

Molecular Modes of Attosecond Charge Migration

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First-principles calculations are employed to elucidate the modes of attosecond charge migration (CM) in halogenated hydrocarbon chains. We use constrained density functional theory (DFT) to emulate the creation of a localized hole on the halogen and follow the subsequent dynamics via time-dependent DFT. We find low-frequency CM modes (~ 1 eV) that propagate across the molecule and study their dependence on length, bond order, and halogenation. We observe that the CM speed (~ 4 Å/fs) is largely independent of molecule length, but is lower for triple-bonded versus double-bonded molecules. Additionally, as the halogen mass increases, the hole travels in a more particlelike manner as it moves across the molecule. These heuristics will be useful in identifying molecules and optimal CM detection methods for future experiments, especially for halogenated hydrocarbons which are promising targets for ionization-triggered CM.

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When forced out of equilibrium, electrons in matter can respond exceedingly fast, on timescales approaching the attosecond [1–11], where their dynamics are driven by many-body correlations and they are not yet impacted by the coupling to nuclear motion [2,8,12]. An important example of this principle is charge migration (CM), which was first predicted by Cederbaum and Zobeley in their pioneering work [1]. CM involves the rapid movement of positively charged holes in a molecule following ionization [1–4,12,13] or excitation [14,15]. The complex quantum evolution underlying CM can potentially expose correlations between electrons and holes that are otherwise hidden in the static properties of the system [1,16]. These correlations, and the dynamics they evoke, can impact fundamental processes, such as charge transport and photoelectric energy conversion.

Only a few experimental studies have documented the presence of CM, using either pump-probe ionization in amino acids (phenylalanine and tryptophan) [3,8] or via high-harmonic spectroscopy in the small linear molecule iodoacetylene [4]. Although a larger number of theoretical studies have appeared [1,2,13,14,17–20], there are still a number of open questions that impact future experiments, including the following. Which molecules are expected to support CM? Does CM manifest in generic ways so that its periodicity and visibility can be predicted to follow simple rules? Does the manner in which CM is initiated influence how it proceeds? To address these questions, it is useful to consider classes of molecules that have common characteristics but that also allow enough

variation to identify which modes of CM are generic and which are not.

In this Letter, we use first-principles calculations to investigate the characteristics of CM in halogenated hydrocarbon chains, which have been shown to support the creation of a localized hole via either strong-field ionization (SFI) [21–23] or inner-shell ionization [24–26]. In particular, we define metrics of CM and study how these are influenced by chemically accessible properties such as the length of the molecule, the type of bonding (single, double, or triple), and the halogen functionalization. We emulate a hole created by strong-field ionization by using constrained density functional theory (DFT) [27] to initiate a localized hole on the halogen atom, followed by time-dependent DFT (TDDFT) to propagate the density in time [28–31]. By isolating the low-frequency modes (~ 1 eV) and studying the time-dependent hole dynamics, we identify a number of trends that could be used to make general predictions for future experiments. We find that the double- and triple-bonded molecules all support robust CM that progresses via hopping from π bond to π bond. This occurs with a speed that is largely independent of the molecular length, but that is lower for the triple-bonded than for the double-bonded chains. We also show that chains with higher-atomic-number halogen atoms support CM in which the hole is more localized and slightly slower as it moves along the molecular backbone.

Our numerical simulations involve three steps: emulation of a hole, time propagation, and extraction of CM modes from the density. To prepare the initial state we use

