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Velocity-Gauge Real-Time Time-Dependent Density Functional Tight-Binding for Large-Scale Condensed Matter Systems

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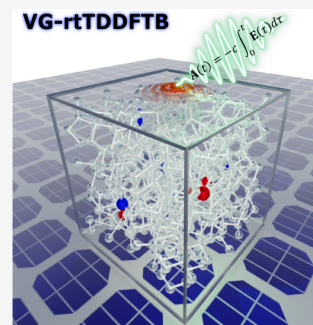
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ABSTRACT: We present a new velocity-gauge real-time, time-dependent density functional tight-binding (VG-rtTDDFTB) implementation in the open-source DFTB+ software package (<https://dftbplus.org>) for probing electronic excitations in large, condensed matter systems. Our VG-rtTDDFTB approach enables real-time electron dynamics simulations of large, periodic, condensed matter systems containing thousands of atoms with a favorable computational scaling as a function of system size. We provide computational details and benchmark calculations to demonstrate its accuracy and computational parallelizability on a variety of large material systems. As a representative example, we calculate laser-induced electron dynamics in a 512-atom amorphous silicon supercell to highlight the large periodic systems that can be examined with our implementation. Taken together, our VG-rtTDDFTB approach enables new electron dynamics simulations of complex systems that require large periodic supercells, such as crystal defects, complex surfaces, nanowires, and amorphous materials.



1. INTRODUCTION

Real-time time-dependent density functional theory (rtTDDFT)^{1–3} is a powerful approach for predicting the electron dynamics of quantum systems via solution of the time-dependent Kohn–Sham (KS) equations.^{4–13} rtTDDFT simulations can probe real-time electron dynamics in the presence of time-dependent external fields, which can be used to understand light–matter interactions and predict the linear/nonlinear response of materials. The most common usage/implementation of rtTDDFT is for molecular (i.e., nonperiodic) systems since the length gauge, which is used to calculate quantum dynamics in nonperiodic systems, is relatively straightforward. However, the length-gauge formalism cannot be used for periodic systems since it breaks the translational symmetry of the Hamiltonian.^{14–16} For condensed matter systems, the time-dependent KS equations can be formally integrated under periodic boundary conditions¹⁷ using the velocity-gauge (VG) formalism,^{11,16,61} which has been used to probe laser-induced electron dynamics in a variety of solid-state systems.^{11,15,18–21}

Despite its broad applicability, the high computational expense of rtTDDFT calculations prohibits its use for large material systems such as crystal defects, complex surfaces, heterostructures, and amorphous systems, which require large supercells. To enable these large-scale electron dynamics simulations, an alternate theoretical formalism with a low computational cost is required. To address this need, we present the first velocity-gauge real-time time-dependent density functional tight-binding (VG-rtTDDFTB) implementation in the open-source DFTB+ software package (<https://dftbplus.org>) for large-scale and long-time electron dynamics

simulations with periodic boundary conditions. Our VG-rtTDDFTB implementation makes use of the density functional tight-binding (DFTB) formalism,^{22,23} which is computationally efficient, relatively accurate, and scales extremely well with system size compared to full density functional theory (DFT).^{24–29}

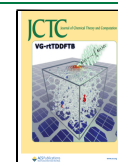
In this work, we derive the theoretical formalism and present a numerical implementation of VG-rtTDDFTB for electron dynamics simulations of large-scale condensed matter systems. Section 2 commences with a description of the VG-rtTDDFTB theoretical formalism. Section 3 provides computational details and benchmark calculations to demonstrate its accuracy and computational parallelizability on a variety of large material systems. Finally, we present an example of laser-induced electron dynamics in amorphous silicon to highlight the large periodic systems that can be examined with our approach, and we conclude with future prospects/applications of our VG-rtTDDFTB implementation.

2. THEORETICAL FORMALISM

The time-dependent KS formalism with periodic boundary conditions in atomic units ($\hbar = e = m_e = 1$) is given by

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$$i\frac{\partial}{\partial t}|\psi_{nk}\rangle = \hat{H}_{\text{KS}}|\psi_{nk}\rangle \quad (1)$$

where ψ_{nk} is the wave function in the Bloch representation. In the long-wavelength limit, $\lambda \gg V^{1/3}$, where λ and V are the laser wavelength and volume of the simulation cell, respectively. Within this regime, the spatial variation of the electromagnetic field is negligible,^{30,31} which allows us to calculate macroscopic dielectric properties of solid-state systems.³² In the long-wavelength approximation, the VG-KS Hamiltonian is given by^{11,16,30}

$$\begin{aligned} \hat{H}_{\text{KS}} &= \frac{1}{2}\left[\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}(t)\right]^2 + \hat{V}_{\text{eff}}[\rho] \\ &= \frac{1}{2}\hat{\mathbf{p}}^2 + \hat{V}_{\text{eff}}[\rho] + \frac{1}{c}\mathbf{A}(t)\cdot\hat{\mathbf{p}} + \frac{1}{2c^2}|\mathbf{A}(t)|^2 \\ &\quad \underbrace{\hspace{10em}}_{\hat{H}_{\text{ext}}(t)} \end{aligned} \quad (2)$$

where $\hat{\mathbf{p}}$ and \hat{V}_{eff} are the momentum and effective potential operators, respectively; c denotes the speed of light in vacuum, $\rho(r) = \frac{1}{N_{\mathbf{k}}}\sum_{n\mathbf{k}}^{\text{occ.}} |\psi_{n\mathbf{k}}(r)|^2$ is the electron density, $N_{\mathbf{k}}$ is the number of k -points or the number of unit cells in the Born-von-Karman supercell used in the calculation,^{33,34} and $\hat{H}_{\text{ext}}(t)$ is the Hamiltonian containing the external vector potential, which is given by

$$\mathbf{A}(t) = -c \int_0^t \mathbf{E}(\tau) d\tau \quad (3)$$

where \mathbf{E} is the external electric field; e.g., $\mathbf{E}(t) = \mathbf{E}_0\delta(t)$ for a delta function “kick” field, and $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$ corresponds to a monochromatic “laser” field with frequency ω . Note that the last term in eq 2 is a function of time that only gives rise to an overall phase factor of the form $\exp(-i\int_0^t |\mathbf{A}(\tau)|^2 d\tau / (2c^2))$ in the time-dependent wave function.¹ This overall phase factor does not affect observables and density matrices in our implementation.

