THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Perspective

Cite This: J. Phys. Chem. Lett. 2020, 11, 229−237

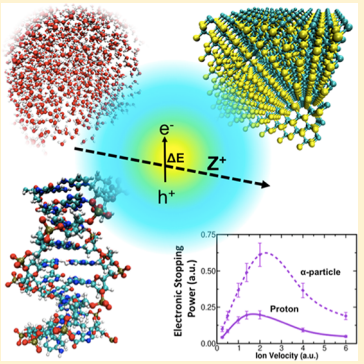
pubs.acs.org/JPCL

First-Principles Modeling of Electronic Stopping in Complex Matter under Ion Irradiation

Dillon C. Yost, Yi Yao, and Yosuke Kanai*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514-3290, United States

ABSTRACT: Electronic stopping refers to the dynamical energy-transfer process to electrons in matter from highly energetic charged particles such as high-velocity protons. We discuss recent progress in theoretical studies of electronic stopping in condensed matter under ion irradiation, focusing on modern electronic structure theory's role in enabling the study of electronic excitation dynamics that result from the energy transfer. In the last few decades, first-principles simulation approaches based on real-time time-dependent density functional theory have greatly advanced the field. While linear response theory is widely used to study electronic stopping processes, especially for simple solids, novel first-principles dynamics approaches now allow us to study chemically complex systems and also yield detailed descriptions of electronic excitations at the molecular scale. Outstanding challenges for further advancement of electronic stopping modeling are also discussed from the viewpoint of electronic structure theory.



When an irradiating ion penetrates matter, the projectile ion transfers its kinetic energy via collisions with the nuclei and electrons in the target matter. Understanding this stopping process of highly energetic ions is essential for the advancement of modern technologies ranging from nuclear fission/fusion reactors,[10] to semiconductor devices for space missions,[12] to cancer therapy based on ion beam radiation.[15] The kinetic energy of irradiating energetic ions is dissipated in the target matter in the stopping process, and the deposited energy becomes available for inducing further structural changes through various mechanisms. The rate of energy transfer from the projectile ion to the target matter is generally measured relative to a unit distance of the projectile ion movement, and this velocity-dependent energy-transfer rate is referred to as the stopping power. Conceptually, the stopping process is divided into two regimes, depending on the type of excitation produced (see Figure 1):[20] At low ion velocities, the dominant effect is called nuclear stopping, which primarily results in excitations of the lattice (i.e., nuclei) and atom displacements. At higher velocities (typically > keV), the relevant excitations are electronic, hence the term "electronic stopping." In electronic stopping, quantum-mechanical excitations of electrons are produced by the energy transfer from the projectile ion. From the viewpoint of electronic structure theory, electrons are excited in response to the highly heterogeneous time-varying electric field around the projectile ion, making it distinctively different from optical excitation.

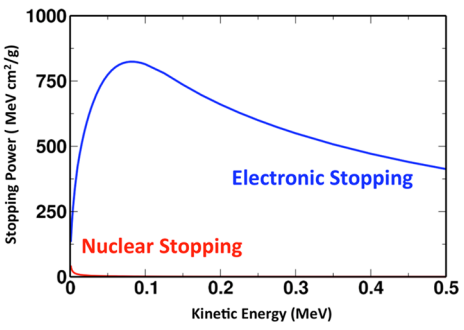


Figure 1. Electronic stopping power (Bethe theory) and experimental nuclear stopping power of liquid water for protons from NIST database.[1]

Ever since Curie proposed in 1900 that an α-ray is actually a particle that loses its energy in matter,[21] a number of theoretical formalisms have been developed for describing such a dynamical phenomenon, now referred to as electronic stopping.[13,22−29] Linear response theory is the most widely used formalism for calculating the electronic stopping power in a simple analytic form:[22,30]

$$S(v) = \frac{4\pi Z^2}{v^2} L(v) \tag{1}$$

where S is the electronic stopping power, v is the projectile ion velocity and $L(v)$ is a velocity-dependent quantity called the stopping logarithm. The stopping logarithm is usually given in terms of the mean excitation energy of the target matter as in the pioneering Bethe theory[13] or the dielectric function as in the seminal work by Lindhard who studied the homogeneous electron gas using the random phase approximation (RPA) in 1954.[27,28,31] These linear response theory approaches work surprisingly well despite their simplicity, especially for the high-velocity regime. In the last few decades, first-principles calculation of the dielectric function has become possible

Received: October 9, 2019
Accepted: December 12, 2019
Published: December 12, 2019

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

using electronic structure theory. Early work on calculating the microscopic dielectric matrix for solids relied on the RPA;[32,33] this amounts to neglecting the exchange−correlation (XC) kernel in the Dyson-like equation that relates the density response function to that of corresponding noninteracting electrons (i.e., Kohn−Sham system). Recent work by Shukri et al. demonstrated the electronic stopping power calculation by employing time-dependent density functional theory (TDDFT) with the adiabatic local density approximation to the XC kernel for calculating the dielectric matrix.[14] In contrast to computation of optical excitation spectra, obtained in the limit of vanishing momentum transfer (i.e., $q = 0$) in the dielectric matrix, more careful attention to convergence with respect to various computational parameters is necessary for the calculation of the full dielectric matrix.[34] Nevertheless, because of the advancement of electronic structure methodologies, the Lindhard formula can now be employed with ingredients from first-principles calculations, without relying on empirical or experimental inputs.

While linear response theory provides a convenient and relatively simple formulation for calculating electronic stopping power, experimental measurements show that such a description is not adequate in many cases.

While linear response theory provides a convenient and relatively simple formulation for calculating electronic stopping power, experimental measurements show that such a description is not adequate in many cases. The periodic oscillation of the stopping power with respect to the projectile ion charge (Z), so-called Z_1 oscillation, in experimental measurements is a notable example of how the expected $\propto Z^2$ behavior of the linear response theory is not obeyed.[35] Another notable failure is its inability to capture the so-called Barkas effect;[36,37] experimental measurements show that protons ($Z = +1$) and antiprotons ($Z = -1$) yield different stopping powers.[38] Several avenues have been pursued to improve the linear response theory description. In order to take into account drastic deviations like the Barkas effect, higher-order expansion terms in powers of Z need to be included. Recognizing that the projectile ion charge can be screened, some have advocated for the use of velocity-dependent charge state model, $Z(v)$,[39] as well as calculating fractions for different ion charge states as a function of the velocity.[40] These approaches have the advantage of retaining a relatively simple analytic expression of linear response theory and its perturbative expansion while possibly reproducing the experimentally observed behavior. Unfortunately, these additional corrections have made the approach more empirical and susceptible to the typical problem of adjusting many interdependent parameters.[41,42] Distinct from building mathematical models by extending the linear response theory, treating the electronic stopping from the viewpoint of scattering theory[43] is another appealing approach from a physics viewpoint. By considering the electronic stopping phenomenon as electron scattering by a projectile ion, the stopping power can be related to the transport cross section.[44] Calculating the transport cross section generally requires the scattering potential, and first-principles electronic structure theory such as density functional theory (DFT) has been used also in this context.[45,46] The atomic character of the projectile ion is fully described in the scattering approach,[47] and taking into account such details is important especially in the low-velocity regime. There are a number of reviews available on theoretical approaches to modeling electronic stopping.[44,48,49]