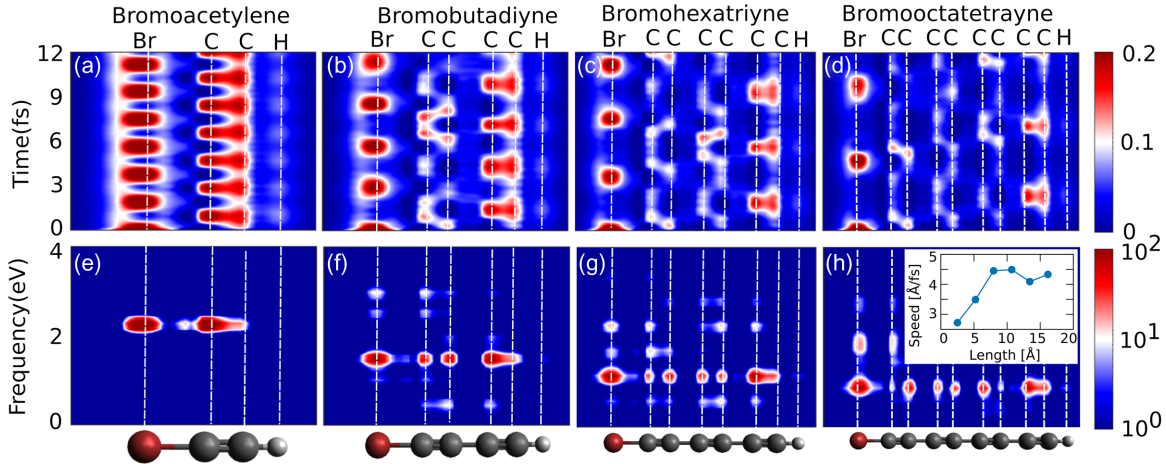


FIG. 1. The effect of molecule length on charge migration in the linear alkyne family. (a)–(d) The time-dependent hole density in (bromoacetylene, bromobutadiyne, bromohexatriyne, and bromooctatetrayne) following sudden ionization from the Br atom. (e)–(h) The intensity of the Fourier transforms of the hole densities. We show the positive part of the hole density integrated over the directions perpendicular to the molecular axis. The inset in (h) shows the computed CM speeds for linear poly-yne $\text{Br-C}_n\text{H}$, where $n = 2, 4, 6, 8, 10, 12$.

constrained DFT (CDFT) [27]; i.e., we combine standard energy minimization techniques with the requirement of having a localized hole on the halogen. This emulates a rapid SFI process, which is known to leave the system in a nonstationary state with a halogen-localized hole [23]. This is a significant improvement over arbitrarily creating hole(s) in the ground state Kohn-Sham valence orbital(s), which exhibit significant delocalization errors and give qualitatively incorrect dynamics [27]. In contrast, the CDFT procedure mixes multiple orbitals, resulting in a more multielectron, multideterminantlike excitation, similar to using ΔSCF (self-consistent field) for excited states [32–34]. This localized initial hole thus involves a superposition of multiple states that results in particlelike propagation created by the localized ionization on the halogen.

Following the creation of the hole, we calculate the subsequent dynamics using Gaussian-basis-set real-time TDDFT in a development version of NWChem [29,35]. Our singly ionized initial state circumvents well-known challenges for adiabatic exchange-correlation functionals [36–41]. For all calculations we use the hybrid PBE0 functional, which has been shown to give accurate CM dynamics, likely due to reduced self-interaction and improved long-range Coulomb interactions [18]. For the basis set we use cc-pVDZ for H/C and Stuttgart RLC ECP for F/Cl/Br. We tested the basis-set convergence using def2-TZVP for the chlorobutadiyne case, which gave essentially identical results. For all simulations we use a time step of 0.2 a.u. (0.005 fs) and propagate the dynamics up to 1200 a.u. (29 fs).






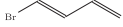





We interpret the dynamics following the singly ionized initial state in terms of the hole density, $\rho^H(\mathbf{r}, t)$, defined as the difference between the neutral ground state density and that of the cation: $\rho^H(\mathbf{r}, t) = \rho^0(\mathbf{r}) - \rho^+(\mathbf{r}, t)$. For simpler visualization, we integrate the hole density over directions

transverse to the CM axis (long axis of the molecule) yielding the reduced hole density $\rho^H(z, t)$. From this we quantify the characteristic CM time t_{CM} , the hole migration distance z_{CM} , and the corresponding speed v_{CM} as described in the following. For each molecule that exhibits CM, we find that the hole moves from the halogen to the terminal double or triple bond. We therefore define z_{CM} as the distance between these two sites. Additionally, we define t_{CM} as the time it takes the hole to travel this distance. This time can be read directly from plots of the time-dependent hole density or inferred from their Fourier transforms: $t_{\text{CM}} = T_{\text{CM}}/2 = \pi/\omega_{\text{CM}}$, where T_{CM} and ω_{CM} are the period and frequency of the mode, respectively (see Fig. 1 for illustration). Our simulations, which focus on the first few oscillations, do not include nuclear motion and thus there is no dephasing of the hole motion. In an actual experiment, the timescale t_{CM} is expected to be much faster than the dephasing processes, and holes are expected to survive at least one half-period in real systems, if not longer [12,42,43].