The self-consistent-charge density functional tight-binding (SCC-DFTB) formalism²² uses nonorthogonal pseudoatomic basis sets, $\{|\phi_{\mu}^{\zeta}\rangle\}$, and effective potentials in a two-center approximation. The collective index μ represents (I, l, m) such that $|\phi_{\mu}^{\zeta}\rangle$ denotes the orbital centered on the l th atom of the ζ th periodic cell image in real space with (l, m) angular momentum quantum numbers, where $\phi_{\mu}(\mathbf{r} - \mathbf{R}_I - \mathbf{L}_{\zeta}) = \langle \mathbf{r} | \phi_{\mu}^{\zeta} \rangle$, \mathbf{R}_I and \mathbf{L}_{ζ} are the positions of the l th atom and ζ th periodic image, respectively. The Bloch state in the SCC-DFTB formalism can be rewritten as

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\zeta} \sum_{\mu=1}^{N_b} C_{n\mathbf{k}\mu}^{\zeta} e^{i\mathbf{k}\cdot\mathbf{L}_{\zeta}} |\phi_{\mu}^{\zeta}\rangle \quad (4)$$

where N_b is the number of atomic basis functions in the unit cell. Combining eqs 1 and 4, the time-dependent DFTB equations in matrix form becomes

$$i\frac{\partial}{\partial t} \mathbf{C}_{n\mathbf{k}} = \mathbf{S}_{\mathbf{k}}^{-1} \mathbf{H}_{\mathbf{k}} \mathbf{C}_{n\mathbf{k}} \quad (5)$$

where $\mathbf{C}_{n\mathbf{k}} = [C_{n\mathbf{k}\mu}^1, C_{n\mathbf{k}\mu}^2, \dots]^T$ is the coefficient vector of the n th state. Alternatively, the equation of motion for the k -dependent density matrices can be obtained from eq 5 as

$$i\frac{\partial}{\partial t} \mathbf{D}_{\mathbf{k}} = \mathbf{S}_{\mathbf{k}}^{-1} \mathbf{H}_{\mathbf{k}} \mathbf{D}_{\mathbf{k}} - \mathbf{D}_{\mathbf{k}} \mathbf{H}_{\mathbf{k}} \mathbf{S}_{\mathbf{k}}^{-1} \quad (6)$$

where the k -dependent density matrix is defined as $\mathbf{D}_{\mathbf{k}} = \sum_n^{\text{occ.}} \mathbf{C}_{n\mathbf{k}} \mathbf{C}_{n\mathbf{k}}^{\dagger}$, and the elements of the k -dependent overlap ($\mathbf{S}_{\mathbf{k}}$) and Hamiltonian ($\mathbf{H}_{\mathbf{k}}$) matrices are given by

$$\mathbf{S}_{\mathbf{k}}^{\mu\nu} = \sum_{\zeta} e^{-i\mathbf{k}\cdot\mathbf{L}_{\zeta}} \langle \phi_{\mu}^{\zeta} | \phi_{\nu}^{\zeta} \rangle = \sum_{\zeta} e^{-i\mathbf{k}\cdot\mathbf{L}_{\zeta}} \bar{\mathcal{S}}^{\mu\nu}(\mathbf{L}_{\zeta}) \quad (7)$$

$$\mathbf{H}_{\mathbf{k}}^{\mu\nu} = \sum_{\zeta} e^{-i\mathbf{k}\cdot\mathbf{L}_{\zeta}} \langle \phi_{\mu}^{\zeta} | \hat{H}_{\text{DFTB}} | \phi_{\nu}^{\zeta} \rangle = \sum_{\zeta} e^{-i\mathbf{k}\cdot\mathbf{L}_{\zeta}} \bar{\mathcal{H}}^{\mu\nu}(\mathbf{L}_{\zeta}) \quad (8)$$

To numerically evaluate the VG Hamiltonian, the $\bar{\mathcal{H}}^{\mu\nu}(\mathbf{L}_{\zeta})$ term in eq 8 can be rewritten within the SCC-DFTB approximation as

$$\bar{\mathcal{H}}^{\mu\nu}(\mathbf{L}_{\zeta}) = \bar{\mathcal{H}}_{(0)}^{\mu\nu}(\mathbf{L}_{\zeta}) + \bar{\mathcal{H}}_{(2)}^{\mu\nu}(\mathbf{L}_{\zeta}) + \bar{\mathcal{H}}_{\text{ext}}^{\mu\nu}(\mathbf{L}_{\zeta}) \quad (9)$$