Recent advances in high-performance computers and electronic structure methodologies have made it possible to calculate the dielectric function and other parameters from first-principles, enabling the use of linear response theory models without empirical/experimental inputs. However, these approaches still rely on the approximated perturbative model framework, which limits its applicability as discussed above. With increasing computational power, it has also become possible to numerically simulate the quantum-mechanical dynamics involved in the electronic stopping process; specifically, the electron dynamics can be simulated to calculate the rate with which electrons gain energy quantum-

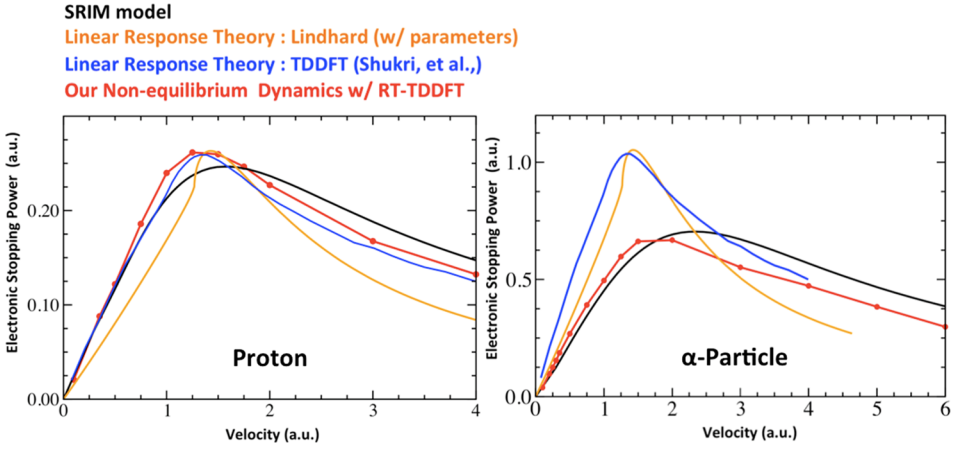


Figure 2. (Left) Electronic stopping power in bulk aluminum for protons, according to our RT-TDDFT result[2] (red), SRIM model[9] (black), linear response theory with Lindhard's dielectric function[2] (orange), and linear response theory with the dielectric matrix calculated using linear response TDDFT[14] (blue). (Right) Electronic stopping power in bulk aluminum for α-particles.The linear response theory: TDDFT result (blue) is obtained using the Z^2 dependence of the linear response theory because the dielectric matrix for the aluminum is the same as for the proton case.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

mechanically in the form of electronic excitations. The stopping power is defined as the amount of energy transferred, E, per unit distance of the projectile ion movement, R, moving at a constant velocity v (i.e., $S(v) = \mathrm{d}E/\mathrm{d}R$). Thus, the time-dependent response of electrons to the perturbing electric field of the projectile ion can be simulated to obtain this energy-transfer rate. For modeling the quantum dynamics of electrons on the atomistic scale, real-time TDDFT (RT-TDDFT) provides a particularly convenient approach. A number of reviews on RT-TDDFT methodologies are available,[50,51] and its discussion is omitted here for brevity. For calculating the stopping power, a set of electron dynamics simulations are performed with a range of projectile ion velocities of interest, and the electronic stopping power curve is obtained by using

$$S(v) = \left\langle \frac{\mathrm{d}E[\{\phi_i(t)\}]}{\mathrm{d}R} \right\rangle_v \tag{2}$$

where E is the electronic energy functional of the time-dependent electron density, given by the set of time-dependent Kohn−Sham (KS) single-particle orbitals, $\phi_i(\mathbf{r}, t)$. In non-equilibrium simulations where the projectile ion velocity is held constant, the increase in the DFT-KS energy corresponds to the work done by the projectile ion on electrons when the so-called adiabatic approximation[52] is adapted to the XC effect.[53] The energy change with respect to the projectile ion displacement is calculated after a steady state is reached in the simulations and is averaged over the projectile ion positions and paths as denoted by the classical ensemble bracket (eq 2). For brevity here, readers are referred to refs 2 and 54 for computational details of performing these simulations. The computationally intensive part is the time propagation of complex KS single-particle orbitals via the time-dependent KS (TD-KS) equations. The TD-KS equations take the form of a nonlinear Schrödinger equation, and numerical integration of such nonlinear partial differential equations remains an active area of research in general.[53,55] It is worthwhile to note that the use of planewaves as the basis functions is particularly convenient for describing the dynamics of high-energy electronic excitations involved in electronic stopping.[2]

Figure 2 shows the results of the RT-TDDFT approach on a prototypical system of crystalline aluminum for the electronic stopping of protons and α-particles (He^{2+} ion) in comparison to other approaches. The stopping and range of ions in matter (SRIM) model is based on the so-called Lindhard−Scharff−Schiott theory[9] with experimental inputs, and it is widely used as a standard reference, especially for solids. As can be seen, the RT-TDDFT result agrees very well with the standard SRIM model data for the protons, and the agreement is quite good also for the α-particle stopping, especially considering the experimental uncertainties that go into the SRIM model. Importantly, the RT-TDDFT approach yields a reliable α-particle stopping power curve, which is a particularly challenging case for the linear response theory. In addition to calculating the stopping power from these simulations, RT-TDDFT gives access to a wealth of information on how the electronic structure changes in response to the projectile ion, allowing us to obtain scientific insights on the atomistic scale. Today, the quantum dynamics of electrons in large complex systems with tens of thousands of electrons can be simulated using RT-TDDFT, as we highlight from our recent studies in the following sections. Early RT-TDDFT studies of electronic stopping focused mainly on bulk metals.[2,56,57] Metals have been widely studied using the Lindhard model, and the uniform gas description for the dielectric function works quite well. Also conveniently, the simplest local density approximation is satisfactory for describing the XC effect to examine the RT-TDDFT approach for modeling electronic stopping. In more recent years, there are increasing efforts on semiconductor materials.[58−60] Because of a number of reliable experimental measurements, crystalline silicon has been studied as a prototypical semiconductor solid to examine the RT-TDDFT approach in detail, analyzing the effects of various computational parameters such as the Brillouin zone integration, the periodically repeated simulation cell size, the basis set size, and the time integration step size, as well as the influence of the XC approximation.[54] Interestingly, excitation of semicore electrons was found to be crucial for accurately modeling the electronic stopping power in the high-velocity regime. Only when semicore electron excitations are taken into account through a correction was the electronic stopping power found to agree well with the experimental measurements in the high velocity regime. The work called for further technical development of the planewave-pseudopotential (PW-PP) formalism for RT-TDDFT simulations,[53] and some key challenges have since been overcome for describing core−electron excitations in the context of modeling electronic stopping processes.[3]

Electronic stopping in water and DNA has become a topic of great interest because of the central roles these biological materials play in radiation-induced cell death.