To give an approximate measure of the experimental sensitivity needed to probe CM, we furthermore quantify the visibility of the hole to an experimental probe of the local density (e.g., high-harmonic spectroscopy or x-ray absorption spectroscopy, or ionization spectroscopy) by calculating the hole contrast γ_{site}^H , where “site” denotes either the halogen or the terminal double or triple bond. This is computed from the time-dependent integrated hole number on a site of interest n_{site}^H , which we fit to an offset oscillation $n_{\text{site}}^H = A + B \sin(\omega_{\text{CM}}t + \phi)$. The contrast is given by the ratio $\gamma_{\text{site}}^H = B/A$. In Table I, we tabulate values for the CM metrics defined above.

We start by discussing the relationship between migration time t_{CM} and molecule length in quasi-one-dimensional

TABLE I. Metrics of charge migration as a function of molecule length, bonding, and halogen functionalization.

Compound		CM time [fs]	CM distance [Å]	CM speed [Å/fs]	Contrast at halogen site	Contrast at terminal bond
Length	Bromoacetylene 	0.92	2.50	2.72	0.37	0.65
	Bromobutadiyne 	1.50	5.23	3.49	0.55	0.60
	Bromohexatriyne 	1.79	7.96	4.45	0.58	0.75
	Bromooctatetrayne 	2.38	10.69	4.49	0.67	0.84
Bonding	Bromobutane ^a 
	Bromobutadiene 	0.87	4.86	5.58	0.39	0.50
	Bromobutadiyne 	1.50	5.23	3.49	0.55	0.60
Halogen	Fluorobutadiyne ^a 
	Chlorobutadiyne 	1.19	5.09	4.28	0.48	0.52
	Bromobutadiyne 	1.50	5.23	3.49	0.55	0.60
	Iodobutadiyne ^b 	1.43	5.41	3.78	0.65	0.81

^aNo CM modes observed (see text)^bNo spin-orbit coupling in simulation (see SM [45])

halogenated hydrocarbon molecules. Changing the length of a molecule may offer an intuitive avenue for tuning the CM time [44], but many questions remain about the effects of molecule length on the migration. To address this, we consider CM in the family of linear bromoalkyne molecules, which contain alternating single and triple bonds. Figures 1(a)–1(d) show the time-dependent hole densities of bromoacetylene (BrC_2H), bromobutadiyne (BrC_4H), bromohexatriyne (BrC_6H), and bromooctatetrayne (BrC_8H), where we use CDFT to create a hole on the Br atom. In bromoacetylene [Fig. 1(a)], the dynamics involve a hopping between the halogen and $\text{C}\equiv\text{C}$, which takes 0.92 fs; this is consistent with the previously studied iodoacetylene molecule [4]. For the diyne [Fig. 1(b)], triyne [Fig. 1(c)], and tetrayne [Fig. 1(d)], the dynamics involve hopping from $\text{Br}\rightarrow\text{C}\equiv\text{C}\rightarrow\text{C}\equiv\text{C}$, with CM times of 1.50, 1.79, and 2.38 fs, respectively. A movie of the hole density in bromobutadiyne demonstrating CM via hopping is available in the Supplemental Material (SM) [45]. Figures 1(e)–1(h) show the intensities of the Fourier transforms of the hole densities. For the poly-ynes [Figs. 1(f)–1(h)], the spectrograms have a dominant feature at the CM-mode frequency ω_{CM} , as well as numerous other weaker modes. These modes are both harmonics of ω_{CM} (a result of the hopping mechanisms) as well as higher-frequency modes arising from the CDFT hole creation. To display the time dependence of the mode around ω_{CM} clearly, we have removed the high-frequency contributions in all time-dependent plots of $\rho^{\text{H}}(z, t)$, filtering via a convolution with a \sin^4 window with a 1 fs total duration (360 as FWHM).

