

The Lack of Resonance Problem in Coherent Control with Real-Time Time-Dependent Density Functional Theory

Shampa Raghunathan and Mathias Nest*

Theoretische Chemie, TU München, Lichtenbergstr. 4, 85747 Garching, Germany

ABSTRACT: We will show that adiabatic real-time TDDFT predicts a time- and energy-dependent electronic structure of molecules, which makes it hard to combine TDDFT with coherent control schemes that depend on resonance conditions. In this study, we use sequences of ultrashort pulses, separated by long intervals of field free evolution, to illustrate this phenomenon for two molecules and two functionals. In coherent control scenarios, long laser pulses, with many oscillation periods, excite the system continuously and, in this way produce, a time-dependent electronic structure.

1. INTRODUCTION

Time-dependent density functional theory (TDDFT)^{1,2} is a promising tool for the coherent control of excited state electron dynamics in real time^{3,4} (RT), with a reasonable accuracy at moderate computational cost. Unfortunately, the exact form of the time-dependent exchange-correlation functional is unknown,^{5–8} so that in practice the so-called adiabatic approximation⁹ of TDDFT is invoked, where the xc potential $v_{xc}(\mathbf{r}, t)$ depends only on the instantaneous electron density $\rho(\mathbf{r}, t)$. Hence, the adiabatic approximation neglects memory effects that are necessary to incorporate the influence of the history of the density $\rho(\mathbf{r}', t')$ for $t' < t$. Despite certain limitations of adiabatic TDDFT, a wide number of applications such as high harmonic generation, Coulomb explosion, laser-induced photodissociation,¹⁰ optical response of metal clusters,^{11–15} multielectron excited states of H_2 and HeH^+ ,¹⁶ strong-field ionization rates of H_2 ,¹⁷ etc. have been performed, yielding satisfactory results. On the other hand, adiabatic TDDFT has been found to give unsatisfactory results, e.g., for the knee structure of ionization yields^{18,19} and Rabi oscillations.^{20,21}

Recently, we began to investigate the limits of the combination of adiabatic TDDFT and coherent control.^{22–24} As others before us,^{2,5,9} we found that it is extremely difficult to perform a state-to-state transition with TDDFT. Another finding was²³ that simple wave packets can be created, if certain conditions are fulfilled, like keeping a significant part of the population in the ground state and not breaking the symmetry of the molecule too much. Maybe most curiously we found in ref 24 that the vertical excitation energies that can be extracted from the TDDFT calculations depend on the fluence of the laser pulse that created the wave packet. In this paper, we study this phenomenon further and show that it is equivalent to a time-dependent or energy-dependent electronic structure of the molecule under investigation. Obviously, this is a consequence of the adiabatic and ground state functional approximations. This is especially important for combinations of TDDFT with coherent control, if resonance conditions have to be fulfilled.

Our procedure to elucidate this phenomenon is as follows. In a quantum dynamical simulation of a control experiment for electrons, ultrashort laser pulses of typically 1–10 fs duration

will be used. However, it is very difficult to extract the electronic structure information from the orbitals in such a scenario. To circumvent this problem, we insert several intervals of field free evolution into the dynamics, as a purely mathematical tool, to analyze the dynamics. More precisely, we use a soft, broadband laser pulse to excite the electrons in a molecule to form a wave packet and obtain electronic structure information from the oscillating dipole moment during the field free evolution. How this is done can most easily be seen by expressing the time dependence in an eigenstate basis:

$$\langle \vec{\mu} \rangle(t) = \sum_{n,m} c_n^* c_m \vec{\mu}_{nm} e^{-i(E_m - E_n)t/\hbar} \quad (1)$$

So even if nothing is known about the excitation energies and populations a priori, this information can be obtained from the dipole moment, which is a “good” observable in TDDFT. The autocorrelation function, which is otherwise often used in quantum dynamics, however, is not. Now, this procedure is repeated, and more energy is pumped into the system. Although the populations may change, the energies should not. However, it is one of the findings of this work that the energies do change, and sometimes quite systematically so. To make sure that our results are not too dependent on the specific system and functional, we performed calculations for two molecules, Li_2C_2 and $LiCN$, and two functionals, LDA and the hybrid functional X3LYP. Atomic units are used throughout, if not stated otherwise.

