Cite this: *Nanoscale*, 2015, 7, 19012

Optical field terahertz amplitude modulation by graphene nanoribbons

Hong Zhang,^{*a} Yoshiyuki Miyamoto,^b Xinlu Cheng^c and Angel Rubio^{d,e,f}Received 28th August 2015,
Accepted 9th October 2015
DOI: 10.1039/c5nr05889a

www.rsc.org/nanoscale

In this study, first-principles time-dependent density functional theory calculations were used to demonstrate the possibility to modulate the amplitude of the optical electric field (E-field) near a semiconducting graphene nanoribbon. A significant enhancement of the optical E-field was observed 3.34 Å above the graphene nanoribbon sheet, with an amplitude modulation of approximately 100 fs, which corresponds to a frequency of 10 THz. In general, a six-fold E-field enhancement could be obtained, which means that the power of the obtained THz is about 36 times that of incident UV light. We suggest the use of semiconducting graphene nanoribbons for converting visible and UV light into a THz signal.

Introduction

Since the isolation of single-layer graphene sheets has been successfully demonstrated,^{1–3} graphene has become one of the major research topics in condensed matter physics.⁴ Several studies have addressed the use of graphene for generating terahertz (THz) radiation,^{5–12} which is fundamental for the detection of organic matter in bio-systems. Optically pumped graphene plasmons were used to generate THz radiation.^{5–9} Furthermore, graphene has recently been used as a part of an optical cavity structure that converts light into a THz signal.¹⁰ Intensity modulation of the THz signal¹¹ and tunability of THz frequency using a graphene-based metamaterial¹² were also demonstrated utilizing the peculiar electronic structure of graphene (Dirac cone).

In this work, we propose an alternative approach for the successful generation of THz radiation based on a THz amplitude modulation of optical field near graphene nanoribbons. Graphene nanoribbons have been successfully prepared based on either a top-down¹³ or a bottom-up approach.^{14–16} Thermodynamically, graphene nanoribbons with armchair edges are energetically more stable than nanoribbons with zigzag edges.¹⁷ Therefore, we propose to use armchair-type graphene nanoribbons for the amplitude modulation of the optical field

of UV light with THz frequencies. The THz radiation was generated by modulating the photoinduced current in a graphene-covered UV photoconductor. Although it is also possible to modulate the amplitude of the optical field by mixing coherent laser beams,¹⁸ the utilization of graphene nanoribbons requires a smaller device size compared to the laser-mixing and makes it less difficult to provide stable THz radiation.

Instead of proposing a practical THz device we concentrated on studying the feasibility of controlling the THz amplitude modulation of the optical field of UV light close to the graphene nanoribbon. We considered semiconducting armchair-type graphene nanoribbons with an energy gap depending on the ribbon width,¹⁹ focusing on armchair graphene nanoribbons with widths $N = 7, 9$, and 11 according to the convention for denoting the ribbon width.¹⁹ The selected N s cover the family of $3m, 3m + 1$, and $3m + 2$ with m as an integer, which are common in discussing electronic properties of graphene nano-ribbons and carbon nanotubes. The $N = 11$ nanoribbon has the same width as the thinnest one as reported in ref. 13 and thinner ones should be capable of being synthesized with the bottom-up synthesis as reported in ref. 14–16. Thus we conclude that we have covered all typical widths of graphene nanoribbons in the current study. We computed the induced electric field (E-field) near the nanoribbon triggered by an alternating E-field with a visible to UV frequency range, and with polarization parallel to the graphene sheet and normal to the ribbon axis, which mimics the optical field. Depending on the frequency of the alternating E-field, the electronic response resulted in an E-field showing not only the same frequency as the applied E-field but also a modulation in amplitude with a much longer period; the longest period corresponded to the THz frequency range, and a six-fold increase in amplitude was observed as the maximum

^aCollege of Physical Science and Technology, Sichuan University, Chengdu 610065, China. E-mail: hongzhang@scu.edu.cn

^bNanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan

^cKey Laboratory of High Energy Density Physics and Technology of Ministry of Education; Sichuan University, Chengdu, 610064, China

^dMax Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

^eNano-Bio Spectroscopy group, Universidad del País Vasco CFM CSIC-UPV/EHU-MPC DIPC, 20018 San Sebastian, Spain

^fEuropean Theoretical Spectroscopy Facility (ETSF)

modulation of the optical E-field. This modulation was not caused by a lattice vibration in the THz frequency range but instead resulted from the interference of electronic excitations in the semiconducting graphene nanoribbon.