We illustrate here how the RT-TDDFT approach has allowed us to study electronic stopping phenomena in contexts of great societal importance. Understanding electronic stopping processes is central to various modern technologies and medicine today, especially with ion-beam radiation oncology being a burgeoning area that could benefit greatly from physics-based understanding. Specifically, electronic stopping in water and DNA has become a topic of great interest because of the central roles these biological materials play in radiation-induced cell death. Electronic stopping in water and DNA has become a topic of great interest because of the central roles these biological materials play in radiation-induced cell death.Fast-moving ions like protons, α-particles, and carbon ions have shown clinical promise in radiation oncology because of their distinctive energy dose−depth distributions.[61,62] The depth-dependent energy deposition profile of ions is largely determined by the electronic stopping power curve.[63,64] Unlike high-energy photons such as X/γ-rays, irradiating ions deposit the vast majority of their kinetic energy at the end of their penetration range and do not give rise to any exit dose[65,66] because of the well-defined peak in the stopping power curve. This allows for more precise targeting of tumor sites and increased preservation of surrounding healthy tissue.[67] With water being the primary component of tissue, various empirical models have been developed for its electronic stopping power.[11,17−19,68−72] However, only limited experimental measurements are available near the stopping power maximum[5,6] for comparison.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

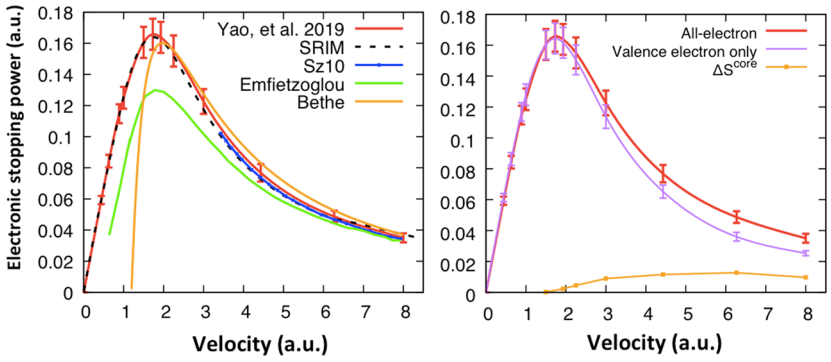


Figure 3. (Left) Electronic stopping power of liquid water for protons, from our first-principles simulation (Yao et al. 2019)[3], in comparison to the experimental data by Shimizu et al.[5,6] (Sz10), SRIM[11] model, the Bethe model[13] with I = 78 eV recommended by International Commission on Radiation Units and Measurement,[16] and Emfietzoglou's model.[17−19] (Right) The contribution from the K-shell core electronic excitations is obtained from the difference between the calculations with and without the core electrons.

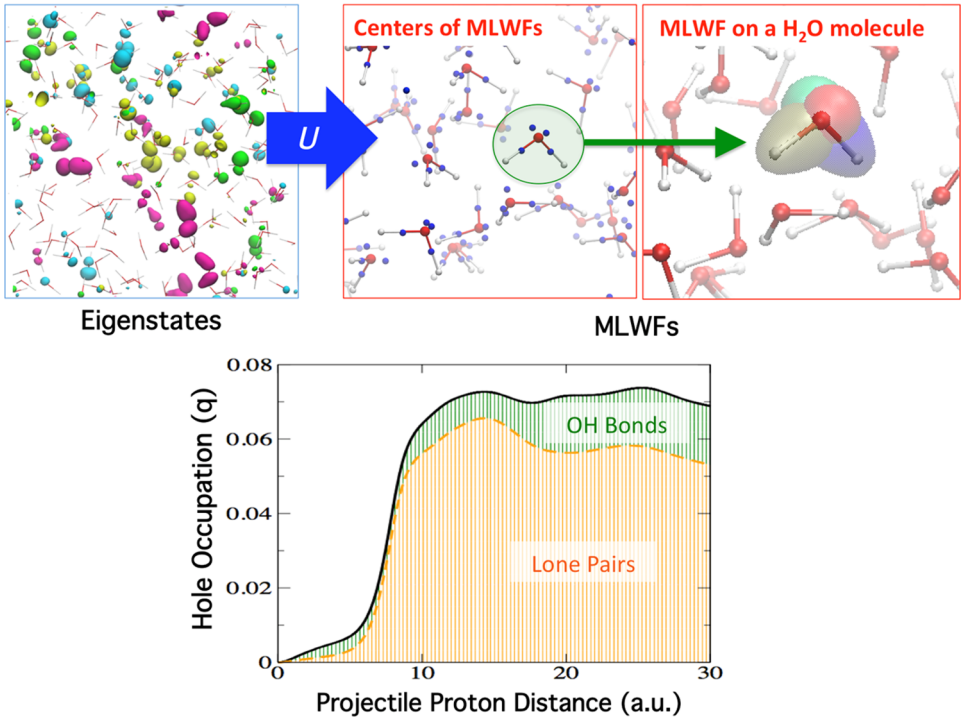


Figure 4. (Top) Maximally localized Wannier functions (MLWFs). The geometric centers of the MLWFs are shown for liquid water, and the four MLWFs localized on individual H_2O molecules are shown for one of the molecules. (Bottom) Using these MLWFs that correspond to the OH bonds and lone pair electrons, contributions to the hole generation from these chemical moieties are obtained as a function of the projectile proton movement.[8]

In addition to determining the stopping power of water, deciphering the molecular-level mechanisms of how the energy deposition leads to DNA damage is a pressing scientific challenge in ion-beam cancer therapy. Generally, DNA radiation damage is discussed in the context of direct and indirect effects. Direct effects comprise processes in which the DNA molecule itself is directly excited and/or ionized by the radiation, leading to critical sugar−phosphate side-chain damage such as a double-strand break (DSB).[73,74] Here, a molecular-level understanding of the electronic stopping process on DNA is essential. On the other hand, indirect effects comprise events in which the radiation induces secondary electron generation and/or creation of reactive species (e.g., water radiolysis products like OH radicals), which can then proceed to chemically react with the DNA molecule, inducing damage.[75,76] The common view is that DSBs and/or clustering of DSBs play a key role in cell death.[73,74] Despite the progress being made in deciphering DNA damage mechanisms, substantial debate remains, even for X/γ-ray photon radiation.[77,78] Our understanding in the case of ion radiation is considerably limited at the present time. In proton beam therapy, a simple empirical correction, called relative biological effectiveness, is widely used to take into account the differences between the proton radiation and X-ray photon radiation, but many now call for a better mechanistic understanding of the radiations in terms of the electronic excitation at the molecular level.[79]

Water. In order to accurately determine the electronic stopping power in water for protons, our recent work found that the excitation of oxygen atom's core electrons (K-shell) is