2. COMPUTATIONAL DETAILS

Here, we give a brief description of the methodology used in this study. The TDKS equations are given by

$$\dot{\phi}_j(\mathbf{r}, t) = -i\hat{H}_{KS}[\rho(\mathbf{r}, t)]\phi_j(\mathbf{r}, t) \quad (2)$$

where the KS Hamiltonian contains a coupling to a laser field in the dipole approximation:

Received: December 19, 2011

Published: February 9, 2012

$$\hat{H}_{KS}[\rho(\mathbf{r},t)] = -\frac{\nabla^2}{2} + v_H[\rho(t)](\mathbf{r},t) + v_{xc}[\rho(t)](\mathbf{r},t) + \underbrace{v_{Ne}(\mathbf{r}) - \mu f(t) \cos(\omega t)}_{v_{ext}(\mathbf{r},t)} \quad (3)$$

The Hamiltonian consists of Hartree v_H , exchange–correlation v_{xc} , and external v_{ext} potentials. The external potential contains the nuclear–electron attraction and the laser–electron interaction. The particular laser pulse sequence employed in this work has the following shape:

$$f(t) = f_0 \sum_i \cos^2\left(\frac{\pi}{2\sigma}(t - t_i)\right) \text{ if } |t - t_i| < \sigma \quad (4)$$

and is zero at all other times. Here, at times t_i , the pulse is maximal, σ is the full width at half-maximum (fwhm), 2σ is the total pulse length, and f_0 contains the polarization and maximum pulse amplitude.

The TDDFT calculations were carried out using the real-space, pseudopotential code Octopus.^{25,26} In all of the calculations, we used norm-conserving, nonlocal, ionic Troullier–Martins²⁷ pseudopotentials to model the electron–ion interactions. Two xc functionals are employed, namely, the local-density approximation (LDA) with the Perdew–Zunger parametrization,^{28–30} and the extended hybrid functional combined with Lee–Yang–Parr correlation functional (X3LYP).³¹

3. RESULTS

We now show that the electronic structure as obtained from real-time TDDFT calculations is time- and energy-dependent. To do so, we proceed as follows: A sequence of soft and ultrashort laser pulses is applied to the electrons of a molecule, with a comparatively long (around 20 fs) field free evolution between the pulses. During the field free evolution, we record the oscillating dipole moments and Fourier transform them so as to obtain spectra from which information about the eigenenergies of the system can be obtained. Because each laser pulse pumps more energy into the system, the height of the peaks in the spectra may change, but their positions should not. We begin this investigation with the Li_2C_2 molecule, for which we found in previous studies that TDDFT works rather well.

3.1. Li_2C_2 Molecule. The equilibrium geometry parameters of Li_2C_2 are $r_{\text{Li-C}} = 3.611 a_0$ and $r_{\text{C-C}} = 2.398 a_0$, with an orientation along the z axis as in our earlier study.²³ For the real-space simulations, we used a sphere of radius of $10 a_0$ and a uniform grid spacing of $0.4 a_0$. For the laser control simulations, we chose a frequency of $\omega = 4.0$ eV and a sequence of three pulses with a duration of $2\sigma = 2T$, where $T = 2\pi/\omega = 1.03$ fs, with the electric field parallel to the molecular axis, i.e., the z axis. The field strength was comparatively low at $0.01 E_h/ea_0$, as can be seen from the energy uptake after three pulses (3.59 eV for LDA, and 3.35 eV for X3LYP). As a note of caution, we have to say that for the X3LYP functional, the total energy fluctuated during the field free evolution by up to about 20 meV. We checked that this could not be improved by choosing another spatial grid or smaller integration time step. The reason is still unclear, but as the effect is small, we report the results here nevertheless.

Before we report the results of our simulations, we would like to point out that we did not employ exactly 20 fs field free

evolution between the pulses in all cases. The reason is that the action of an ultrashort pulse on an excited system depends on the relative phase between the pulse and the system. Therefore, a difference of a few tenths of a femtosecond in the timing t_i can make the difference between further excitation or de-excitation. For Li_2C_2 , we have chosen the interval between two pulses always in such a way that only excitations occur. The energies pumped into the molecule with each pulse will be given below.

