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Article

Linear-Response Time-Dependent Density Functional Theory with **Stochastic Range-Separated Hybrids**

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decomposition of the Coulomb convolution (J. Phys. Chem. A 2016, 120, 3071). Here, we extend the stochastic RSH approach to excited states within the framework of linear-response generalized Kohn-Sham time-dependent density functional theory (GKS-TDDFT) based on the plane-wave basis. As a validation of the stochastic GKS-TDDFT method, the excitation energies of small molecules N_2 and CO are calculated and compared to the deterministic results. The computational efficiency of the stochastic method is demonstrated with a two-dimensional MoS_2 sheet (~1500 electrons), whose excitation energy, exciton charge density, and (excited state) geometric relaxation are determined in the absence and presence of a point defect.

 $\left[\eta_{\sigma} \rangle \langle \eta_{\sigma}^{\pm} \right]$

I. INTRODUCTION

Understanding, predicting, and ultimately controlling excitedstate behavior are central to diverse chemical, molecular, and material problems, including photovoltaics, light-emitting devices, photocatalysis, photosynthesis, plasmonics, molecular electronics, and biosensors. Nowadays, time-dependent density functional theory (TDDFT)^{1,2} has become one of the most powerful tools to probe the electronic structure and optical excitations, balancing computational accuracy and efficiency. In particular, linear-response TDDFT has been widely employed to compute the excitation energy, ionic force, and nonadiabatic coupling of excited states in molecular- and solid-state materials.^{3–15}

density matrix with stochastic orbitals and a stochastic

Exchange-correlation (XC) functionals play a critical role in both DFT and TDDFT. It is well-known that semi-local XC functionals, such as the generalized-gradient approximation (GGA) and the local density approximation, do not accurately predict excited-state properties in extended systems because of the incorrect description of long-range electron–electron and electron–hole interaction.^{16–18} In contrast, generalized Kohn-Sham (GKS)^{19,20} DFT and TDDFT methods with a nonlocal exchange interaction (hybrid functionals)^{21,22} have been shown to yield accurate one- and two-particle excitations, for both molecular and extended systems.²³⁻²⁹ Note that here, GKS refers specifically to the inclusion of explicit exchange but not to the use of mixed-spin orbitals.

The majority of existing GKS-TDDFT codes uses atomcentered (AO) basis sets with target applications in molecular chemistry.³⁰⁻³² The most important advantage of AO bases is that hybrid functionals are readily computed with short-range AOs; the scaling of operating with a nonlocal exchange is $O(N^2)$ in a local basis (but with a possibly large prefactor, depending on the AO basis and its degree of localization). In contrast, a plane-wave basis is a natural choice for periodic and extended systems, thanks to its simplicity and completeness. In addition, it is free of Pulay forces that plague AO basis methods. The drawback of plane waves is that hybrid functionals are computationally demanding because the nonlocal exchange is obtained from the density matrix rather than the density, increasing the scaling from $O(N^2 \log N)$ in KS-TDDFT to $O(N^3 \log N)$ in GKS-TDDFT.

Cost: GKS-TDDFT ≈ KS-TDDFT

To alleviate the cost of hybrid functionals, one can unitarily transform all occupied orbitals into spatially localized ones.³³⁻³⁵ The nonlocal exchange potential and the corresponding exchange energy are then calculated efficiently with the localized orbitals.^{36–38} Recently, Lin has introduced an adaptively compressed exchange operator with a low rank that



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significantly reduces the computational cost of nonlocal exchange.³⁹ These methods work well in GKS-DFT, as it involves only the occupied orbitals.

Here, we extend the recently developed stochastic orbital method to efficiently describe excited states in plane-wave based linear-response GKS-TDDFT, by significantly reducing the cost of the exchange operator. With the stochastic approach, the numerically expensive explicit-exchange GKS Hamiltonian becomes, for large systems, as cheap as a local-potential KS Hamiltonian.⁴⁰ Recently, a real time GKS-TDDFT with a stochastic hybrid functional (the same functional used here) was developed and applied to calculate absorption spectra for large finite phosphorene sheets containing up to 2000 electrons.⁴¹ Furthermore, stochastic KS-DFT,⁴² stochastic GW,⁴³ and stochastic Bethe–Salpeter equation (BSE)⁴⁴ were successfully applied to systems with thousands of electrons.