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

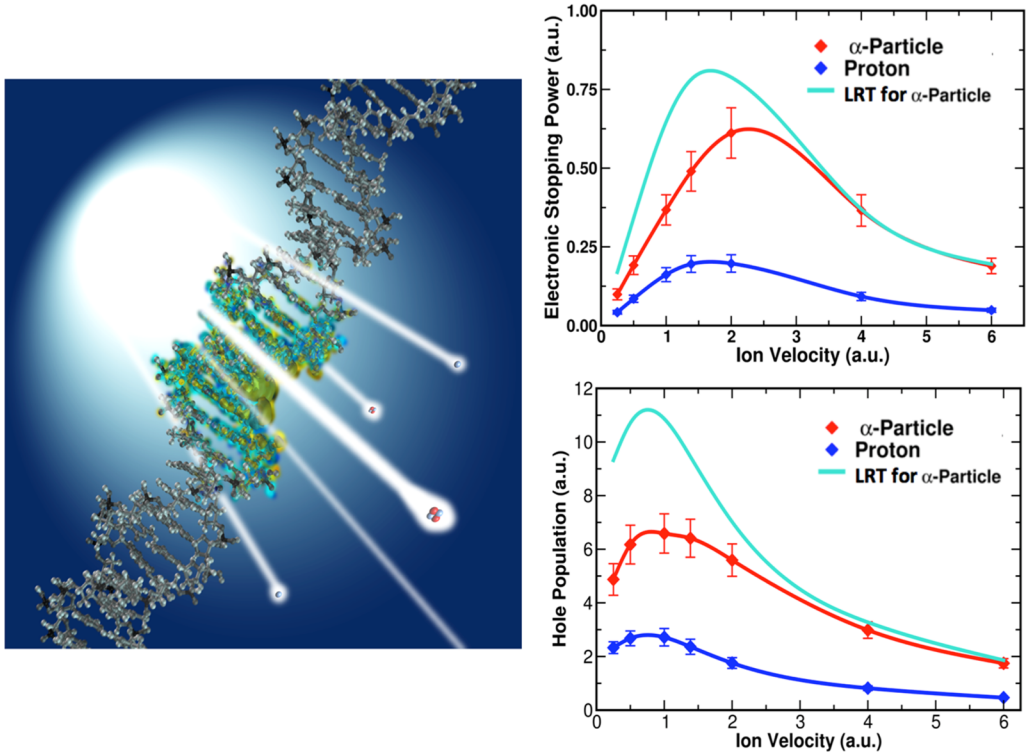


Figure 5. (Left) Illustration of DNA under proton and α-particle irradiation. Electronic stopping power (top-right) and hole population (lower-right) for protons and α-particles.[4] The linear-response theory (LRT) result for α-particles based on the proton curve is also shown.

crucial,[3] being responsible for as much as one-third of the stopping power at the large proton velocity of 8.0 au (1.6 MeV) as shown in Figure 3. Also, the core−electron excitation influences the valence electron excitation significantly and provides an additional channel for the energy transfer. This behavior is similar to the "shake-up" effect often discussed in the context of X-ray absorption.[80] By projecting the TD-KS wave functions onto the KS eigenstates, the generation of electron−hole pairs can be quantified by calculating the occupation number changes for the eigenstates. The simulation showed that the generated holes remain highly localized within a few angstroms around the irradiating proton paths while the electrons are excited away, showing the ionizing radiation behavior. In spite of their significant contribution to the stopping power, the K-shell core electrons play a rather minor role in terms of the excitation density (i.e., electron−hole pairs); only one percent of the excited electrons originate from the K-shell even at the large velocity of 8.0 au. Although both X/γ-ray and proton radiations are often considered as ionizing radiation and are usually treated on the same footing,[79] our work revealed that the nature of excitation and ionization behaviors involved is distinctly different.[3]

The atomistic RT-TDDFT simulations also contain a wealth of information from which chemical insights can be derived. For example, the TD-KS wave functions can be projected onto the maximally localized Wannier functions (MLWFs) which are localized on familiar chemical moieties such as bonds and lone pairs. The MLWFs form a set of single-particle orbitals that are maximally localized in space, and it is obtained from the unitary transform of the KS eigenstates. In liquid water, for instance, four MLWFs can be identified on an individual water molecule: two of them for the OH bonds and the other two for the lone pair electrons on the oxygen atom, as seen in Figure 4. By projecting the TD-KS wave functions onto the MLWFs that are localized on individual molecules, we can quantify where and how the electrons are excited from in terms of the chemical moieties.[8] The simulation showed, for example, that the excitation under proton irradiation derives mostly from the oxygen lone pair electrons rather than from the OH bond electrons (Figure 4), diminishing the possibility of OH bonds directly dissociated in the initial excitation process. Modeling of liquid water remains an active area of physical chemistry research,[81−84] and the MLWF analysis also gives atomistic insights into important structural properties in modeling electronic stopping.

DNA. Many spectroscopic measurements of photon-induced and ion-induced DNA damage are performed on *dry* (not in solution) DNA for convenience.[85] Our recent work also on a strand of dry DNA in vacuum revealed some remarkable features in the excitation behavior under proton/α-particle irradiation. As perhaps expected, the electronic excitations are mostly ionizations, and more than 90% of the excited electrons are promoted above the vacuum level.[4] At the same time, holes are generated mostly in the high-lying valence states near the highest occupied molecular orbital (HOMO), predominantly within the energy range of ~10 eV. The simulation also showed that the excited hole generation is highly localized along the projectile/irradiating ion path at all velocities, and its spatial distribution does not show significant selectivity with regard to the local chemical composition of the DNA (i.e., nucleobase types, side chain, etc.). The electronic excitation quickly decays away from the ion track within a nanometer, as is consistent with the DNA damage behavior found in the experimental work by Souici et al.[86] Between the two, the α-particle case shows somewhat stronger localization of the hole generation along the ion track than the proton case. An intriguing experimental observation was that the maximum DNA damage response was measured for a proton velocity that

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

is higher than the velocity that corresponds to the stopping power maximum.[86] One might have hypothesized that excited hole generation (ionization) is maximized also at this higher proton velocity. However, our simulations show that the hole generation is maximized at a velocity that is lower than the maximal stopping power velocity for both protons and α-particles (Figure 5). These first-principles simulations of electronic stopping processes are anticipated to play an important role in deciphering the complicated damage mechanisms of DNA under ion irradiation. Simulating DNA under physiological conditions is a next key challenge, with many current experiments and simulations being performed under this isolated "dry" condition. Our development of a massively parallel RT-TDDFT method[57] enables scientific investigation into such complex situations. Figure 6, for instance, shows how such a large simulation is possible for studying the effect of water solvation on the electronic stopping in DNA. These simulations can be extremely large and complicated with approximately 13 000 electrons (DNA and over 1000 water molecules) and over six million plane-waves as the basis functions, and the combination of modern high-performance computers (HPCs) and massively parallel electronic structure method development now allows us to perform simulations of these increasingly more realistic and complex environments.