where $\bar{\mathcal{H}}_{(0)}^{\mu\nu}(\mathbf{L}_{\zeta}) \equiv \langle \phi_{\mu}^{\zeta} | \frac{1}{2}\hat{\mathbf{p}}^2 + \hat{V}_{\text{eff}}[\rho_0] | \phi_{\nu}^{\zeta} \rangle$, $\bar{\mathcal{H}}_{(2)}^{\mu\nu}(\mathbf{L}_{\zeta})$, and $\bar{\mathcal{H}}_{\text{ext}}^{\mu\nu}(\mathbf{L}_{\zeta})$ include contributions from the self-consistent-charge (SCC), non-SCC, and external potential terms in DFTB, respectively. In SCC-DFTB, all of the $\bar{\mathcal{S}}^{\mu\nu}(\mathbf{L}_{\zeta})$ and $\bar{\mathcal{H}}_{(0)}^{\mu\nu}(\mathbf{L}_{\zeta})$ matrix elements are pretabulated using Slater-Koster techniques³⁵ with a reference density ρ_0 . The diagonal elements of $\bar{\mathcal{H}}_{(0)}^{\mu\nu}(\mathbf{L}_{\zeta})$ correspond to the atomic orbital energies, and the off-diagonal elements are calculated in a two-centered approximation.²² The SCC-term $\bar{\mathcal{H}}_{(2)}^{\mu\nu}(\mathbf{L}_{\zeta})$ is defined as

$$\bar{\mathcal{H}}_{(2)}^{\mu\nu}(\mathbf{L}_{\zeta}) = \frac{1}{2} \bar{\mathcal{S}}^{\mu\nu}(\mathbf{L}_{\zeta}) \sum_K (\gamma_{IK} + \gamma_{JK}) \Delta q_I \Delta q_J \quad (10)$$

where eq 10 depends on the Mulliken population $q_I = \frac{1}{2N_{\mathbf{k}}} \sum_{n\mathbf{k}}^{\text{occ.}} \sum_{\mu \in I, \nu} C_{n\mathbf{k}\mu}^{\mu*} \mathbf{S}_{\mathbf{k}}^{\mu\nu} C_{n\mathbf{k}\nu}^{\nu} + \text{c.c.} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{\mu \in I} |\mathbf{D}_{\mathbf{k}} \mathbf{S}_{\mathbf{k}}|^{\mu\mu}$, and $\Delta q_I = q_I - Z_I$ is the charge fluctuation with respect to the ion charge Z_I . The μ th and ν th basis indices denote orbitals centered on the I th and J th atoms, respectively. γ_{IJ} is defined as²²

$$\gamma_{IJ} = \frac{1}{R_{IJ}} - S(U_I, U_J; R_{IJ}) \quad (11)$$

where $R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J|$ and U_I is the chemical hardness or Hubbard parameter of the I th atom. The first term of eq 11 is the long-range Coulomb interaction, and S is the short-range term that decays exponentially.²² For periodic boundary conditions, the long-range part of eq 10 can be evaluated using the standard Ewald summation,^{36,37} whereas the short-range part can be summed over a few neighbor periodic images of the central unit cell ($\zeta = 0$).

From eq 2, the external potential term, $\bar{\mathcal{H}}_{\text{ext}}^{\mu\nu}(\mathbf{L}_{\zeta})$, can be written as

$$\begin{aligned} \bar{\mathcal{H}}_{\text{ext}}^{\mu\nu}(\mathbf{L}_{\zeta}) &= \langle \phi_{\mu}^{\zeta} | \hat{H}_{\text{ext}} | \phi_{\nu}^{\zeta} \rangle \\ &= \frac{1}{c} \mathbf{A}(t) \cdot \langle \phi_{\mu}^{\zeta} | \hat{\mathbf{p}} | \phi_{\nu}^{\zeta} \rangle + \frac{1}{2c^2} |\mathbf{A}(t)|^2 \bar{\mathcal{S}}^{\mu\nu}(\mathbf{L}_{\zeta}) \end{aligned} \quad (12)$$

where the first term can be obtained from the expression $\langle \phi_{\mu}^{\zeta} | \hat{\mathbf{p}} | \phi_{\nu}^{\zeta} \rangle = -i \langle \phi_{\mu}^{\zeta} | \nabla | \phi_{\nu}^{\zeta} \rangle = i \langle \phi_{\mu}^{\zeta} | \nabla_J | \phi_{\nu}^{\zeta} \rangle$, ∇_J denotes the gradient with respect to atomic position \mathbf{R}_J , and $\nu \in J$ th atom.³⁸ The overlap matrix $\mathbf{S}_{\mathbf{k}}$ and Hamiltonian $\mathbf{H}_{\mathbf{k}}$ in eqs 5 and 6 can be calculated using eqs 3, 7–12. The coefficient vectors or density matrices can be updated by integrating eq 5 or 6, respectively.