Figure 1 shows a clear increase in t_{CM} with molecule length. Looking at the corresponding CM speed (v_{CM}), the molecule with two carbon atoms, Fig. 1(a), for which CM involves a halogen-to-bond CM mechanism, has a speed of 2.72 Å/fs (see Table I). The three poly-yne molecules, Figs. 1(b)–1(d), for which CM occurs via bond-to-bond

hopping, have v_{CM} of 3.49 Å/fs for the four-carbon chain, 4.45 Å/fs for the six-carbon chain, and 4.49 Å/fs for the eight-carbon chain. The inset of Fig. 1(h) shows the computed CM speeds for linear poly-ynes $\text{Br}-\text{C}_n\text{H}$, where $n = 2, 4, 6, 8, 10, 12$. For the shorter molecules, the CM speed increases with length before leveling off to a constant of ~ 4 Å/fs for larger molecules. The similarity of their v_{CM} suggests a picture of CM reminiscent of conductivity in conjugated molecules where electrons move via hopping from π site to π site [46,47]. Since this mobility depends primarily on the overlap of neighboring π bonds, conductivity is an intensive property (independent of system length). Likewise in CM, the mobility of a hole arises from the ability of a neighboring π bond to donate electrons to fill it. This “bucket brigade” mechanism of hole mobility [15] likewise results in a speed that is dictated by the overlap of the π bonds. We further speculate that there are two characteristic speeds in the dynamics: the hole migration from the halogen to or from the chain occurs at one (slower) speed, whereas the hole hopping down the chain occurs at another (faster) speed. We note that these speeds are similar in magnitude to those reported previously for CM in unfunctionalized poly-ynes [44], although different in initial condition and length dependence: Kuleff and collaborators found CM speed to increase with length when initiated by delocalized valence-orbital hole [44] (see Fig. S1 in SM for comparison [45]).

To illustrate in more detail how CM is affected by chemical bonding, the horizontal row of Figs. 2(a)–2(c) shows the filtered hole dynamics for the family of molecules where Br functionalizes four-carbon molecules with single-, double-, and triple-bonded backbones. For bromobutane (BrC_4H_9), the hole stays mostly localized on the Br, with a small amount of hole density spread throughout the chain. We posit that this nonmigrating motion is a consequence of the lack of a π system, i.e., an inability of a

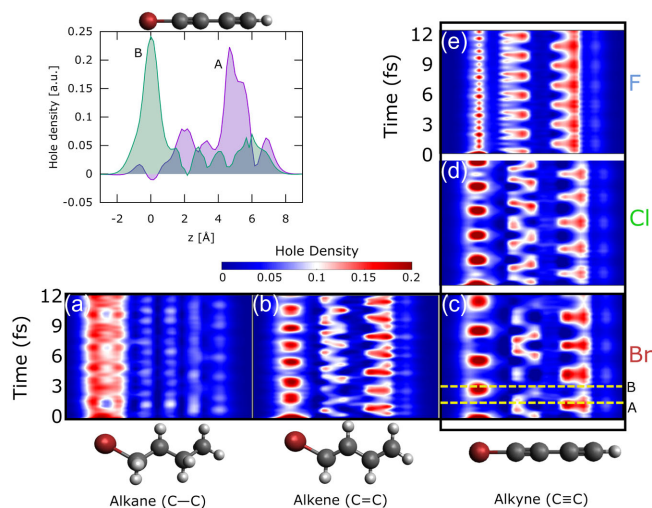


FIG. 2. Time-dependent perpendicular-integrated hole densities in linear halohydrocarbons as a function of bond order and halogen atomic number (Z) following sudden ionization from the halogen. Top left-hand inset: lineout of the hole densities in bromobutadiyne at two extrema of the CM (A, hole on terminal $C\equiv C$; B, hole on Br).

saturated chain to donate electrons to fill the hole on the Br. For this reason, we predict that alkanes are not likely to support long-range CM.