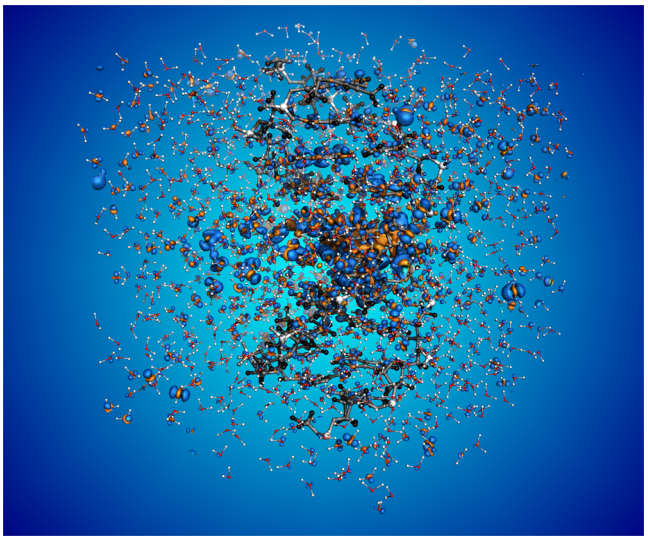


Figure 6. Snapshot from RT-TDDFT nonequilibrium electron dynamics simulation of solvated DNA under proton irradiation. Blue and orange show the electron density increase and decrease with respect to the equilibrium electron density. The simulation consists of approximately 13 000 electrons with the periodic boundary condition.

Over the past decade, first-principles modeling of electronic stopping processes has greatly advanced, thanks to the development of RT-TDDFT simulation methods and modern HPCs. Building on more than a century of work on theory and modeling of electronic stopping phenomena, mainly in the realm of condensed matter physics, new computational advances now enable us to study increasingly complex chemical systems like DNA solvated in water. In addition to utilizing our newly gained scientific knowledge for addressing problems in medicine and engineering, we emphasize the importance of continued computational method development as an enabler of modern theoretical science in the context of

Building on more than a century of work on theory and modeling of electronic stopping phenomena, mainly in the realm of condensed matter physics, new computational advances now enable us to study increasingly complex chemical systems like DNA solvated in water.

studying electronic stopping. Achieving better accuracy and efficiency continues to be a key avenue in computational chemistry and physics, and developing novel approaches is also necessary for distilling scientific insights from increasingly complex simulations. One such effort that we are pursuing is the propagation of MLWFs in RT-TDDFT.[7] Within RT-TDDFT simulations, the gauge freedom of the time-dependent electronic orbitals can be exploited for numerical and scientific convenience while the unitary transformation does not alter physical properties calculated from the quantum dynamics of electrons. MLWFs are spatially localized on chemical moieties, and performing quantum dynamics simulations in this MLWF gauge allows us to analyze electronic stopping of complex systems like water-solvated DNA in terms of chemically distinguishable parts. By propagating the MLWFs in time, we can obtain the frequency-dependent conductivity, for example, in electronic stopping as can be done for the optical excitation. Figure 7 demonstrates such an idea for a simple case of a benzene molecule. Comparing this "electronic stopping spectrum" to the optical spectrum, we observe that at low proton velocities (v = 0.625 au and v = 1.25 au), the electronic stopping excitations are similar to the electronic excitation represented by the sharp peak at ∼7 eV in the optical excitation, mostly characterized by HOMO → LUMO transition. With increasing proton velocity, however, there is a trend toward a broadband spectrum, with high-frequency components contributing more.[7]

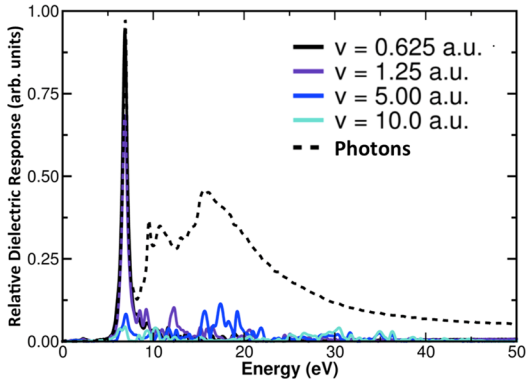


Figure 7. Dielectric response spectra for a benzene molecule with a proton projectile with different velocities, v, in comparison to the optical excitation spectrum (i.e., under photoirradiation).[7]

In addition to gaining scientific insights from increasingly complicated simulations, another important computational method development challenge is modeling high-Z projectile ion cases, beyond "light" ions like protons and α-particles.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

Electronic stopping process with high-Z ions is of great interest, for example, for modeling of nuclear reactor/fuel materials.[87] In addition to charged particles like α-particles and high-energy electrons (i.e., β-particles) as byproducts of nuclear reactions, lattice atoms/ions can be displaced in reactor/fuel materials via the elastic collision with fast neutrons. The resulting energetic ions, often of high-Z, can lead to electronic stopping within the materials and beyond. Additionally, other highly energetic high-Z ions can be potentially present as the nuclear transmutation products. For high-Z ion projectiles, the electronic energy dissipation within the projectile ion in addition to the charge-transfer dynamics between the projectile ion and target matter complicates the physics involved.[88] On the technical side, accurate modeling of core electrons also continues to be a great challenge in the RT-TDDFT framework, especially for the PW-PP formalism,[53] while some recent progress has been made.[3,54] On the side of more fundamental theoretic challenges, the infamous issue of the XC approximation needs to be mentioned. Standard XC approximations such as the generalized gradient approximation (GGA)[89] appear satisfactory for modeling electronic stopping phenomena in systems like crystalline silicon[54] and liquid water,[3,90] and increasing availability of more advanced XC functionals (e.g., meta-GGA and hybrid-GGA approximations) for efficient RT-TDDFT simulations is encouraging. However, a more difficult challenge is presented for the adiabatic approximation in the context specific to TDDFT, in which the history dependence of XC functional is neglected (i.e., the XC functional has no "memory"). Within this adiabatic approximation, the XC potential depends only on the instantaneous electron density, or equivalently on the instantaneous time-dependent KS orbitals.[91,92] Nazarov et al. examined the adiabatic approximation in the context of electronic stopping for homogeneous electron gas through the dynamical XC kernel in TDDFT.[93] Their work showed the adiabatic approximation becomes increasingly erroneous for higher-Z projectile ions. Extending TDDFT beyond this adiabatic approximation remains as an active area of modern DFT research.[94−96] For calculating the stopping power, the adiabatic approximation to the XC effect is inherently assumed in the RT-TDDFT approach described above. By deriving the time-dependent change of the DFT-KS electronic energy,[53] the energy change can be shown to be equivalent to the work done by the projectile ion on the electronic system of the target matter if the adiabatic approximation is adapted. As discussed by Ullrich in the context of TD-current DFT,[92] deriving an analytical expression that ensures a constant total energy can be quite complicated when the adiabatic approximation is not used. One might consider obtaining an alternative stopping power expression by deriving the nonadiabatic force from the semiclassical action for the electrons−nuclei system that includes the nonadiabatic XC effect.[97]