Computational methods

The presented calculations were performed based on the time-dependent density functional theory TDDFT,²⁰ and electron-ion dynamics (TDDFT-MD) on a real-time axis within the Ehrenfest approximation.²¹ The adopted code FPSEID^{22,23} was used to employ the split-operator scheme^{24,25} for calculating the time-evolution under alternating E-field mimicking laser irradiation.²⁶ To obtain the real-time electron dynamics we solved the time-dependent Kohn–Sham equation

$$i\hbar \frac{\partial \psi_{n,k}^{\text{KS}}(r,t)}{\partial t} = (H^{\text{KS}}(r,t) + V_{\text{ext}}(r,t))\psi_{n,k}^{\text{KS}}(r,t) \quad (1)$$

where $\psi_{n,k}^{\text{KS}}$ denotes the time-dependent Kohn–Sham orbital with band number n and k -vector of the Bloch state, and sum of the norm of all occupied Kohn–Sham orbitals is the time-dependent charge density $\rho(r,t)$. Meanwhile $H^{\text{KS}}(r,t)$ denotes the time-dependent Kohn–Sham Hamiltonian which is uniquely determined as the function of the $\rho(r,t)$ ²⁰ resulting in a self-consistent relationship between $H^{\text{KS}}(r,t)$ and $\psi_{n,k}^{\text{KS}}$. The alternating E-field is given as a gradient of the scalar potential $V_{\text{ext}}(r,t)$ and the strength of the E-field was set to $0.03 \text{ V \AA}^{-1}$. Then, we monitored time-evolution of the total E-field, which is sum of the applied E-field and the gradient of the self-consistent field, *i.e.*, the Coulomb potential of electrons and ions plus the exchange–correlation potential. The gradient of the self-consistent field is denoted as “induced field”.

The E-field intensity ($E = 0.03 \text{ V \AA}^{-1}$) of a continuous laser beam corresponds to a power of $1.214 \times 10^{10} \text{ W cm}^{-2}$. We therefore examined the stability of the graphene nanoribbon under laser irradiation as well as the influence of the lattice dynamics on the modulation of the E-field by using the Ehrenfest approximation for the electron-ion dynamics. (Validation of this approach has been described in ref. 27–29 in detail.) In our simulations, the average kinetic energies of the ions did not exceed 0.2 meV. Thus we concluded that the influence of lattice dynamics is negligible and that the graphene nanoribbons can be considered to be robust. Furthermore, for the calculations, the local density approximation (LDA)³⁰ and norm-conserving pseudopotentials³¹ were employed. Further details concerning the computational conditions are given in the footnote.[†]

[†]The calculations were performed using the plane-wave basis set to describe valence wavefunctions of electrons with a cutoff energy of 59 Ry. The unit cell has a shape of rectangular box $x \times y \times z = 6.68 \text{ \AA} \times 4.26 \text{ \AA} \times 21.84 \text{ \AA}$ for $N = 7$. For nano-ribbons $N = 9$ and $N = 11$, the box sizes in z directions are increased as 24.30 and 26.76 Å, respectively. Here y and z axes are as denoted in Fig. 1, while the x axis is normal to the graphene sheet. The length of the y axis corresponds to the period of the unit-length of the armchair nano-ribbon, while the length of the z axis was set to keep inter-ribbon distance as 12.63 Å. The fictitious dynamical

Fig. 1 (Color online) Structure and electronic properties of the armchair-type graphene nanoribbon: (a) structure of hydrogenated armchair-type graphene nanoribbon ($N = 7$). The small hatched (blue) dots represent hydrogen atoms, and the other open circles are the carbon atoms. The y -axis is parallel to the ribbon-axis and the z -axis is normal to the axis. The nanoribbon sheet lies in the yz plane, whereas the x -axis (not shown) is normal to the sheet. The vertical arrow with letter “E” indicates the assumed polarization vector of light. The dot-dashed (blue) line running through the center of the nanoribbon indicates the position assumed for monitoring the time-evolution of the E-field. (b) The corresponding energy-band structure of the nanoribbon with k vector aligned parallel to the y axis. The 0 eV on the energy axis denotes the top of valence band. The curves below 0 eV (blue) and above 0 eV (red) are the valence and conduction bands, respectively. The eigenvalues at the 16 k -points used for the simulations are represented by the dots. (c) The calculated photo-absorption spectra with optical polarization vector aligned parallel to the z axis are plotted by solid (red) lines, obtained through the TDDFT (top panel), and by static DFT (bottom panel), respectively. For the DFT calculations, the energy broadening factor was set to 0.1 eV. The dotted (blue) line and the dashed (green) line denote spectra with the optical polarization vectors aligned parallel to the x axis and the y axis, respectively.