Unlike for saturated chains, we see clear evidence of CM in bromobutadiene (BrC_4H_5) and bromobutadiyne (BrC_4H). CM in these molecules involves hopping from the halogen to the middle and terminal double or triple bonds, as shown in the inset of Fig. 2, which shows $\rho^H(z, t)$ at the time when the hole is on Br (labeled B) and at the time it is on the terminal $C\equiv C$ (labeled A). For these two molecules, t_{CM} increases as bond strength increases, with the resulting v_{CM} (Table I) slower in the triple-bonded (3.49 Å/fs) versus double-bonded case (5.58 Å/fs). In terms of a hopping picture, the faster CM in alkenes is a result of the $C=C/C=C$ sites being closer to each other than the $C\equiv C/C\equiv C$, i.e., more overlap, stronger coupling, and thus higher hole mobility.

An alternative method of modulating CM without changing the molecular structure is to use chemical functionalization. The vertical column of Figs. 2(c)–2(e) shows the effect of halogenation on CM for the four-carbon polyalkyne chain (XC_4H with $X = F, Cl, Br$). Rounding out the series, we have included the results for iodobutadiyne in the SM (Fig. S2) [45]. The three heavier halobutadiynes ($X = Cl, Br, I$) all exhibit a clear hopping-type CM from the X to the terminal $C\equiv C$ bond. Table I shows that the CM speed is higher for the Cl than the Br case (4.28 Å/fs vs 3.49 Å/fs). This can be understood from the higher electronegativity of Cl^+ , which allows it more readily to give up its hole than Br^+ . The I case is similar to the Br case (with a speed of 3.78 Å/fs; see the SM [45]). In contrast, for fluorobutadiyne (FC_4H),

the hole on the F oscillates with one frequency while the hole in the chain hops from triple bond to triple bond at another frequency. This weak coupling of the F from the chain is a result of the lower electronegativity of alkyl groups compared to F, which manifests as a large energy spacing between the F and chain molecular orbitals. Similar effects are seen in hole localization resulting from SFI in fluoromethane [21,23]. Furthermore, the CM in the fluorine case is suppressed as a result of the relative delocalization of the initial hole (see SM, Fig. S3 [45]). In contrast to the localized holes on Cl and Br, the large electronegativity of the F atom causes the CDFT ground state to involve significant hole density on the two $C\equiv C$ bonds; i.e., the F draws electrons from the chain. This results in fast F-C dynamics and slow intrachain dynamics instead of the hopping-type CM mode observed in the other halogenated compounds.

To quantify the visibility of a hole to an experimental probe during the CM process, Table I also shows the contrasts on the halogen and the terminal double or triple bond for all molecules. For the XC_4H case, the contrast on X increases going from Cl to I. This is consistent with previous observations that SFI in higher Z halogens results in a more localized hole [21,23]. Interestingly, the contrast on the terminal $C\equiv C$ also increases with Z . This suggests it is also easier to experimentally observe the hole on the other end of the molecule. Combined with the slower CM speeds, this makes bromine (or possibly iodine) functionalized molecules excellent candidates for CM experiments. Finally, as shown in Table I, the hole contrast on both the halogen and terminal π bond also increases with molecule length and bond order. This suggests that CM is likely easier to observe in longer molecules than shorter ones, and in triple-bonded molecules than in double-bonded ones.

In summary, we have used first-principles simulations to compute CM in linear halohydrocarbons, and computed the corresponding physical metrics including migration length, time, speed, and hole contrast. These measures are useful for interpreting observations and for motivating the choice of molecules for future experiments. Many techniques work best when the dynamics occur at a timescale comparable to the experimental laser probe period (e.g., high-harmonic spectroscopy), pump-probe delay, and/or when there is a large difference in density in one region of the molecule (e.g., inner-shell spectroscopy).