Despite many existing challenges, electronic structure theory has greatly advanced in the last several decades, and the study of electronic stopping has benefitted tremendously from the advancement. Modern electronic structure theory has prompted a recent paradigm shift away from the traditional linear response theory like the Bethe model and Lindhard formula, and an increasing number of researchers are adapting a new dynamical approach in which the quantum dynamics of electrons are simulated using first-principles electronic structure theory like RT-TDDFT. The first-principles approach has allowed us to extend the investigation beyond simple solid-state systems like metals and semiconductor solids, and we are now able to investigate electronic stopping in chemically complex systems like solvated DNA, semiconductors with defects,[98] and nanomaterials with complex surface structures.[99]

AUTHOR INFORMATION

ORCID

Dillon C. Yost: 0000-0003-0854-1218

Yi Yao: 0000-0002-9957-6979

Yosuke Kanai: 0000-0002-2320-4394

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grants No. CHE-1565714 and No. OAC-1740204. An award of computer time was provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. This research used resources of the Argonne Leadership Computing Facility, which is a U.S. DOE Office of Science User Facility supported under Contract No. DE-AC02−06CH11357.

REFERENCES

(1) Berger, M. J.; Coursey, J. S.; Zucker, M. A.; Chang, J. *Stopping-Power and Range Tables for Electrons, Protons, and Helium Ions, NISTIR 4999*; National Institute of Standards and Technology: Gaithersburg, MD, 2019.

(2) Schleife, A.; Kanai, Y.; Correa, A. A. Accurate atomistic first-principles calculations of electronic stopping. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 014306.

(3) Yao, Y.; Yost, D. C.; Kanai, Y. *K*-Shell Core-Electron Excitations in Electronic Stopping of Protons in Water from First Principles. *Phys. Rev. Lett.* **2019**, *123*, 066401.

(4) Yost, D. C.; Kanai, Y. Electronic Excitation Dynamics in DNA under Proton and α-Particle Irradiation. *J. Am. Chem. Soc.* **2019**, *141*, 5241−5251.

(5) Shimizu, M.; Hayakawa, T.; Kaneda, M.; Tsuchida, H.; Itoh, A. Stopping cross-sections of liquid water for 0.3−2.0 MeV protons. *Vacuum* **2010**, *84*, 1002−1004.

(6) Shimizu, M.; Kaneda, M.; Hayakawa, T.; Tsuchida, H.; Itoh, A. Stopping cross sections of liquid water for MeV energy protons. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2009**, *267*, 2667−2670.

(7) Yost, D. C.; Yao, Y.; Kanai, Y. Propagation of maximally localized Wannier functions in real-time TDDFT. *J. Chem. Phys.* **2019**, *150*, 194113.

(8) Reeves, K. G.; Kanai, Y. Electronic Excitation Dynamics in Liquid Water under Proton Irradiation. *Sci. Rep.* **2017**, *7*, 40379.

(9) Lindhard, J.; Nielsen, V.; Scharff, M.; Thomsen, P. Integral equations governing radiation effects. *Mater. Fys. Medd. Dan. Vid. Selsk* **1963**, *33* (10), 1−42.

(10) Odette, G. R.; Wirth, B. D. Radiation effects in fission and fusion reactors. In *Handbook of materials Modeling*; Springer, 2005; pp 999−1037.

(11) Ziegler, J. F.; Ziegler, M. D.; Biersack, J. P. SRIM − The stopping and range of ions in matter (2010). *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1818−1823.

(12) Zeller, H. Cosmic ray induced failures in high power semiconductor devices. *Microelectron. Reliab.* **1997**, *37*, 1711−1718.

(13) Bethe, H. Zur theorie des durchgangs schneller korpuskular-strahlen durch materie. *Ann. Phys.* **1930**, *397*, 325−400.

(14) Shukri, A. A.; Bruneval, F.; Reining, L. *Ab initio* electronic stopping power of protons in bulk materials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 035128.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