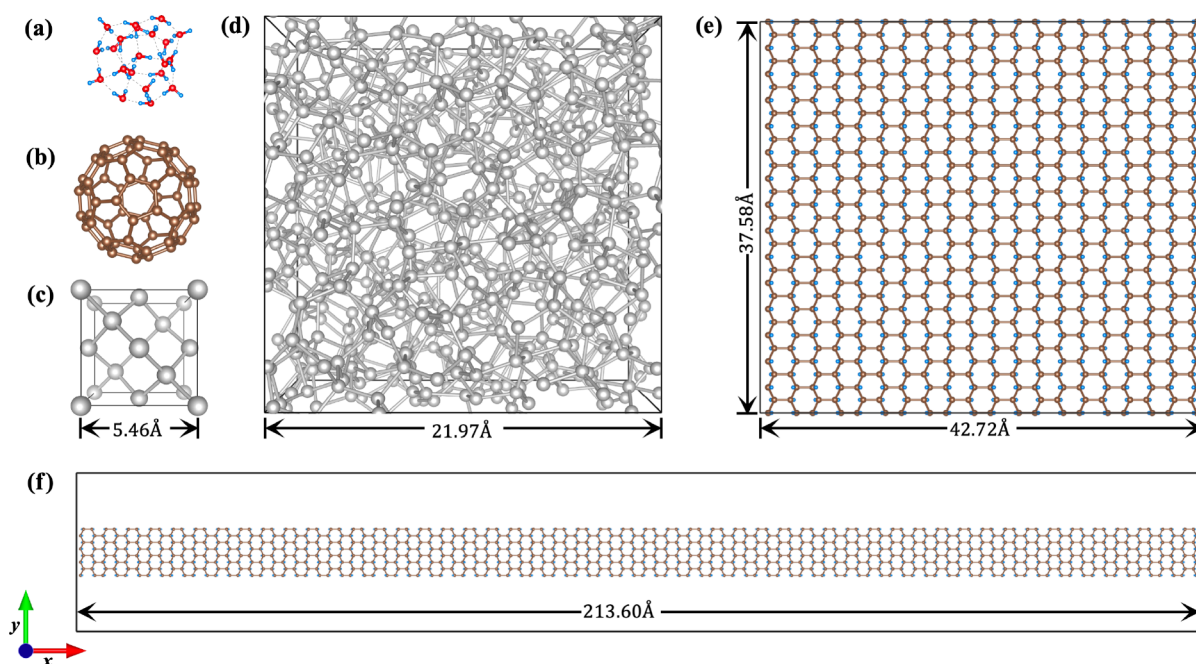


Figure 1. Molecular and periodic structures examined with our VG-rtTDDFTB approach: (a) (H₂O)₂₁ cluster, (b) C₆₀r, (c) c-Si, (d) a-Si, (e) 2D-graphane (C₆₀₀H₆₀₀), and (f) 1D-graphane (C₈₀₀H₈₀₀).

In our implementation, we use the leapfrog algorithm to integrate eq 6 for the k -dependent density matrix, \mathbf{D}_k :

$$\mathbf{D}_k(t + dt) = \mathbf{D}_k(t - dt) + 2\dot{\mathbf{D}}_k(t)dt \quad (13)$$

One can also integrate eq 5 using the unitary Crank-Nicolson^{39,40} time evolution of the coefficient vectors (which we have also implemented in our code). Our resulting VG-rtTDDFTB electron dynamics simulations give the time-dependent Mulliken charge and current $\mathbf{J}(t)$:¹¹

$$\begin{aligned} \mathbf{J}(t) &= -\frac{1}{2\Omega N_k} \sum_{nk}^{\text{occ.}} \mathbf{C}_{nk}^\dagger(t) \mathbf{\Pi}_k(t) \mathbf{C}_{nk}(t) + c. c. \\ &= -\frac{1}{\Omega N_k} \sum_k \text{Tr}[\mathbf{D}_k(t) \mathbf{\Pi}_k(t)] \end{aligned} \quad (14)$$

where Ω denotes the volume of the unit cell, and the elements of the current-momentum matrix is $\mathbf{\Pi}_k^{\mu\nu}(t) = \sum_c e^{-ik \cdot \mathbf{L}_c} \langle \phi_\mu^c | \hat{\mathbf{p}} | \phi_\nu^c \rangle + \frac{1}{c} \mathbf{A}(t) S_k^{\mu\nu}$, which is a 3-component vector. The frequency-dependent conductivity, $\sigma(\omega)$, and dielectric function, $\epsilon(\omega)$, can be derived using the time-dependent current generated by the δ -function “kick” field in the linear-response regime:¹¹

$$\sigma_{ij}(\omega) = \frac{1}{E_{0j}} \int_0^T e^{i\omega\tau} J_i(\tau) f(\tau) d\tau \quad (15)$$

$$\epsilon_{ij}(\omega) = 1 + \frac{4\pi i \sigma_{ij}(\omega)}{\omega} \quad (16)$$

where $f(\tau) = e^{-\tau/\tau_0}$ is a filtering function with τ_0 set to 200 au in this work. With these quantities calculated, the absorption spectrum is given by the imaginary part of the dielectric function $\text{Im}[\epsilon(\omega)]$. Note that eq 15 does not contain any spatial dependence because of the long-wavelength approximation.³¹