The present work merges the efficiency of the stochastic approach in describing hybrid functionals with the efficiency of frequency-based TDDFT in describing low-frequency excitations. Specifically, we reformulate plane-wave based linearresponse GKS-TDDFT by using a stochastic representation of hybrid functionals. We concentrate on long-range-separated hybrid (RSH) functionals with an optimally tuned rangeseparation parameter.⁴⁵⁻⁴⁹ In Section II, we first present GKS-TDDFT with a deterministic RSH functional. The stochastic formulation of the RSH functional is introduced. Then, we briefly analyze the cost saving with stochastic GKS-TDDFT. Lastly, we present the implementation of the projector augmented-wave (PAW) pseudopotential^{50,51} and the required modification of the stochastic exchange formula. In Section III, the method is validated for two small molecules, N₂ and CO, and is then applied to a two-dimensional (2D) MoS₂ sheet with almost 1500 electrons. Finally, we conclude in Section IV.

II. METHODOLOGY

We only consider the Γ -point in the Brillouin zone, where we use real KS orbitals. In the following, we use the indices *i*, *j*, *k* ... to label occupied KS orbitals; σ , τ ... to denote their spins; and α , β ... to label excited states.

A. TDDFT Formalism Using Deterministic RSHs. The action of the GKS Hamiltonian on each KS orbital is

$$H^{\sigma}|\psi_{i\sigma}\rangle = \left(-\frac{1}{2}\nabla^{2} + V_{\rm loc}^{\sigma} + V_{\rm NL} + k_{\sigma}^{\gamma}\right)|\psi_{i\sigma}\rangle \tag{1}$$

where V_{loc}^{σ} is the KS effective local potential, consisting of Hartree, local XC, and local pseudopotential terms. $V_{\rm NL}$ is the nonlocal pseudopotential. k_{σ}^{γ} is the range-separated exchange operator that acts on the KS orbital as

$$k_{\sigma}^{\gamma}|\psi_{i\sigma}\rangle = -\sum_{j} \int \psi_{j\sigma}(r) u_{\rm C}^{\gamma}(|r-r'|)\psi_{j\sigma}^{*}(r')\psi_{i\sigma}(r')\mathrm{d}r'$$
⁽²⁾

Here, $u_{\rm C}^{\gamma}(r) = r^{-1} \operatorname{erf}(\gamma r)$ accounts for long-range contributions to the nonlocal exchange and γ is the range-separation parameter. The ground-state GKS-DFT equation is then

$$H^{\sigma}|\psi_{i\sigma}\rangle = \sum_{j} \epsilon_{ij\sigma}|\psi_{j\sigma}\rangle$$
(3)

with the orthonormal condition $\langle \psi_{i\sigma} | \psi_{j\tau} \rangle = \delta_{ij} \delta_{\sigma\tau}$ and $\epsilon_{ij\sigma} = \delta_{ij} \epsilon_{i\sigma}$ is the energy of the *i*th KS orbital.

The excited-state energies and wave functions can be obtained by solving a non-Hermitian eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_{\alpha}^{+} \\ \boldsymbol{\psi}_{\alpha}^{-} \end{pmatrix} = \omega_{\alpha} \begin{pmatrix} -\mathbf{I} & 0 \\ 0 & \mathbf{I} \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}_{\alpha}^{+} \\ \boldsymbol{\psi}_{\alpha}^{-} \end{pmatrix}$$
(4)

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which is analogous to Casida's equation.³ Here, ω_{α} is the α th excitation energy, I is the identity matrix, and ψ_{α}^{\pm} is the linearresponse orbital. Note that the linear-response orbital $|\psi_{i\sigma}^{+}\rangle$ corresponds to $\sum_{b} X_{ib\sigma} |\psi_{b\sigma}\rangle$ in Casida's equation and $|\psi_{i\sigma}\rangle$ corresponds to $\sum_{b} Y_{ib\sigma} |\psi_{b\sigma}\rangle$, where *b* labels the unoccupied KS orbitals. $\sum_{i} (|\psi_{i\sigma}\rangle \langle \psi_{i\sigma}^{+}| + |\psi_{i\sigma}^{-}\rangle \langle \psi_{i\sigma}|)$ represents the KS transition density matrix. The linear-response orbital is directly expanded by the plane-wave basis in the virtual space which is orthogonal to the occupied orbitals. The use of the plane-wave representation with a projector to remove the contribution of the occupied space avoids the need to obtain all the (unknown) virtual orbitals and enables the efficient calculations of absorption spectra. ^{52,53}