Results

Electronic and optical properties

Fig. 1(a) shows the stable structure of a hydrogen-terminated armchair-type nanoribbon with $N = 7$, including 7 lines of C–C bonds parallel to the y -axis along the width direction of the nanoribbon.¹⁹ The corresponding energy-band structure is shown in Fig. 1(b), and the k -vector is parallel to the y -axis which is indicated in Fig. 1(a). The observed energy gap at Γ point is in agreement with the results in the literature.¹⁹ As a semiconducting material, this armchair-type nanoribbon features the optical properties displayed in Fig. 1(c). The real-time dynamics of electron polarization against short pulse was computed, and the polarization was Fourier-transformed in the frequency domain,³² see the top panel of Fig. 1(c). The Fourier transformation was performed in the time-range from 1.96 to 19.60 fs. Three major peaks were observed, corresponding to absorption energies 2.67, 5.87, and 6.53 eV, respectively. The results were then compared with those obtained through static

cal charge of positive and negative polarities was set in the edge of the vacuum region to generate E-field parallel to the z -axis, which was the reason to keep almost double inter-ribbon distance in the z -axis compared to that in the x -axis. 16 irreducible k -points including Γ and Y points were used in a one-dimensional Brillouin Zone of the armchair nano-ribbon with k -vector parallel to the y -axis, which are dense enough to draw the band-dispersion as denoted in Fig. 1(b) and 4(a). For the real-time evolution of electron wavefunctions, we set interval of the time-step as 0.03 atomic unit (7.2610×10^{-4} fs).

DFT calculations, shown in the bottom panel in Fig. 1(c) using optical transition matrix elements of the Kohn–Sham orbitals and Kohn–Sham eigenvalues. (The spectra obtained for x and y polarizations are also shown in the bottom panel of Fig. 1(c).) The results obtained for the optical absorption energy through the DFT calculations, which are usually a little bit too low, should be improved when switching to the TDDFT simulation without affecting the conclusions presented here. The effect of exciton in the current low-dimensional model is partly considered by TDDFT.³³ Direct comparison of the computed optical properties with polarization of incident light would be straightforward when experiment with highly oriented graphene nanoribbon becomes accessible.

The analysis of the optical matrix element reveals that the broader absorption peak at 2.67 eV can mainly be attributed to transitions from the second highest occupied state (HOMO–1) to the lowest unoccupied state (LUMO) and transition from HOMO to LUMO+1 at the Γ point in the momentum space, whereas the sharper absorption peaks at 5.87 eV and 6.53 eV corresponds to transitions from HOMO–1 to LUMO and from HOMO to LUMO+1 at the Y point, respectively. The optical matrix elements for the latter two peaks are higher by a factor of two compared to the peak 2.67 eV. Furthermore, the band dispersions in the band-gap region are narrower at the Y point than at the Γ point. Therefore the sharper peaks at 5.87 eV and 6.53 eV can be attributed to a higher optical joint density of states.

Simulation for optical-field modulation

The time evolution of the total E-field (the applied field plus the induced field) was monitored at a distance of 3.34 Å above the graphene nanoribbon averaged for the period along the central line (see Fig. 1(a)), and the results are shown in Fig. 2(a)–(d) for photon energies of 2.67 eV, 5.87 eV, 6.20 eV, and 6.53 eV, respectively. Since the E-field was monitored apart from the graphene sheet, the E-field variation in sheet parallel directions should be weak, thus we believe that the current way for averaging the field is adequate.

Fig. 2 (Color online) Time evolution of the applied E-field (thick (blue) lines), and the total E-field consisting of applied E-field and induced E-field (thin (red) lines), obtained through TDDFT simulation for different photon energies (a) 2.67 eV, (b) 5.87 eV, (c) 6.20 eV, and (d) 6.53 eV.