From our CM-mode analysis, we can address the questions posed at the start of the Letter, and draw some general conclusions about the types of molecules best suited to future CM studies. Firstly, molecules with conjugation are likely to be the best candidates for supporting particlelike CM, since the π system supports facile hole motion. Triple-bonded molecules give rise to more localized and slower CM than double-bonded ones, although their highly reactive nature may make experiments challenging. We also observe that, at least in alkene or alkynes,

CM does indeed manifest in a generic way, where the hole moves down the molecular backbone via hopping between π bonds. Absent dephasing or energy loss, these dynamics are model-like and periodic. As a result, holes migrate within the chain with a speed relatively independent of molecule length and CM can be intuitively controlled via molecular geometry (e.g., length, rings) to match the timescale and/or length scale of a particular experimental probe. Regarding the role of initial condition, although we have not explicitly studied different types of ionization, we observe that starting CM via a localized hole on a halogen (Cl, Br, I) results in coherent CM. Fluorine-functionalized chains, in contrast, do not exhibit CM as the high electronegativity of F results in a delocalized hole across the molecule when using CDFT to emulate SFI. Moreover, higher-atomic-number halogens result in slower and more localized holes, which is advantageous for experimental measurements that probe the local electron density at different ends of the molecule. Going forward, these simple heuristics will form a set of guiding principles, not only for identifying molecules that exhibit charge migration, but also for developing the experimental means of measuring it. In the near future, halogen-functionalized conjugated molecules are an ideal framework for systematic charge migration studies, where bonding, length, and halogen functionalization can all be used to control CM to match experimental timescales and sensitivities.

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- [1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.* **307**, 205 (1999).
- [2] M. Vacher, M. J. Bearpark, and M. A. Robb, *J. Chem. Phys.* **140**, 201102 (2014).
- [3] F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva *et al.*, *Science* **346**, 336 (2014).
- [4] P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyanyan, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen *et al.*, *Science* **350**, 790 (2015).
- [5] N. V. Golubev and A. I. Kuleff, *Phys. Rev. A* **91**, 051401(R) (2015).
- [6] J. Breidbach and L. S. Cederbaum, *Phys. Rev. Lett.* **94**, 033901 (2005).
- [7] M. F. Kling and M. J. Vrakking, *Annu. Rev. Phys. Chem.* **59**, 463 (2008).
- [8] M. Lara-Astiaso, M. Galli, A. Trabattoni, A. Palacios, D. Ayuso, F. Frassetto, L. Poletto, S. De Camillis, J. Greenwood, P. Decleva, I. Tavernelli, F. Calegari, M. Nisoli, and F. Martín, *J. Phys. Chem. Lett.* **9**, 4570 (2018).
- [9] M. Nisoli, P. Decleva, F. Calegari, A. Palacios, and F. Martín, *Chem. Rev.* **117**, 10760 (2017).
- [10] F. Calegari, A. Trabattoni, A. Palacios, D. Ayuso, M. C. Castrovillani, J. B. Greenwood, P. Decleva, F. Martín, and M. Nisoli, *J. Phys. B* **49**, 142001 (2016).
- [11] H. J. Wörner, C. A. Arrell, N. Banerji, A. Cannizzo, M. Chergui, A. K. Das, P. Hamm, U. Keller, P. M. Kraus, E. Liberatore *et al.*, *Struct. Dyn.* **4**, 061508 (2017).
- [12] V. Despré, A. Marciniak, V. Lorient, M. Galbraith, A. Rouzée, M. Vrakking, F. Lépine, and A. Kuleff, *J. Phys. Chem. Lett.* **6**, 426 (2015).
- [13] F. Remacle and R. D. Levine, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 6793 (2006).
- [14] F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. B. Greenwood *et al.*, *IEEE J. Sel. Top. Quantum Electron.* **21**, 1 (2015).
- [15] A. D. Dutoi, M. Wormit, and L. S. Cederbaum, *J. Chem. Phys.* **134**, 024303 (2011).
- [16] H. Hennig, J. Breidbach, and L. S. Cederbaum, *J. Phys. Chem. A* **109**, 409 (2005).
- [17] S. Lünemann, A. I. Kuleff, and L. S. Cederbaum, *Chem. Phys. Lett.* **450**, 232 (2008).
- [18] A. Bruner, S. Hernandez, F. Mauger, P. M. Abanador, D. J. LaMaster, M. B. Gaarde, K. J. Schafer, and K. Lopata, *J. Phys. Chem. Lett.* **8**, 3991 (2017).
- [19] A. I. Kuleff, S. Lünemann, and L. S. Cederbaum, *Chem. Phys.* **414**, 100 (2013).
- [20] M. Lara-Astiaso, A. Palacios, P. Decleva, I. Tavernelli, and F. Martín, *Chem. Phys. Lett.* **683**, 357 (2017).
- [21] P. Hoerner and B. Schlegel, *J. Phys. Chem. A* **121**, 5940 (2017).
- [22] P. Hoerner and H. B. Schlegel, *J. Phys. Chem. C* **122**, 13751 (2018).
- [23] M. P. Sándor, A. Sissay, F. Mauger, M. W. Gordon, T. T. Gorman, T. D. Scarborough, M. B. Gaarde, K. Lopata, K. J. Schafer, and R. R. Jones, *J. Chem. Phys.* **151**, 194308 (2019).
- [24] F. Keller and H. Lefebvre-Brion, *Z. Phys. D* **4**, 15 (1986).
- [25] R. Boll, B. Erk, R. Coffee, S. Trippel, T. Kierspel, C. Bomme, J. D. Bozek, M. Burkett, S. Carron, K. R. Ferguson *et al.*, *Struct. Dyn.* **3**, 043207 (2016).
- [26] K. Schnorr, A. Senftleben, M. Kurka, A. Rudenko, G. Schmid, T. Pfeifer, K. Meyer, M. Kübel, M. F. Kling, Y. Jiang *et al.*, *Phys. Rev. Lett.* **113**, 073001 (2014).
- [27] H. Eshuis and T. V. Voorhis, *Phys. Chem. Chem. Phys.* **11**, 10293 (2009).
- [28] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- [29] K. Lopata and N. Govind, *J. Chem. Theory Comput.* **7**, 1344 (2011).
- [30] M. R. Provorse and C. M. Isborn, *Int. J. Quantum Chem.* **116**, 739 (2016).