Having laid out the basic setup of our calculations, we now turn to the results. Figure 1 shows the spectra we obtained from

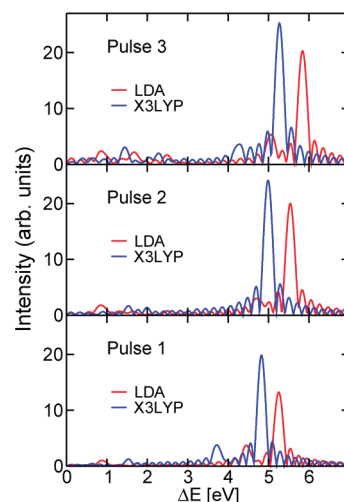


Figure 1. Spectra of the oscillations of the z component of the dipole moment of Li_2C_2 after one, two, and three laser pulses.

the z component of the dipole moment after one, two, and three ultrashort pulses. The units of the intensities are arbitrary, but they are also the same in all graphs, so that peak heights can be compared. The spectra are quite similar, but there is a clearly visible shift in the peak positions. According to eq 1, this corresponds to different values for vertical excitation energies during the first, second, and third periods of field free evolution.

To emphasize this result, we show in Figure 2 the position of the two main peaks as a function of the energy that has been

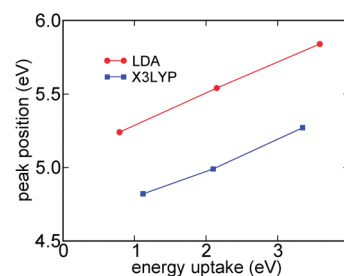


Figure 2. Shift of the positions of the main peaks, and thus the vertical excitation energies, according to Figure 1. Both functionals show an almost linear shift of 0.2 eV per eV energy uptake.

pumped into the system. The relation is almost linear, with a slope of 0.2 eV per eV of absorbed energy. This value is the same for both functionals, to within the accuracy with which a straight line can be fitted to the data points. As a result, we can conclude that the electronic structure predicted by TDDFT is indeed energy dependent. To illustrate our points, we have pumped the energy in short bursts into the system, with long

intervals in between. In a typical coherent control simulation, longer pulses would be used, leading to a shift of excitation energies as a function of time. It is this time-dependence, that will make it hard for adiabatic TDDFT to be used together with coherent control, where often resonance conditions need to be fulfilled.

How can this result be understood? In general, such a thing has to be expected always when a time-dependent basis is used to represent the state of the system, i.e., in this case, time-dependent orbitals. Initially, the orbitals are optimal to represent the ground state of the system, but at later times they also contain an overlap with excited states, so that these states are described with a time- and energy-dependent quality during the propagation. A similar phenomenon, time-dependent state averaging, has been observed in multiconfiguration time-dependent Hartree–Fock (MCTDHF),^{32–36} which also employs time-dependent orbitals. In contrast, TDCI for example uses a basis of canonical Hartree–Fock orbitals and produces therefore a time-independent electronic structure. However, several open questions remain: How much does this phenomenon depend on the specifics of the molecule? What is the reason for the positive sign of the slope in Figure 2, which is opposite of what was found for MCTDHF?³⁶ And, in which way do the functionals have to be improved to repair this problem?

In the next section, we will address the first question, by looking at a different molecule, LiCN.

3.2. LiCN MOLECULE. The equilibrium geometry of LiCN has bond lengths of $r_{\text{Li-C}} = 3.683 a_0$ and $r_{\text{C-N}} = 2.168 a_0$, orienting along the z axis as in our earlier study.²² In the real-space TDDFT simulations, a sphere of radius $12 a_0$ and a uniform grid spacing of $0.38 a_0$ are used. We employed a sequence of five short laser pulses of frequency $\omega = 6.0$ eV with a duration of $2\sigma = 4T$, where $T = 2\pi/\omega = 0.69$ fs, with the electric field perpendicular to the molecular axis, i.e., along the x axis.

Again, the intervals between two pulses have been chosen in such a way that always significant excitations occur, with one exception. The exception is the second laser pulse, which changes the energy of the system only marginally (-4 meV for LDA and $+160$ meV for X3LYP). This will lead us to further insights into the properties of TDDFT.

Figure 3 shows the spectra obtained from the x component (perpendicular to the molecular axis) of the oscillating dipole moment. These spectra have a richer structure, although this time four-cycle pulses instead of two-cycle pulses have been used, and less energy is pumped into the system (see below). At a first glance, we can see that the LDA spectra are all qualitatively the same and differ mostly only in the height of the peaks. Compared to that, the X3LYP spectra change significantly from one pulse to another. Only one peak, between 4.5 and 5 eV, can be identified in all graphs. As in the previous section, we begin by looking at the energy dependence of the peak positions. For this, we selected the X3LYP peak just mentioned and the two highest LDA peaks, see Figure 4. The X3LYP peak shows the strongest energy dependence that we found, with 0.4 eV per eV of absorbed energy. At the same time, the LDA peaks show almost no energy dependence. In the lower panel, it can be seen that the peak has shifted a little bit, although the energy after the first laser pulse is almost the same as after the second pulse. This is just one aspect of the difference between the pulse 1 and pulse 2 spectra in Figure 3: The spectra should be (almost) identical, but they are not. In