The strength of the total E-field obtained for a photon energy of 2.67 eV shows lower amplitude than the applied E-field up to a time-range of 10 fs corresponding to a screening. Then, the screening becomes weaker in a longer time range. At 20 fs, the amplitude and phase of the total E-field were almost identical to the amplitude and the phase of the applied E-field. Meanwhile, the simulations for photon energies of 5.87 eV, 6.20 eV, and 6.53 eV revealed a rapid increase in the strength of the total E-field beyond the strength of the applied field, corresponding to an enhancement effect. In case of enhancement, the phase of the total E-field starts diverging from the phase of the applied field, which indicates that the amplitude of the induced E-field significantly exceeds the amplitude of the applied field. Such an increase in amplitude of the induced field can be explained by an amplified electron motion similar to a pendulum in resonance. The presence of the edge of the nanoribbon is another factor contributing to the large induced E-field. Such an enhancement in the total E-field has previously also been observed inside semiconducting carbon nanotubes.³⁴

The significant difference between the dynamics of the total E-field obtained for photon energy of 2.67 eV and those obtained for photon energies higher than 5.87 eV is correlated with the corresponding absorption peaks shown in the top panel of Fig. 1(c). The absorption peaks observed for photon energies of 5.87 eV and 6.53 eV are rather higher and sharper than that for a photon energy of 2.67 eV, as mentioned before. On the other hand, it is remarkable that the field-enhancement effect was also observed for a photon energy of 6.20 eV, which is in a valley between the neighboring peaks, as shown in Fig. 1(c).

Amplitude modulation in longer-time simulation

Next we studied the longer-time behavior of the E-field modulation for photon energies higher than 6 eV. Fig. 3 shows the modulation of the alternating E-field for frequencies corresponding to photon energies of 6.20 eV and 6.53 eV, respectively, with a longer time-constant than in Fig. 2. The amplitude

Fig. 3 (Color online) Time evolution of the applied E-field (thick (blue) lines), and the total E-field consisting of the applied E-field and the induced E-field (thin (red) lines) for photon energies of 6.20 and 6.53 eV, respectively. Top and bottoms correspond to Fig. 2(c) and (d), respectively, however, for a longer time-constant.

of the total E-field reaches its maximum approximately 70 fs for these photon energies, 195 fs (for 6.20 eV) and 170 fs (for 6.53 eV), respectively, the amplitude again shows a peak. Therefore, the modulation period is ≈ 100 fs, which correspond to a frequency of approximately 10 THz: for both cases. *i.e.*, a photon energy of 6.20 eV and 6.53 eV, the intensity of the enhanced E-field is significant, and reaches $0.3 \text{ V } \text{\AA}^{-1}$ for photon energy of 6.20 eV, which is stronger in magnitude than the given E-field. The energy accumulation due to continuous irradiation with UV light near the resonant frequency of electron-cloud motion resulted in an increase of amplitude of an induced E-field.

An amplitude modulation of an incident light was previously observed in a semiconductor quantum well which features two major photo-absorption peaks from light and heavy hole states,³⁵ and the modulation period was assessed according to the energy-level difference between heavy and light hole-states, *i.e.*, the modulation period was inversely proportional to the energy-interval of the absorption peak. Meanwhile in our case, the photo-absorption peaks in Fig. 1(c) do not correspond to a few broader peaks but to a superposition of many peaks obtained by an inter-band transition at each of the k -points. Therefore, we expect that the interference between several excited states with different resonant frequencies is responsible for the E-field modulations.

E-field modulation in wider nano-ribbons

We have also simulated wider nanoribbons, with $N = 9$ and $N = 11$. The band structures of these nanoribbons are shown in Fig. 4(a), and are in good agreement with results published previously.¹⁹ However, with polarization normal to the ribbon

Fig. 4 (Color online) Energy-band structure and photo-absorption spectrum for armchair-type graphene nanoribbons with $N = 9$ and $N = 11$: (a) energy-band structure for $N = 9$ (left) and $N = 11$ (right) and the k vector aligned parallel to the y axis. The 0 eV on the energy axis denotes the top of valence band. The curves below (blue) and above 0 eV (red) are valence and conduction bands, respectively. The eigenvalues at the 16 k -points used for the simulations are denoted as dots. (b) Photo-absorption spectrum with the optical polarization vector aligned parallel to the z axis in Fig. 1(a) obtained through TDDFT calculations for $N = 9$ (bottom) and $N = 11$ (top). The absorption intensity is given in an arbitrary but common unit.

Fig. 5 (Color online) Time evolution of the applied E-field (thick (blue) lines), and the total E-field consisting of the applied E-field and the induced E-field (thin (red) lines) for a photon energy of 6.01 eV and a nanoribbon width $N = 9$ (bottom), and for a photon energy of 5.69 eV and a nanoribbon width $N = 11$ (top).

edge and parallel to the ribbon sheet, the absorption spectrum in Fig. 4(b) does not show a significant difference regarding the peak positions besides the difference in absorption intensity, and is even similar to the spectrum obtained for $N = 7$. For investigating the E-field modulation, we therefore focused on the photon energies of 6.01 eV for $N = 9$, and 5.69 eV for $N = 11$, which are located between the two main peaks as denoted by arrows in Fig. 4(b).