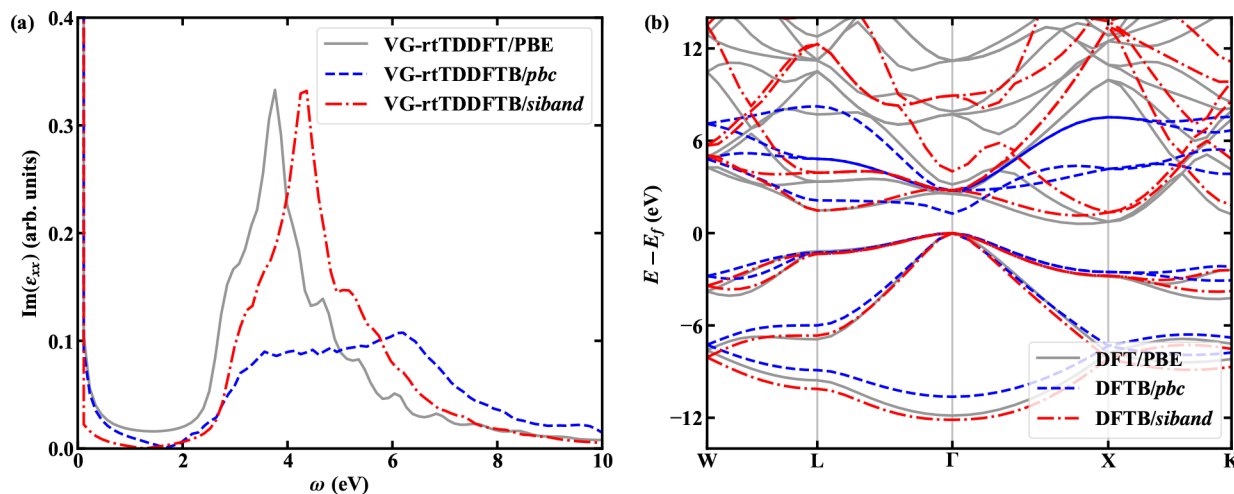
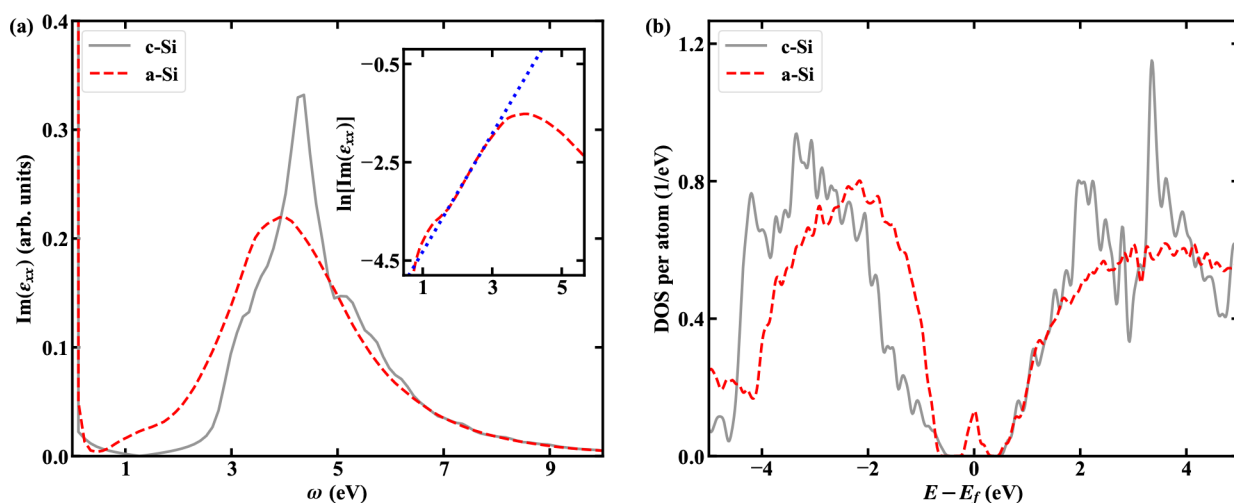
3. RESULTS AND DISCUSSION

3.1. Computational details. We first calculated the electronic ground state with SCC-DFTB using the DFTB+ package.^{22,23} The subsequent electron dynamics were then calculated with the VG-rtTDDFTB framework developed in this work. We performed electron dynamics simulations on representative chemical/material systems ranging from 0D (cluster) to 3D (bulk) geometries. Figure 1(a) shows the optimized structure of a (H₂O)₂₁ cluster using the TIPSP potential.^{41–43} The C₆₀ and crystal silicon (c-Si) structures shown in Figures 1(b) and (c), respectively, were optimized with the SCC-DFTB method. The amorphous silicon (a-Si) structure containing 512 atoms in Figure 1(d) was obtained from the last molecular dynamics step of a GAP-MD simulation with a slow quench rate (10¹¹ K/s) from 1800 to 500 K,⁴⁴ which has been shown to generate reliable structures for a-Si compared to experiments.⁴⁴ For the partially periodic systems in Figures 1(e) and (f), we built the 2D- and 1D-graphane structures from the 10 × 15 × 1 and 50 × 4 × 1 supercells, respectively, of the boat conformer of graphane.⁴⁵ We used a 30 Å vacuum space along the nonperiodic directions for all the clusters and partially periodic systems in this work.

For our DFTB/VG-rtTDDFTB calculations, we used the *mio*²² and *pb*⁴⁶ Slater-Koster (SK) parameter sets for clustered and bulk/1D/2D systems, respectively. We found that the *siband*^{47,48} SK set for c-Si and a-Si gave more accurate electronic structures and absorption spectra. We used maximum angular momenta of *s*, *p*, and *d* for H, C/O, and Si elements, respectively. To benchmark our VG-rtTDDFT calculations, ground-state DFT and VG-rtTDDFT calculations were carried out with the real-space based OCTOPUS package^{18,19} using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional⁴⁹ with a 0.15 Å grid spacing for c-Si. For our absorption spectra calculations, we applied a δ -pulse electric field of $E_x(t) = E_0\delta(t)$ and $E_0 = 0.005$ eV/Å applied along the *x*-axis at $t = 0$ for all systems. The average current is subtracted from the total current induced by the kick

Table 1. Walltime for Various VG-rtTDDFTB Simulations (18000 steps, 36 fs) on the NERSC *Perlmutter* Supercomputer

System	Periodicity	SK set	k mesh	Number of basis functions	Number of cores	Walltime (h)
(H ₂ O) ₂₁	0	<i>mio</i>	1 × 1 × 1	126	1	0.01
C ₆₀	0	<i>mio</i>	1 × 1 × 1	240	1	0.06
c-Si	3	<i>siband</i>	16 × 16 × 16	72	64	0.35
a-Si	3	<i>siband</i>	1 × 1 × 1	4608	128	11.51
C ₆₀₀ H ₆₀₀	2	<i>pbz</i>	1 × 1 × 1	3000	64	2.43
C ₈₀₀ H ₈₀₀	1	<i>pbz</i>	1 × 1 × 1	4000	128	5.37

Figure 2. (a) Imaginary part of the dielectric function ϵ_{xx} and (b) electronic band structures calculated with DFT (PBE) and DFTB using the *pbz* and *siband* Slater-Koster sets for crystalline Si.Figure 3. (a) Imaginary part of the dielectric function ϵ_{xx} calculated by our VG-rtTDDFTB implementation. The dotted blue line in the inset is the least-squares fitting of the Urbach region using the expression $\ln[\text{Im}(\epsilon_{xx})] = \omega/E_U - 5.52$ with $E_U = 0.83$ eV. (b) Density of states calculated with DFTB using the *siband* Slater-Koster set for c-Si and a-Si.