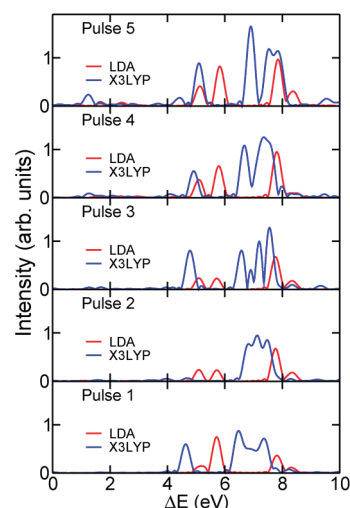


Figure 3. Spectra of the oscillations of the x component of the dipole moment of LiCN after up to five laser pulses.

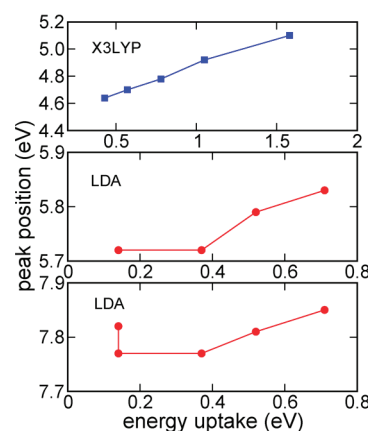


Figure 4. Shift of the positions of the main peaks in Figure 3, after up to five laser pulses.

particular, the almost disappeared X3LYP peak at 4.7 eV is striking.

When we turn our attention to the z component of the dipole moment, Figure 5, we see that the spectra change so much that it becomes impossible to identify peaks in different panels with each other, at least for X3LYP. We would like to emphasize that only very little energy is pumped into the system, so that the dynamics should not be very chaotic. For LDA, there is one stable peak at around 2.7 eV, which is also energy independent. In this way, the example of LiCN shows us the range of changes that can appear in the spectra: from stable peaks that do not change, over linear shifts, to completely uninterpretable spectra. The fact that the result for the z component of the dipole moment of LiCN is worse than for the x component agrees with our previous findings in refs 23 and 24. Adiabatic real-time TDDFT seems to work best, when the permanent dipole moments of the states involved do not differ too much.

4. CONCLUSIONS

We showed that vertical excitation energies of molecules, as described by adiabatic real-time TDDFT, can depend on the amount of energy pumped into the electronic system. If long laser pulses are used, where the energy is absorbed

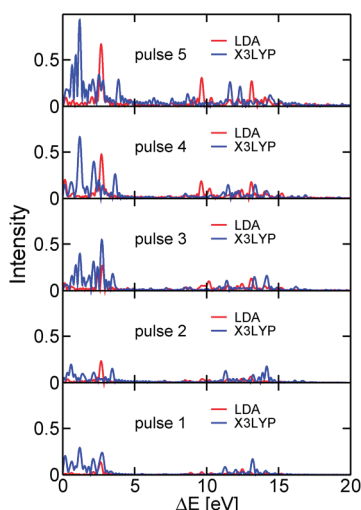


Figure 5. Spectra of the oscillations of the z component of the dipole moment of LiCN after up to five laser pulses.

continuously, the excitation energies will also shift continuously. The result is an effectively time-dependent electronic structure. This will make it very hard to apply coherent control schemes together with TDDFT, if the schemes depend on resonance conditions. As in previous studies, we found that more symmetric systems, like Li_2C_2 or the x axis of LiCN, can be described more reliably, while the different z components of the permanent dipole moments of the excited states of LiCN produce rather chaotic dynamics. The basic phenomenon is present for both functionals, and maybe a little stronger for the hybrid functional. Ideally, the electronic structure should of course be time- and energy-independent. Further studies are needed in order to decide whether better adiabatic functionals are sufficient to improve the situation, or the adiabatic approximation itself needs to be overcome.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mathias.nest@mytum.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the Munich-Centre for Advanced Photonics.