Fig. 5 shows the computed E-field modulations for photon energy of 6.01 eV and $N = 9$, and for photon energy of 5.69 eV and $N = 11$. For both the cases, similar to the case shown in Fig. 3 for photon energy of 6.20 eV and $N = 7$, a significant enhancement of the E-field was observed. For both the cases the amplitude modulation period is approximately 100 fs. Although there is a difference regarding the time the first peak appears when comparing the E-field enhancements by the different armchair-type nanoribbons, the intervals between the first and the second peaks are almost the same.

Discussion and concluding remarks

The E-field enhancement can be attributed to a resonant amplification of the oscillating electron cloud, while the modulation of the amplitude of the E-field can be attributed to interference between many photo-excited states from many k -points. In all three cases, *i.e.*, for $N = 7, 9$ and 11 , the induced E-field was modulated with a long period in the order of 100 fs. Besides the currently studied excitation-energies, photon energies around 5 eV, corresponding to shoulders in absorption peaks (see Fig. 1(c) and 4(b)), may also contribute to E-field modulation.

We now comment on the influence of impurities in the graphene ribbon. The presence of impurity introduces new scattering processes that might modify slightly the findings of the present work; in particular they could tend to suppress the

Fig. 6 (Color online) Schematic illustration of the generation of a THz signal using photo-conducting semiconductor covered by an armchair-type graphene nanoribbon sheet. The current converter denoted by the arrow can convert a one-way modulating current into an alternating current.

E-field enhancement as well as the THz oscillation. However a detailed analysis of this effect is beyond the scope of the present work and it is left for future work.

Next, we discuss possible applications of the present findings. For instance, if a mat of graphene nanoribbons is printed on a surface of photo-conducting semiconductor, the distance from the surface of the mat to the semiconductor should be close to $3.34 \text{ \AA}$. This distance is very close to the distance where we observed the modulation of the E-field of the incident UV light, according to the simulation results. When a photo-conducting semiconductor is irradiated with UV light through the graphene nanoribbon mat, the photon-intensity can be modulated in the photo-conducting semiconductor and thus the photo-current can be modulated as well, as illustrated in Fig. 6.

When this modulated current is then converted into an alternating current by a circuit connected to an antenna, a THz radiation can be generated by the antenna. We assume that the power of the generated THz radiation is governed by two factors: first, the enhancement factor describing the difference between the UV E-field and the modulated UV E-field, which is by factor six according to Fig. 3 and 5. The second factor is the photo-current conversion efficiency of the photo-conducting semiconductor, which was not the focus of this study. Indeed, such a circuit can be built using a current-voltage converter connected with a voltage calibration circuit. In this study, we demonstrated the modulation of E-field of UV light, with a modulation period of approximately 100 fs by graphene nanoribbons with different widths. To obtain a standard THz signal in the range from 0.5 to 5 THz, a longer modulation period needs to be achieved, which should be the aim of further studies. One of the most promising ways to realize such modulation frequencies is using the armchair-

type graphene nanoribbons with larger widths than the ribbons investigated in this study. In addition, using ribbons consisting of other two-dimensional materials is considered another feasible approach in which visible light might be the case of the amplitude modulation.

Acknowledgements

The calculations in this study were performed using the Parallel Computing System at AIST and the High-Performance Computing System of the Cybermedia Center in Osaka University. HZ and XLC acknowledge financial support from the National Natural Science Foundation of China (Grant No. 11474207 and Grant No. 11374217). YM acknowledges the fund from MEXT, Grant-in-Aid for Scientific Research on Innovative Areas "Science of Atomic Layers (SATL)", Japan, and the support from Research organization of Information Science and Technology (RIST) at Tokyo. AR acknowledges financial support from the European Research Council Advanced Grant DYnamo (ERC-2010-AdG-267374), Spanish Grant (FIS2013-46159-C3-1-P), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT578-13) and COST Actions CM1204 (XLIC) and MP1306 (EUSpec).