(15) Obolensky, O.; Surdutovich, E.; Pshenichnov, I.; Mishustin, I.; Solov'Yov, A.; Greiner, W. Ion beam cancer therapy: Fundamental aspects of the problem. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2008**, *266*, 1623−1628.
(16) Recommended values for key data. *J. ICRU* **2014**, *14*, 31−48.
(17) Emfietzoglou, D.; Cucinotta, F. A.; Nikjoo, H. A Complete Dielectric Response Model for Liquid Water: A Solution of the Bethe Ridge Problem. *Radiat. Res.* **2005**, *164*, 202−211.
(18) Emfietzoglou, D.; Garcia-Molina, R.; Kyriakou, I.; Abril, I.; Nikjoo, H. A dielectric response study of the electronic stopping power of liquid water for energetic protons and a new I-value for water. *Phys. Med. Biol.* **2009**, *54*, 3451.
(19) Emfietzoglou, D.; Nikjoo, H.; Pathak, A. Electronic cross sections for proton transport in liquid water based on optical-data models. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *249*, 26−28.
(20) Sigmund, P. Stopping of slow ions. *Bull. Russ. Acad. Sci.: Phys.* **2008**, *72*, 569−578.
(21) Sklodowska-Curie, M. Sur la pénétration des rayons de Becquerel non déviables par le champ magnétique. *Compt. Rend. Acad. Sci.* **1900**, *130*, 76−79.
(22) Kamaratos, E. The mean excitation energy for stopping power I, the Bragg rule, and chemical and phase effects. Application of a statistical treatment to the determination of I for chemically bound particles. *Chem. Rev.* **1984**, *84*, 561−576.
(23) Rutherford, E. LXXIX. The scattering of α and β particles by matter and the structure of the atom. *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1911**, *21*, 669−688.
(24) Thomson, J. J. XLII. Ionization by moving electrified particles. *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1912**, *23*, 449−457.
(25) Darwin, C. G. XC. A theory of the absorption and scattering of the α rays. *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1912**, *23*, 901−920.
(26) Fermi, E.; Teller, E. The capture of negative mesotrons in matter. *Phys. Rev.* **1947**, *72*, 399.
(27) Lindhard, J.; Scharff, M.; Schiøtt, H. E. *Range Concepts and Heavy Ion Ranges*; Munksgaard, 1963.
(28) Lindhard, J.; Winther, A. *Stopping Power of Electron Gas and Equipartition Rule*; Munksgaard, 1964.
(29) Nagy, I.; Aldazabal, I.; Glasser, M. The helium atom in metallic electron gases: a comparative study based on screened Schrödinger Hamiltonians. *J. Phys. B: At., Mol. Opt. Phys.* **2012**, *45*, 095701.
(30) Cabrera-Trujillo, R.; Sabin, J. R. The Theory and Computation of Energy Deposition Properties. *Adv. Quantum Chem.* **2004**, *45*, 1−6.
(31) Lindhard, J. On the properties of a gas of charged particles. *Danske Matematisk-fysiske Meddeleiser* **1954**, *28*, 1−57.
(32) Campillo, I.; Pitarke, J. M.; Eguiluz, A. G. Electronic stopping power of aluminum crystal. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *58*, 10307−10314.
(33) Mathar, R. J.; Sabin, J. R.; Trickey, S. B. Electronic stopping of protons for lithium in the dielectric formulation obtained from first-principles calculations. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *155*, 249−271.
(34) Shukri, A. A.; Al-Qawasmeh, A.; Al Shorman, M. M.; Alsaad, A. Computational investigation of the valid valence states contribution in calculating the electronic stopping power of proton in bulk Al within the linear response approach. *Can. J. Phys.* **2019**. DOI: 10.1139/cjp-2019-0090
(35) Ormrod, J. H.; Duckworth, H. E. Stopping Cross Sections in Carbon for Low-Energy Atoms with $z < 12$. *Can. J. Phys.* **1963**, *41*, 1424−1442.
(36) Barkas, W. H.; Birnbaum, W.; Smith, F. M. Mass-Ratio Method Applied to the Measurement of *L*-Meson Masses and the Energy Balance in Pion Decay. *Phys. Rev.* **1956**, *101*, 778−795.
(37) Barkas, W. H. Masses of the Metastable Particles. *Annu. Rev. Nucl. Sci.* **1965**, *15*, 67−88.
(38) Møller, S. P.; Csete, A.; Ichioka, T.; Knudsen, H.; Uggerhøj, U. I.; Andersen, H. H. Stopping Power in Insulators and Metals without Charge Exchange. *Phys. Rev. Lett.* **2004**, *93*, 042502.
(39) Schiwietz, G.; Grande, P. Improved charge-state formulas. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *175*, 125−131.
(40) Arnau, A.; Pealba, M.; Echenique, P. M.; Flores, F.; Ritchie, R. H. Stopping power for helium in aluminum. *Phys. Rev. Lett.* **1990**, *65*, 1024−1027.
(41) Porter, L. E. Further observations of projectile-z dependence in target parameters of modified Bethe-Bloch theory. *Int. J. Quantum Chem.* **2003**, *95*, 504−511.
(42) Cabrera-Trujillo, R.; Sabin, J. R.; Oddershede, J. Explanation of the observed trend in the mean excitation energy of a target as determined using several projectiles. *Phys. Rev. A: At., Mol., Opt. Phys.* **2003**, *68*, 042902.
(43) Ferrell, T. L.; Ritchie, R. H. Energy losses by slow ions and atoms to electronic excitation in solids. *Phys. Rev. B* **1977**, *16*, 115−123.
(44) Sigmund, P. *Particle Penetration and Radiation Effects*; Springer, 2006.
(45) Echenique, P. M.; Nieminen, R. M.; Ritchie, R. H. Density functional calculation of stopping power of an electron gas for slow ions. *Solid State Commun.* **1981**, *37*, 779−781.
(46) Zaremba, E.; Arnau, A.; Echenique, P. M. Nonlinear screening and stopping powers at finite projectile velocities. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1995**, *96*, 619−625.
(47) Juaristi, J. I.; Arnau, A.; Echenique, P. M.; Auth, C.; Winter, H. Charge State Dependence of the Energy Loss of Slow Ions in Metals. *Phys. Rev. Lett.* **1999**, *82*, 1048−1051.
(48) Race, C.; Mason, D.; Finnis, M.; Foulkes, W.; Horsfield, A.; Sutton, A. The treatment of electronic excitations in atomistic models of radiation damage in metals. *Rep. Prog. Phys.* **2010**, *73*, 116501.
(49) Echenique, P.; Flores, F.; Ritchie, R. Dynamic screening of ions in condensed matter. *Solid State Phys.* **1990**, *43*, 229−308.
(50) Provorse, M. R.; Isborn, C. M. Electron dynamics with real-time time-dependent density functional theory. *Int. J. Quantum Chem.* **2016**, *116*, 739−749.
(51) Goings, J. J.; Lestrange, P. J.; Li, X. Real-time time-dependent electronic structure theory. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2018**, *8*, No. e1341.
(52) Ullrich, C. A. *Time-Dependent Density-Functional Theory, Concepts and Applications*; Oxford Graduate Texts: 2011.
(53) Schleife, A.; Draeger, E. W.; Kanai, Y.; Correa, A. A. Plane-wave pseudopotential implementation of explicit integrators for time-dependent Kohn-Sham equations in large-scale simulations. *J. Chem. Phys.* **2012**, *137*, 22A546.
(54) Yost, D. C.; Yao, Y.; Kanai, Y. Examining real-time time-dependent density functional theory nonequilibrium simulations for the calculation of electronic stopping power. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 115134.
(55) Gómez Pueyo, A.; Marques, M. A. L.; Rubio, A.; Castro, A. Propagators for the Time-Dependent Kohn−Sham Equations: Multistep, Runge−Kutta, Exponential Runge−Kutta, and Commutator Free Magnus Methods. *J. Chem. Theory Comput.* **2018**, *14*, 3040−3052.
(56) Correa, A. A.; Kohanoff, J.; Artacho, E.; Sánchez-Portal, D.; Caro, A. Nonadiabatic Forces in Ion-Solid Interactions: The Initial Stages of Radiation Damage. *Phys. Rev. Lett.* **2012**, *108*, 213201.
(57) Schleife, A.; Draeger, E. W.; Anisimov, V.; Correa, A. A.; Kanai, Y. Quantum Dynamics Simulation of Electrons in Materials on High-Performance Computers. *Comput. Sci. Eng.* **2014**, *16*, 54.
(58) Lee, C.-W.; Schleife, A. Electronic stopping and proton dynamics in InP, GaP, and In0.5Ga0.5P from first principles. *Eur. Phys. J. B* **2018**, *91*, 222.
(59) Yost, D. C.; Kanai, Y. Electronic stopping for protons and α particles from first-principles electron dynamics: The case of silicon carbide. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94*, 115107.
(60) Ullah, R.; Corsetti, F.; Sánchez-Portal, D.; Artacho, E. Electronic stopping power in a narrow band gap semiconductor from first principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 125203.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237