field to reduce noise of the optical spectra. The $16 \times 16 \times 16$ k -point meshes were generated using the Monkhorst-Pack method⁵⁰ for c-Si, and a single Γ -point was used for the calculations of the other large-scale or cluster systems. We used a 0.002 fs time step and the leapfrog integral method for all of our VG-rtTDDFTB electron dynamics simulations. Furthermore, we calculated the density of states (DOS) using a Gaussian function with a width of 0.05 eV for all cases. The Fermi level (E_f) for our DOS and band structure plots were shifted to a 0 eV reference energy. We defined our charge density using a Gaussian broadening of the atomic charges

$$\rho(\mathbf{r}; t) = \sum_I \frac{Q_I(t)}{\sqrt{(2\pi)^3 \eta^3}} e^{-(\mathbf{r}-\mathbf{R}_I)^2/2\eta^2}, \text{ where } Q_I(t) = -\Delta q_I(t)$$

denotes the I th atomic charge, and η was set to 0.55 Å.

3.2. Computational Results on Large Material Systems. We implemented our VG-rtTDDFTB approach with a hybrid MPI/OpenMP parallelization to enable large-scale electron dynamics simulations. Our parallelization is accelerated by distributing the k -point index over MPI ranks because the electron dynamics simulation is largely independent of each k -point and requires only minimal intercore communications. At the node level, for each k -point, the

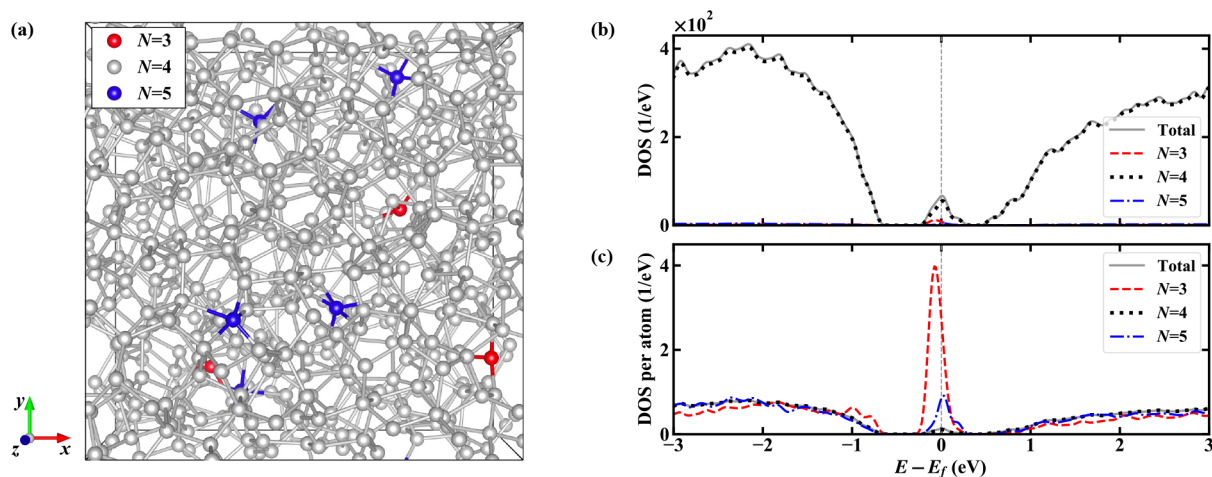


Figure 4. (a) Structure of amorphous Si containing 512 atoms with various N -coordinated atoms. Total/local (b) DOS and (c) DOS per atom for amorphous Si calculated using DFTB with *siband* Slater-Koster set.

