential, we consider as our second study an external potential in which the density is deformed more rapidly than during the ramping process. Instead of adding an external laser field to the electron-nucleus interaction, we directly perturb the soft-core potential according to

$$v_{\mathrm{ext}}(z,t) = -\frac{2e^2}{\sqrt{[z - (0.5\ \mathrm{a.u.})\sin(\omega t)]^2 + 1}}. \quad (8)$$

This forcing mimics an oscillatory motion of the nucleus. It has the benefit of keeping the density relatively well localized, thus allowing for stable solutions in the TDKS-inversion-scheme. The chosen frequency $\omega \approx 0.9$ a.u. is close to the frequency range investigated in earlier work on two-electron systems in the nonadiabatic regime [25,26]. Figure 2 shows that for the external potential (8) the density gets rapidly and strongly deformed and does not return to its initial shape after a full cycle of the forcing. To contain such a density as a ground state, the adiabatically exact KS potential produces additional minima which are not present in its exact, nonadiabatic counterpart. The resulting $v_c^{\mathrm{adia,ex}}$ displayed in the lowest line of Fig. 2 differs markedly from v_c^{ex}, showing that nonadiabatic effects become important.

Finally, in our third study we turn our attention to the practically most relevant case of strong, time-dependent external fields due to powerful laser pulses of the 780 nm wavelength that is typically used in strong-field experiments. The oscillation here is of moderate frequency but the density is strongly displaced from its initial position. This is a setup for which ALDA is known to fail badly [18]. The results shown below are obtained during a 4-cycle pulse with linear turn-on and -off for two cycles each. Our comparison now is done in the way that is most useful to assess the accuracy of the adiabatically exact approximation in practice: We propagate [33] the KS orbital while using at every time step the adiabatically exact approximation of v_c that is obtained self-consistently from the KS density [35].

The TDSE is solved as the exact reference and now is used only for that purpose. To compare the results of the adiabatically exact TDKS calculation to those of the TDSE, we focus on the number of bound electrons,

$$N_b(t) = \int_{-a}^{a} n(z,t)dz, \quad (9)$$

with $|z| \leq a = 5$ a.u. This is a decisive quantity for the

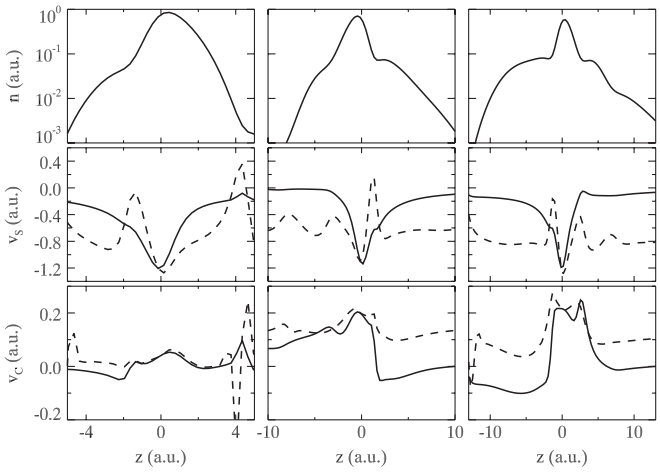

FIG. 2. Same as Fig. 1 but for the two-electron atom during high-frequency excitation according to (8) at $t = \frac{1}{2}T$, $t = T = 2\pi/\omega$ and $t = \frac{3}{2}T$ (from left to right). The initial situation at $t = 0$ is the same as in Fig. 1.

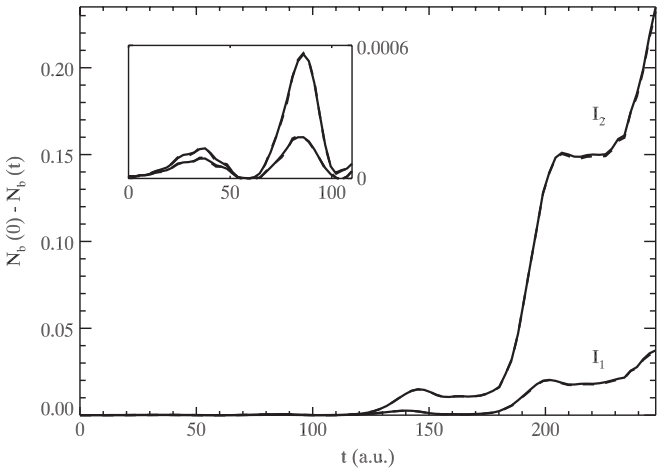

FIG. 3. Total ionization during the interaction of the two-electron atom with a laser pulse of maximum intensity $I_1 = 4 \times 10^{14}$ W/cm^2 (lower two curves) and $I_2 = 7 \times 10^{14}$ W/cm^2 (upper two curves). Solid curves: exact TDSE calculation; dashed curves: adiabatically exact TDKS scheme. The inset shows a magnification of the first part of the curve.

interpretation of the ionization results, as the DI yields depend crucially on it [18,19]. It is also well suited for the comparison, because it can be calculated directly from the density without making additional approximations. Figure 3 shows the time evolution of the total ionization, $N_b(0) - N_b(t)$, for two different maximum laser intensities typical of experimental conditions. The striking result is that the curves obtained from the adiabatically exact TDKS calculation lie virtually on top of the exact ones. Thus, the time evolution is not influenced by memory effects for the intensities within the crucial NSI region.