The matrix operators ${\bf A}$ and ${\bf B}$ act on the linear-response orbitals

$$[\mathbf{A}\boldsymbol{\psi}^{\pm}]_{i\sigma} = \sum_{j} (H^{\sigma}\delta_{ij} - \epsilon_{ij\sigma})|\boldsymbol{\psi}_{j\sigma}^{\pm}\rangle \\ + \sum_{j\tau} \langle P_{c}^{\sigma}\boldsymbol{\psi}_{i\sigma}|K_{\sigma\tau}|\boldsymbol{\psi}_{j\tau}P_{c}^{\tau}\boldsymbol{\psi}_{j\tau}^{\pm}\rangle \\ [\mathbf{B}\boldsymbol{\psi}^{\pm}]_{i\sigma} = \sum_{j\tau} \langle P_{c}^{\sigma}\boldsymbol{\psi}_{i\sigma}|K_{\sigma\tau}|P_{c}^{\tau}\boldsymbol{\psi}_{j\tau}^{\pm}\boldsymbol{\psi}_{j\tau}\rangle$$
(5)

where $P_c^{\sigma} = 1 - \sum_i |\psi_{i\sigma}\rangle \langle \psi_{i\sigma}|$ is a projection operator to the virtual space which is required to avoid the explicit use of virtual orbitals and $K_{\sigma\tau}$ is the Hartree and XC kernel. The kernel is labeled as (note that the expression below is a function of r)

Here, $n^{\sigma}(r)$ is the charge density with spin σ and $E_{\rm xc}$ is the local XC functional. The last term in eq 6 is the RSH element, denoted henceforth as $\langle \psi_{j\sigma}|K_{\rm RSH}|\psi_{kr}\psi_{lr}\rangle$. We employ an iterative algorithm⁵⁴ to determine the low-lying eigenvalues and eigenvectors of the large non-Hermitian matrix in eq 4.

A Lagrangian is constructed to calculate the ionic force associated with the α th excited state¹¹

$$\hat{\mathcal{L}}_{\alpha}[x, \psi, \mathbf{Z}, \Gamma] = \mathcal{M}[x, \psi] + \sum_{ij\sigma} \langle Z_{i\sigma} | (H^{\sigma} \delta_{ij} - \varepsilon_{ij\sigma}) | \psi_{j\sigma} \rangle$$
$$- \sum_{i \ge j, \sigma} \Gamma_{ij\sigma} (\langle \psi_{i\sigma} | \psi_{j\sigma} \rangle - \delta_{ij})$$
(7)

by enforcing the Brillouin condition and the orthonormal condition for the KS orbitals, where x denotes the ionic coordinate. In the abovementioned equation, the functional \mathcal{M} is

$$\mathcal{M} \equiv (\boldsymbol{\psi}_{\alpha}^{+} \ \boldsymbol{\psi}_{\alpha}^{-}) \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + \omega_{\beta} \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix} \right] \begin{pmatrix} \boldsymbol{\psi}_{\alpha}^{+} \\ \boldsymbol{\psi}_{\alpha}^{-} \end{pmatrix}$$
(8)

The multipliers **Z** and Γ are determined from the stationary condition of the Lagrangian $\delta \hat{\mathcal{L}}_{\alpha} / \delta \psi_i = 0$. The ionic force in the excited states is the partial derivative of the Lagrangian with respect to the ionic coordinate $F_{\alpha} = -\partial \hat{\mathcal{L}}_{\alpha} / \partial x$, while the charge density of the α th excited state is obtained from the derivative of the Lagrangian with respect to the external potential, $\rho_{\alpha}^{\text{ex}} = -\delta \hat{\mathcal{L}}_{\alpha} / \delta V_{\text{ext}}$.