- [31] J. J. Goings, P. J. Lestrangle, and X. Li, *Comput. Mol. Sci.* **8**, e1341 (2018).
- [32] N. A. Besley, A. T. B. Gilbert, and P. M. W. Gill, *J. Chem. Phys.* **130**, 124308 (2009).
- [33] Y. Liang, J. Vinson, S. Pemmaraju, W. S. Drisdell, E. L. Shirley, and D. Prendergast, *Phys. Rev. Lett.* **118**, 096402 (2017).
- [34] P. Ramos and M. Pavanello, *J. Chem. Phys.* **148**, 144103 (2018).
- [35] E. Apra, E. Bylaska, W. de Jong, N. Govind, K. Kowalski, T. Straatsma, M. Valiev, H. van Dam, Y. Alexeev, J. Anchell *et al.*, *J. Chem. Phys.* **152**, 184102 (2020).
- [36] J. I. Fuks, P. Elliott, A. Rubio, and N. T. Maitra, *J. Phys. Chem. Lett.* **4**, 735 (2013).
- [37] N. T. Maitra and D. G. Tempel, *J. Chem. Phys.* **125**, 184111 (2006).
- [38] K. Giesbertz and E. Baerends, *Chem. Phys. Lett.* **461**, 338 (2008).
- [39] M. R. Provorse, B. F. Habenicht, and C. M. Isborn, *J. Chem. Theory Comput.* **11**, 4791 (2015).
- [40] J. I. Fuks, K. Luo, E. D. Sandoval, and N. T. Maitra, *Phys. Rev. Lett.* **114**, 183002 (2015).
- [41] S. Raghunathan and M. Nest, *J. Chem. Theory Comput.* **8**, 806 (2012).
- [42] M. Vacher, M. J. Bearpark, and M. A. Robb, *J. Chem. Phys.* **140**, 201102 (2014).
- [43] K. Spinlove, M. Vacher, M. Bearpark, M. Robb, and G. Worth, *J. Chem. Phys.* **482**, 52 (2017).
- [44] V. Despre and A. Kuleff, *Theor. Chem. Acc.* **138**, 110 (2019).
- [45] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.126.133002> for more details.
- [46] W. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).
- [47] D. C. Yost, Y. Yao, and Y. Kanai, *J. Chem. Phys.* **150**, 194113 (2019).