In summary, we calculated the adiabatic xc potential by inverting the interacting SE. Thus, we were able to visualize the nonadiabatic effects in $v_{\mathrm{xc}}(\mathbf{r}, t)$ exactly, providing a procedure to directly track down this fundamental but elusive feature of TDDFT. As a test of immediate practical relevance we have performed a nonlinearized, nonperturbative Kohn-Sham calculation of strong-field ionization which consistently used the adiabatically exact approximation for v_{xc}. While memory effects in v_{xc} are known to be crucial for the description of phenomena like, e.g., double excitations, our results show that they are negligible for typical strong-field excitations, and, in particular, for the paradigm process of the helium DI. Here, the adiabatically exact TDDFT approach yields excellent results.

S. K. acknowledges support by the Deutsche Forschungsgemeinschaft.

[1] P. B. Corkum and F. Krausz, Nature Phys. **3**, 381 (2007).
[2] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory*, edited by R. F. Nalewajski (Springer, Berlin, 1996), p. 81.
[3] S.-I. Chu, J. Chem. Phys. **123**, 062207 (2005).
[4] F. Calvayrac *et al.*, Phys. Rep. **337**, 493 (2000).
[5] D. N. Fittinghoff *et al.*, Phys. Rev. Lett. **69**, 2642 (1992).
[6] B. Walker *et al.*, Phys. Rev. Lett. **73**, 1227 (1994).
[7] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[8] A. Becker and F. H. M. Faisal, J. Phys. B **29**, L197 (1996); Phys. Rev. A **59**, R1742 (1999).
[9] D. Dundas *et al.*, J. Phys. B **32**, L231 (1999).
[10] W.-C. Liu *et al.*, Phys. Rev. Lett. **83**, 520 (1999).
[11] M. Lein, E. K. U. Gross, and V. Engel, Phys. Rev. Lett. **85**, 4707 (2000).
[12] J. S. Prauzner-Bechcicki *et al.*, Phys. Rev. Lett. **98**, 203002 (2007).
[13] R. Moshammer *et al.*, Phys. Rev. Lett. **84**, 447 (2000).
[14] T. Weber *et al.*, Phys. Rev. Lett. **84**, 443 (2000).
[15] T. Weber *et al.*, Nature (London) **405**, 658 (2000).
[16] D. Bauer, Phys. Rev. A **56**, 3028 (1997).
[17] D. G. Lappas and R. van Leeuwen, J. Phys. B **31**, L249 (1998).
[18] M. Petersilka and E. K. U. Gross, Laser Phys. **9**, 105 (1999).
[19] F. Wilken and D. Bauer, Phys. Rev. Lett. **97**, 203001 (2006).
[20] M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005); M. Mundt and S. Kümmel, Phys. Rev. Lett. **95**, 203004 (2005).
[21] J. P. Perdew *et al.*, Phys. Rev. Lett. **49**, 1691 (1982).
[22] M. Lein, E. K. U. Gross, and J. P. Perdew, Phys. Rev. B **61**, 13431 (2000).
[23] I. V. Tokatly and O. Pankratov, Phys. Rev. Lett. **86**, 2078 (2001).
[24] N. T. Maitra *et al.*, J. Chem. Phys. **120**, 5932 (2004).
[25] C. A. Ullrich and I. V. Tokatly, Phys. Rev. B **73**, 235102 (2006); C. A. Ullrich, J. Chem. Phys. **125**, 234108 (2006).
[26] P. Hessler, N. T. Maitra, and K. Burke, J. Chem. Phys. **117**, 72 (2002).
[27] Y. Kurzweil and R. Baer, Phys. Rev. B **73**, 075413 (2006).
[28] I. D'Amico and G. Vignale, Phys. Rev. B **59**, 7876 (1999).
[29] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).
[30] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[31] J. T. Chayes, L. Chayes, and M. B. Ruskai, J. Stat. Phys. **38**, 497 (1985).
[32] D. G. Lappas *et al.*, J. Phys. B **29**, L619 (1996).
[33] A. S. de Wijn, S. Kümmel, and M. Lein, J. Comput. Phys. **226**, 89 (2007).
[34] K. Peirs, D. Van Neck, and M. Waroquier, Phys. Rev. A **67**, 012505 (2003).
[35] A similar procedure has been used in H. O. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008).