B. Stochastic Representation of RSHs in TDDFT. Following ref 40, we introduce an occupied-projected random orbital

$$|\eta_{\sigma}\rangle = \sum_{i} |\psi_{i\sigma}\rangle \langle \psi_{i\sigma} |\xi\rangle \tag{9}$$

Here, $\xi(r) = \pm 1/\sqrt{\Delta V}$ are random functions, with a random sign at each real-space grid point, and ΔV is the volume per grid point. A stochastic representation of the identity operator is expressed as⁵⁵

$$[|\xi\rangle\langle\xi|]_{\xi} = 1 \tag{10}$$

where $[\cdots]_{\xi}$ denotes the average over all random functions ξ . Thus, we use the stochastic orbitals to calculate the zero-order KS density matrix

$$[|\eta_{\sigma}\rangle\langle\eta_{\sigma}|]_{\xi} = \sum_{ij} [|\psi_{i\sigma}\rangle\langle\psi_{i\sigma}|\xi\rangle\langle\xi|\psi_{j\sigma}\rangle\langle\psi_{j\sigma}|]_{\xi} = \sum_{i} |\psi_{i\sigma}\rangle\langle\psi_{i\sigma}|$$
(11)

The range-separated exchange kernel is also determined stochastically

$$u_{C}^{\gamma}(|r - r'|) = [\zeta(r)\zeta^{*}(r')]_{\varphi}$$
(12)

with

$$\zeta(r) = \frac{1}{(2\pi)^3} \int \sqrt{\overline{u}_C^{\gamma}(k)} e^{i\varphi(k)} e^{ik\cdot r} dk$$
(13)

where $\overline{u}_{C}^{\prime}(k)$ is the Fourier transform of $u_{C}^{\prime}(r)$ and $\varphi(k)$ is a random phase (with a value between 0 and 2π) at each k point. By defining a stochastic orbital $|\chi_{\sigma}\rangle$,

$$|\chi_{\sigma}\rangle = \zeta(r)|\eta_{\sigma}\rangle \tag{14}$$

we then have the stochastic formulation of the RSH in the GKS Hamiltonian as

$$k_{\sigma}^{\gamma}|\psi_{i\sigma}\rangle = -[|\chi_{\sigma}\rangle\langle\chi_{\sigma}|\psi_{i\sigma}\rangle]_{\xi,\varphi}$$
⁽¹⁵⁾

In actual applications, we construct and store in memory a priori a finite number N_{χ} of pairs of random functions $\{\xi(r),\zeta(k)\}$. The stochastic orbitals $|\chi_{\sigma}\rangle$ are calculated on the fly with the updated KS-occupied orbitals $|\psi_{i\sigma}\rangle$.

Next, we present the stochastic formulation of RSHs in the context of eq 5. The occupied-projected random linear-response orbital is introduced as

$$\left|\eta_{\sigma}^{\pm}\right\rangle = \sum_{i} \left|\psi_{i\sigma}^{\pm}\right\rangle \langle\psi_{i\sigma}|\xi\rangle \tag{16}$$

which leads to a stochastic representation of the first-order KS density matrix as

$$\sum_{i} (|\psi_{i\sigma}\rangle\langle\psi_{i\sigma}^{\pm}| + |\psi_{i\sigma}^{\pm}\rangle\langle\psi_{i\sigma}|) = [|\eta_{\sigma}\rangle\langle\eta_{\sigma}^{\pm}| + |\eta_{\sigma}^{\pm}\rangle\langle\eta_{\sigma}|]_{\xi}$$
(17)

The stochastic linear-response orbital $|\chi_{\sigma}^{\pm}\rangle$ is then defined as

 $|\chi_{\sigma}^{\pm}\rangle = \zeta(r)|\eta_{\sigma}^{\pm}\rangle \tag{18}$

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The RSH components in eq 5 can thus be calculated stochastically because

$$\sum_{j} \langle \psi_{i\sigma} | K_{\rm RSH} | \psi_{j\sigma} \psi_{j\sigma}^{\pm} \rangle = -[|\chi_{\sigma}^{\pm} \rangle \langle \chi_{\sigma} | \psi_{i\sigma} \rangle]_{\xi,\varphi}$$
(19)

and

$$\sum_{j} \langle \psi_{i\sigma} | K_{\text{RSH}} | \psi_{j\sigma}^{\pm} \psi_{j\sigma} \rangle = -[|\chi_{\sigma}\rangle \langle \chi_{\sigma}^{\pm} | \psi_{i\sigma} \rangle]_{\xi,\varphi}$$
(20)

In linear-response TDDFT, all occupied orbitals $|\psi_{i\sigma}\rangle$ are fixed and the stochastic linear-response orbitals $|\chi_{\sigma}^{\pm}\rangle$ are calculated on the fly by using the updated linear-response orbitals $|\psi_{i\sigma}^{\pm}\rangle$.