Notes and references

- 1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197–200.
- 3 Y. Zhang, Y.-W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201–204.
- 4 K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab and P. Kim, *Nature*, 2012, **490**, 192–200.
- 5 L. Ju, B. Geng, J. Horng, C. Girit, M. Martin, Z. Hao, H. A. Bechtel, X. Liang, A. Zettl, Y. R. Shen and F. Wang, *Nat. Nanotechnol.*, 2011, **6**, 630–634.
- 6 M. Tamagnone, J. S. Gómez-Díaz, J. R. Mosig and J. Perruisseau-Carrier, *Appl. Phys. Lett.*, 2012, **101**, 214102.
- 7 H. Yan, F. Xia, Z. Li and P. Avouris, *New J. Phys.*, 2012, **14**, 1–14.
- 8 D. Sun, C. Divin, J. Rioux, J. E. Sipe, C. Berger, W. A. de Heer, P. N. First and T. B. Norris, *Nano Lett.*, 2010, **10**, 1293–1296.
- 9 L. Prechtel, L. Song, D. Schuh, P. Ajayan, W. Wegscheider and A. W. Holleitner, *Nat. Commun.*, 2012, **3**, 646.
- 10 R. Yu, V. Pruneri and F. Javier García de Abajo, *ACS Photonics*, 2015, **2**, 550.
- 11 B. Sensale-Rodriguez, R. Yan, M. M. Kelly, T. Fang, K. Tahy, W. S. Hwang, D. Jena, L. Liu and H. G. Xing, *Nat. Commun.*, 2012, **3**, 780.
- 12 X. He, *Carbon*, 2015, **82**, 229–237.

- 13 X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, *Science*, 2008, **319**, 1229–1232.
- 14 J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen and R. Fasel, *Nature*, 2010, **466**, 470–473.
- 15 Y. Ishii, T. Sakashita, S. Kawasaki, H. Kato and M. Takatori, *Mater. Express*, 2011, **1**, 36.
- 16 Y. C. Chen, T. Cao, C. Chen, Z. Pedramrazi, D. Haberer, D. G. de Oteyza, F. R. Fischer, S. G. Louie and M. F. Crommie, *Nat. Nanotechnol.*, 2015, **10**, 156–160.
- 17 S. Okada, *Phys. Rev. B: Condens. Matter*, 2008, **77**, 041408 (R).
- 18 A. Nahata, J. T. Yardley and T. F. Heinz, *Appl. Phys. Lett.*, 1999, **75**, 2524.
- 19 Y.-W. Son, M. L. Cohen and S. G. Louie, *Phys. Rev. Lett.*, 2006, **97**, 216803.
- 20 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997–1000.
- 21 P. Ehrenfest, *Z. Phys.*, 1927, **45**, 455–457.
- 22 O. Sugino and Y. Miyamoto, *Phys. Rev. B: Condens. Matter*, 1999, **59**, 2579–2586.
- 23 O. Sugino and Y. Miyamoto, *Phys. Rev. B: Condens. Matter*, 2002, **88**, 089901(E).
- 24 M. Suzuki, *J. Phys. Soc. Jpn.*, 1992, **61**, 3015–3019.
- 25 M. Suzuki and T. Yamauchi, *J. Math. Phys.*, 1993, **34**, 4892–4897.
- 26 A. Castro, M. A. L. Marques, J. A. Alonso, G. F. Bertsch and A. Rubio, *Eur. Phys. J. D*, 2004, **28**, 211–218.
- 27 J. L. Alonso, X. Andrade, P. Echenique, F. Falceto, D. Prada-Gracia and A. Rubio, *Phys. Rev. Lett.*, 2008, **101**, 96403.
- 28 X. Andrade, A. Castro, D. Zueco, J. L. Alonso, P. Echenique, F. Falceto and A. Rubio, *J. Chem. Theor. Comput.*, 2009, **5**, 728–742.
- 29 *Fundamentals of time-dependent density functional theory*, ed. M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross and A. Rubio, Springer, Berlin, 2012, vol. 837.
- 30 J. P. Perdew and A. Zunger, *Phys. Rev. B: Condens. Matter*, 1981, **23**, 5048–5079.
- 31 N. Troullier and J. L. Martins, *Phys. Rev. B: Condens. Matter*, 1991, **43**, 1993–2006.
- 32 K. Yabana and G. F. Bertsch, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 4484–4487.
- 33 G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys.*, 2002, **74**, 601–659.
- 34 H. Zhang and Y. Miyamoto, *Appl. Phys. Lett.*, 2008, **95**, 053109.
- 35 P. C. M. Planken, M. C. Nuss, I. Brener and K. Goossen, *Phys. Rev. Lett.*, 1992, **69**, 3800–3803.