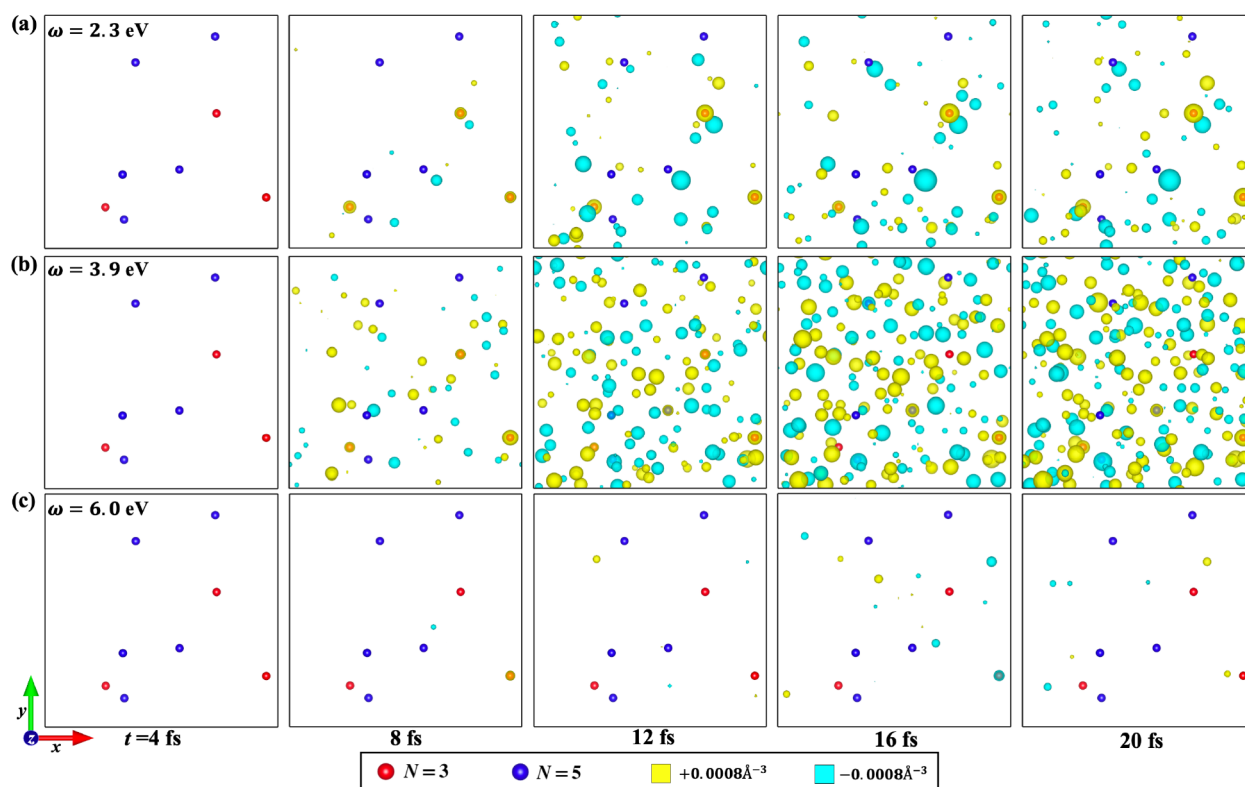


Figure 5. Snapshots of laser-induced total charge density fluctuations $\Delta\rho(\mathbf{r};t) = \rho(\mathbf{r};t) - \rho(\mathbf{r};0)$ for N -coordinated atoms with respect to the ground state at laser frequencies of (a) 2.3, (b) 3.9, and (c) 6.0 eV. The 4-coordinated atoms are not shown for clarity.

computational workloads are distributed among cores using the multithreaded OpenMP parallelization. To evaluate the computational efficiency for our parallelized VG-rtTDDFTB implementation, we simulated various systems for 18000 steps (36 fs) on the NERSC *Perlmutter* supercomputer with a δ -function “kick” field. Table 1 shows that our parallelized VG-rtTDDFTB implementation enables extremely efficient electron dynamics simulations of large complex condensed matter systems that are too computationally expensive with standard rtTDDFT approaches.

To assess the accuracy of our VG-rtTDDFTB calculations for bulk systems, the optical spectra of c-Si were calculated by our VG-rtTDDFTB using *pb*c and *sib*and SK sets in

comparison with VG-rtTDDFT using the PBE functional. As shown in Figure 2(a), the optical spectrum calculated by VG-rtTDDFTB using the *sib*and SK file are slightly blue-shifted, and generally consistent with full VG-rtTDDFT/PBE results. The VG-rtTDDFTB optical spectrum calculated with the *pb*c parameter set, however, shows a significant discrepancy compared to the full VG-rtTDDFT/PBE results. The *sib*and parameter set was specifically constructed to accurately capture the electronic structure of bulk Si,⁴⁷ which is necessary for reproducing its optical spectrum. As shown in Figure 2(b), the DFTB band structures for bulk Si confirm the good agreement between the *sib*and parametrization and the DFT/PBE results. In contrast, the DFTB/*pb*c band structure shows narrow

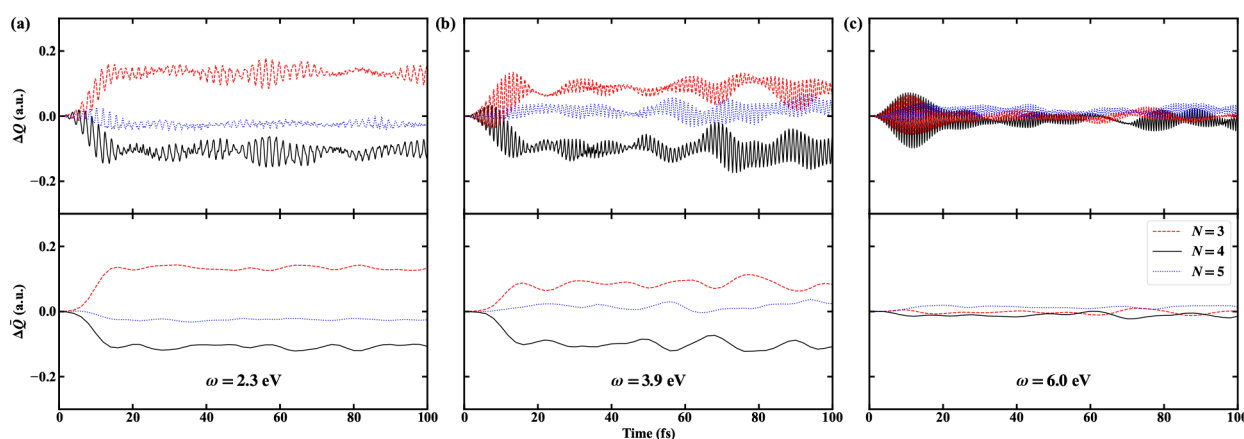


Figure 6. Laser-induced total charge evolution $\Delta Q(t) = Q(t) - Q(0)$ of various N -coordinated atoms at laser frequencies of (a) 2.3, (b) 3.9, and (c) 6.0 eV. The bottom panels depict the charge dynamics averaged every 2 fs.

conduction bands and significant discrepancies compared to the DFT/PBE result.