REFERENCES

- (1) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997.
- (2) Gross, E. K. U.; Burke, K. In *Time-dependent density functional theory*; Marques, M. A. L., Ullrich, C. A., Nogueira, F., Rubio, A., Burke, K., Gross, E. K. U., Eds.; Springer-Verlag: Berlin, Germany, 2006; Lecture Notes in Physics, Vol. 706.
- (3) Shapiro, M.; Brumer, P. *Principles of the Quantum Control of Molecular Processes*; Wiley: New York, 2003.
- (4) Castro, A.; Werschnik, J.; Gross, E. K. U. arXiv:1009.2241v1
- (5) Maitra, N.-T.; Burke, K.; Woodward, C. *Phys. Rev. Lett.* **2002**, *89*, 023002.
- (6) Baer, R.; Kurzweil, Y.; Cederbaum, L. S. *Isr. J. Chem.* **2005**, *45*, 161.
- (7) Schirmer, J.; Dreuw, A. *Phys. Rev. A* **2007**, *75*, 022513.
- (8) Gross, E. K. U.; Kohn, W. *Phys. Rev. Lett.* **1985**, *55*, 2850.
- (9) Burke, K.; Werschnik, J.; Gross, E. K. U. *J. Chem. Phys.* **2005**, *123*, 062206.

- (10) Castro, A.; Marques, M. A. L.; Alonso, J. A.; Bertsch, G. F.; Rubio, A. *Phys. J. D* **2004**, *28*, 211.
- (11) Yabana, K.; Bertsch, G. F. *Phys. Rev. A* **1999**, *60*, 3809.
- (12) Calvayrac, F.; Reinhard, P. G.; Suraud, E.; Ullrich, C. A. *Phys. Rep.* **2000**, *377*, 493.
- (13) Fennel, T.; Meiwe-Broer, K. H.; Tiggesbäumker, J.; Reinhard, P. G.; Dinh, P. M.; Suraud, E. *Rev. Mod. Phys.* **2010**, *82*, 1793.
- (14) Mundt, M.; Kümmel, S. *Phys. Rev. B* **2007**, *76*, 035413.
- (15) Kurzweil, Y.; Baer, R. *Phys. Rev. B* **2006**, *73*, 075413.
- (16) Isborn, C. M.; Li, X. *J. Chem. Phys.* **2008**, *129*, 204107.
- (17) Chu, X. *Phys. Rev. A* **2010**, *82*, 023407.
- (18) Lappas, D. G.; van Leeuwen, R. *J. Phys. B: At., Mol., Opt. Phys.* **1998**, *31*, L249.
- (19) Bauer, D.; Ceccherini, F. *Optics Express* **2001**, *8*, 377.
- (20) Ruggenthaler, M.; Bauer, D. *Phys. Rev. Lett.* **2009**, *102*, 233001.
- (21) Fuks, J. I.; Helbig, N.; Tokatly, I.; Rubio, A. *Phys. Rev. B* **2011**, *84*, 75107.
- (22) Raghunathan, S.; Nest, M. *J. Chem. Theory Comput.* **2011**, *7*, 2492.
- (23) Raghunathan, S.; Nest, M. Submitted.
- (24) Raghunathan, S.; Nest, M. *J. Chem. Phys.* Accepted.
- (25) Marques, M. A. L.; Castro, A.; Bertsch, G. F.; Rubio, A. *Comput. Phys. Commun.* **2003**, *151*, 60.
- (26) Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C. A.; Andrade, X.; Lorenzen, F.; Marques, M. A. L.; Gross, E. K. U.; Rubio, A. *Phys. Stat. Sol. B* **2006**, *243*, 2465.
- (27) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.
- (28) Dirac, P. A. M. *Math. Proc. Cambridge Philos. Soc.* **1930**, *26*, 376.
- (29) Bloch, F. *Z. Phys.* **1929**, *57*, 545.
- (30) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.
- (31) Xu, X.; Goddard, W. A. III. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 2673.
- (32) Zanghellini, J.; Kitzler, M.; Fabian, C.; Brabec, T.; Scrinzi, A. *Laser Physics* **2003**, *13*, 1064.
- (33) Kato, T.; Kono, H. *Chem. Phys. Lett.* **2004**, *392*, 533.
- (34) Nest, M.; Padmanaban, R.; Saalfrank, P. *J. Chem. Phys.* **2007**, *126*, 214106.
- (35) Nest, M.; Remacle, F.; Levine, R. D. *New J. Phys.* **2008**, *10*, 025019.
- (36) Padmanaban, R.; Nest, M. *Chem. Phys. Lett.* **2008**, *483*, 263.