(61) Durante, M.; Loeffler, J. S. Charged particles in radiation oncology. *Nat. Rev. Clin. Oncol.* **2010**, *7*, 37.
(62) Baskar, R.; Lee, K. A.; Yeo, R.; Yeoh, K.-W. Cancer and Radiation Therapy: Current Advances and Future Directions. *Int. J. Med. Sci.* **2012**, *9*, 193−199.
(63) Report 16. *Journal of the International Commission on Radiation Units and Measurements*. 2016; Vol. *os9*.
(64) Besemer, A.; Paganetti, H.; Bednarz, B. The clinical impact of uncertainties in the mean excitation energy of human tissues during proton therapy. *Phys. Med. Biol.* **2013**, *58*, 887.
(65) Newhauser, W. D.; Zhang, R. The physics of proton therapy. *Phys. Med. Biol.* **2015**, *60*, R155.
(66) Stathakis, S. The Physics of Radiation Therapy. *Med. Phys.* **2010**, *37*, 1374−1375.
(67) Paganetti, H. Proton therapy physics. In *Proton Therapy Physics*, 2 ed.; Webster, J. G., Ritenour, E. R., Tabakov, S., Ng, K.-H., Eds.; CRC Press, 2018; pp 9−26.
(68) Report 90. *Journal of the International Commission on Radiation Units and Measurements*. 2014; Vol. *14*.
(69) Ashley, J. C. Optical-data model for the stopping power of condensed matter for protons and antiprotons. *J. Phys.: Condens. Matter* **1991**, *3*, 2741.
(70) Garcia-Molina, R.; Abril, I.; de Vera, P.; Kyriakou, I.; Emfietzoglou, D. A study of the energy deposition profile of proton beams in materials of hadron therapeutic interest. *Appl. Radiat. Isot.* **2014**, *83*, 109−114.
(71) Penn, D. R. Electron mean-free-path calculations using a model dielectric function. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *35*, 482−486.
(72) Ritchie, R. H. Energy losses by swift charged particles in the bulk and at the surface of condensed matter. *Nucl. Instrum. Methods Phys. Res.* **1982**, *198*, 81−91.
(73) Sevilla, M. D.; Bernhard, W. A. Mechanisms of direct radiation damage to DNA. In *Radiation Chemistry: From Basics to Applications in Material and Life Science*; Spotheim-Maurizot, M., Mostafavi, M., Douki, T., Belloni, J., Eds.; EDP Sciences: Les Ulis, 2008; pp 191−201.
(74) Uehara, S.; Nikjoo, H.; Goodhead, D. T. Comparison and assessment of electron cross sections for Monte Carlo track structure codes. *Radiat. Res.* **1999**, *152*, 202−213.
(75) Wishart, J. F.; Rao, B. M. *Recent trends in radiation chemistry*; World Scientific, 2010.
(76) O'Neill, P.; Wardman, P. Radiation chemistry comes before radiation biology. *Int. J. Radiat. Biol.* **2009**, *85*, 9−25.
(77) Nguyen, J.; Ma, Y.; Luo, T.; Bristow, R. G.; Jaffray, D. A.; Lu, Q.-B. Direct observation of ultrafast-electron-transfer reactions unravels high effectiveness of reductive DNA damage. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 11778−11783.
(78) Baccarelli, I.; Bald, I.; Gianturco, F. A.; Illenberger, E.; Kopyra, J. Electron-induced damage of DNA and its components: Experiments and theoretical models. *Phys. Rep.* **2011**, *508*, 1−44.
(79) Durante, M.; Orecchia, R.; Loeffler, J. S. Charged-particle therapy in cancer: clinical uses and future perspectives. *Nat. Rev. Clin. Oncol.* **2017**, *14*, 483.
(80) Persson, P.; Lunell, S.; Szöke, A.; Ziaja, B.; Hajdu, J. Shake-up and shake-off excitations with associated electron losses in X-ray studies of proteins. *Protein Sci.* **2001**, *10*, 2480−2484.
(81) Morawietz, T.; Singraber, A.; Dellago, C.; Behler, J. How van der Waals interactions determine the unique properties of water. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 8368−8373.
(82) Chen, M.; Ko, H.-Y.; Remsing, R. C.; Calegari Andrade, M. F.; Santra, B.; Sun, Z.; Selloni, A.; Car, R.; Klein, M. L.; Perdew, J. P.; Wu, X. Ab initio theory and modeling of water. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 10846−10851.
(83) Markland, T. E.; Ceriotti, M. Nuclear quantum effects enter the mainstream. *Nat. Rev. Chem.* **2018**, *2*, 0109.
(84) Ruiz Pestana, L.; Marsalek, O.; Markland, T. E.; Head-Gordon, T. The Quest for Accurate Liquid Water Properties from First Principles. *J. Phys. Chem. Lett.* **2018**, *9*, 5009−5016.
(85) Brun, É.; Cloutier, P.; Sicard-Roselli, C.; Fromm, M.; Sanche, L. Damage Induced to DNA by Low-Energy (0−30 eV) Electrons under Vacuum and Atmospheric Conditions. *J. Phys. Chem. B* **2009**, *113*, 10008−10013.
(86) Souici, M.; Khalil, T. T.; Muller, D.; Raffy, Q.; Barillon, R.; Belafrites, A.; Champion, C.; Fromm, M. Single- and Double-Strand Breaks of Dry DNA Exposed to Protons at Bragg-Peak Energies. *J. Phys. Chem. B* **2017**, *121*, 497−507.
(87) Nordlund, K. Historical review of computer simulation of radiation effects in materials. *J. Nucl. Mater.* **2019**, *520*, 273−295.
(88) Ullah, R.; Artacho, E.; Correa, A. A. Core Electrons in the Electronic Stopping of Heavy Ions. *Phys. Rev. Lett.* **2018**, *121*, 116401.
(89) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(90) Reeves, K. G.; Yao, Y.; Kanai, Y. Electronic stopping power in liquid water for protons and α particles from first principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94*, 041108.
(91) Maitra, N. T.; Souza, I.; Burke, K. Current-density functional theory of the response of solids. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 045109.
(92) Ullrich, C. A. Time-dependent density-functional theory beyond the adiabatic approximation: Insights from a two-electron model system. *J. Chem. Phys.* **2006**, *125*, 234108.
(93) Nazarov, V. U.; Pitarke, J. M.; Takada, Y.; Vignale, G.; Chang, Y. C. Including nonlocality in the exchange-correlation kernel from time-dependent current density functional theory: Application to the stopping power of electron liquids. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 205103.
(94) Wijewardane, H. O.; Ullrich, C. A. Real-Time Electron Dynamics with Exact-Exchange Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **2008**, *100*, 056404.
(95) Hofmann, D.; Körzdörfer, T.; Kümmel, S. Kohn-Sham Self-Interaction Correction in Real Time. *Phys. Rev. Lett.* **2012**, *108*, 146401.
(96) Thiele, M.; Gross, E. K. U.; Kümmel, S. Adiabatic Approximation in Nonperturbative Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **2008**, *100*, 153004.
(97) Kunert, T.; Schmidt, R. Non-adiabatic quantum molecular dynamics: General formalism and case study H2+ in strong laser fields. *Eur. Phys. J. D* **2003**, *25*, 15−24.
(98) Lee, C.-W.; Schleife, A. Hot-Electron-Mediated Ion Diffusion in Semiconductors for Ion-Beam Nanostructuring. *Nano Lett.* **2019**, *19*, 3939−3947.
(99) Krasheninnikov, A. V.; Nordlund, K. Ion and electron irradiation-induced effects in nanostructured materials. *J. Appl. Phys.* **2010**, *107*, 071301.

DOI: 10.1021/acs.jpclett.9b02975
J. Phys. Chem. Lett. 2020, 11, 229−237