Amorphous silicon has been widely investigated as a noncrystalline material with applications in solar cells,⁵¹ thin-film transistors,⁵² and electrodes in batteries.⁵³ Despite its wide applicability, first-principles calculations for a-Si are rare because of the enormous computational expense of this amorphous system (which requires large supercells). To highlight the capabilities of our VG-rtTDDFTB approach, we calculate optical properties and electron dynamics for the a-Si structure shown in Figure 1(d). As shown in Figure 3(a), the absorption edge of a-Si is broadened and slightly red-shifted compared to that of c-Si, which is generally consistent with the results reported in previous experiments.^{54–56} Furthermore, we observed a clear “Urbach” absorption edge⁵⁷ (from 1.7 to 2.8 eV) in the inset of Figure 3(a), which arises from optical electron transitions between the localized (defected) and extended bands of the DOS shown in Figure 3(b).

To investigate the effect of coordination defects on electron dynamics, we highlighted N -coordinated atoms for a-Si in Figure 4(a) as the red (3-coordinated), silver (4-coordinated), and blue (5-coordinated) balls, which were determined by the bond-length cutoff of 2.85 Å for each atom.⁴⁴ Since 4-coordinated atoms are more prevalent (98.4% of total atoms), the effect of other coordination defects in the total and local DOS [Figure 4(b)] are less pronounced. However, the DOS per atom in Figure 4(c) shows that coordination defects significantly influence the electronic structure near the Fermi level of a-Si. The 3-coordinated atoms have a large peak slightly below the Fermi level due to their localized unbonded character (i.e., dangling bonded atoms), whereas 5-coordinated atoms have a small peak above the Fermi level due to extra bonding, known as “floating bonds”.^{58,59} These states near the Fermi level have a significant influence on low-energy excitations and dynamics, which result in a broadened absorption spectrum.

To further study laser-induced electron dynamics of a-Si, we used a 20 fs \sin^2 -enveloped laser pulse (centered at 10 fs) with frequencies of 2.3, 3.9, and 6.0 eV, which corresponds to the edge, peak, and tail, respectively, of the absorption spectrum of a-Si as shown in Figure 3(a). We applied an electric field along the x -axis with an intensity of 10^{12} W/cm² ($E_0 \approx 0.274$ eV/Å) for our electron dynamics simulations. In Figure 5, we present the instantaneous charge density with respect to the ground state of a-Si for different laser frequencies. We see that charge

transfer under different frequencies is weak during the first 4 fs due to the initialization of the laser pulse, whereas the charge transfer tends to maximize after 12 fs. Figure 5(a) shows that low-frequency excitations at 2.3 eV induces electron transfer among the 3- and 4-coordinated atoms. Specifically, electrons are transferred from dangling-bonded ($N = 3$) atoms for all snapshots after 8 fs. For medium-frequency excitations at 3.9 eV, Figure 5(b) shows that more electron transfer occurs among the 4-coordinated atoms while electron transfer from 3-coordinated atoms to other atoms is still present. It is worth noting that the different floating-bonded ($N = 5$) atoms have different charge transfer modes at the same time. For high-frequency excitations at 6.0 eV, Figure 5(c) shows that the least amount of charge transfer occurs. The 3-coordinated atoms lose electrons at 8 fs and subsequently gain charge at 16 fs. The overall electron dynamics are consistent with the absorption spectra peaks at each frequency shown in Figure 3(a).

We calculated the Mulliken charge fluctuations among 3-, 4-, and 5-coordinated atoms with respect to the ground state as shown in Figure 6. For low-frequency laser excitation (2.3 eV) shown in Figure 6(a), the 3- and 5-coordinated atoms lose and gain electrons, respectively, which is consistent with the electron transfer between localized (near the Fermi level) and conduction bands in the Urbach region of the absorption edge⁵⁷ as mentioned previously. For medium-frequency laser excitations (3.9 eV) shown in Figure 6(b), the 5-coordinated atoms exhibit lose electrons, which is opposite of that shown in Figure 6(a); in addition, electron transfer from 3-/4-coordinated atoms is weaker. These phenomena indicate that the extended valence band starts to transfer electrons to the extended conduction band. Figure 6(c) shows that at high frequencies of 6.0 eV, the time-averaged electron transfer is relatively weak and comparable in magnitude among the N -coordinated atoms, which can be attributed to the high energy electron excitation between the extended valence and conduction bands that are far from Fermi level arising from the 4-coordinated atoms.

4. CONCLUSION

In summary, we have derived and implemented a new velocity gauge, real-time time-dependent density functional tight-binding (VG-rtTDDFTB) method in the open-source DFTB+ software package for electron dynamics simulations

of large, condensed matter systems with periodic boundary conditions. Our VG-rtTDDFTB approach enables electron dynamics simulations of large condensed matter systems containing thousands of atoms with a favorable computational scaling as a function of system size. Our implementation uses a hybrid MPI/OpenMP parallelization scheme for massive parallelization to treat large systems on multicore supercomputers. The computational efficiency of our VG-rtTDDFTB approach enables electron dynamics simulations of complex systems that require larger periodic supercells, such as crystal defects, complex surfaces, nanowires, and amorphous materials.

In conclusion, we have demonstrated that our VG-rtTDDFTB implementation can execute large electron dynamics for periodic systems containing thousands of atoms with an excellent time to solution on the order of seconds per time step. As a representative example, we performed a 100 fs electron dynamics simulation for amorphous silicon (containing 512 atoms) on a modest computer cluster to study laser-induced charge transfer dynamics. Our VG-rtTDDFTB calculations give mechanistic insight into time-resolved electron density fluctuations and electron transfer as the system is irradiated in real time with electromagnetic radiation. Our simulations also allow us to analyze different electron dynamics occurring between differently coordinated atoms at various frequencies as the system is irradiated. We anticipate that our VG-rtTDDFTB approach could find broad usage for large periodic systems, particularly for material systems that are too large to handle with rtTDDFT. Further extensions to accelerate these calculations with specialized hardware accelerators^{25,29,60} are currently underway in our group.

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Notes

The authors declare no competing financial interest.

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