C. Cost Saving with Stochastic TDDFT. The numerically dominant cost is the action of the exchange. We now briefly analyze the savings because of the use of stochastic exchange, following ref 40. In deterministic GKS-DFT and GKS-TDDFT, when acting with the exchange kernel on all occupied orbitals, there are N_{occ}^2 (i.e., all pairs) Coulomb convolution integrals, each costing about $10N_{plw} \log_2 N_{plw}$ double-precision operations. The number of operations is about $200N_{plw}$ for large system sizes with $N_{plw} \approx 10^5 - 10^7$. Thus, the total cost per action of the exchange is about $200N_{occ}^2N_{plw}$. In contrast, in the stochastic exchange [eqs 15, 19, and 20], the cost per occupied orbital is twice that of applying N_{χ} dot products, each costing $2N_{plw}$, that is, the total exchange-kernel cost per iteration is circa $4N_{\chi}N_{occ}N_{plw}$. Therefore, the ratio of the cost between deterministic and stochastic exchange is $50 N_{occ}/N_{\chi}$.

For small systems, where a large range-separation parameter γ is used, N_{χ} is around 1000, so the breakeven point is around 20 occupied orbitals, that is, systems with few tens of electrons. For large systems with thousands of electrons, $N_{\chi} \approx 50-100$ is sufficient to yield converged results. Thus, the stochastic calculation saves about a factor of around $N_{\rm occ}$ relative to the deterministic calculation. For such large systems, the cost of applying the stochastic exchange is no more than that of local-exchange (or no-exchange) KS-TDDFT, where the computationally most demanding step is applying the kinetic energy (circa $200N_{\rm occ}N_{\rm plw}$). Thus, the stochastic exchange GKS-TDDFT for large systems just approximately doubles the cost of no-exchange KS-TDDFT (i.e., linear-response random-phase approximation).

These considerations do not change when we use PAW, as detailed in the next section. Also, note that the underlying TDDFT approach is based on the plane-wave basis so that it is fully converged with respect to the virtual orbital basis. It is possible to also employ similar stochastic-TDDFT approaches with any AO basis sets, highly local or not, although this will not be pursued here.

D. PAW Formalism. Pseudopotentials are routinely used in conjunction with plane-wave methods. Here, we focus on the PAW pseudopotential, which provides a higher transferability and a lower energy cutoff than the norm-conserving pseudopotentials.^{56,57} In PAW, the all-electron (AE) wave function $|\psi_{i\sigma}\rangle$ is a linear transformation of the pseudo-wave-function (PS) $|\tilde{\psi}_i\rangle$

$$|\psi_{i\sigma}\rangle = \mathcal{T}|\widetilde{\psi}_{i\sigma}\rangle = |\widetilde{\psi}_{i\sigma}\rangle + \sum_{I} (|\phi_{I}\rangle - |\widetilde{\phi}_{I}\rangle)\langle \widetilde{p}_{I}|\widetilde{\psi}_{i\sigma}\rangle$$
(21)

where ϕ_I , ϕ_D and \tilde{p}_I are AE partial waves, PS partial waves, and projector functions, respectively, defined in the core region.

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The index I also includes the angular momentum quantum numbers and an additional index for the reference energy. In the following, the tilde symbols represent the PS wave functions and operators, which are evaluated on the planewave grid. By using PAW, the ground-state GKS equation in eq 3 is expressed as

$$\tilde{H}^{\sigma}|\tilde{\psi}_{i\sigma}\rangle = \sum_{j} \epsilon_{ij\sigma} \tilde{S}|\tilde{\psi}_{j\sigma}\rangle$$
(22)

with the orthonormal condition $\langle \tilde{\psi}_{i\sigma} | \tilde{S} | \tilde{\psi}_{j\tau} \rangle = \delta_{ij} \delta_{\sigma\tau}$ and $\tilde{S} = \mathcal{T}^{\dagger} \mathcal{T}$ is the overlap operator.

The action of the GKS Hamiltonian on the PS orbital is given by 51,58

$$\begin{split} \tilde{H}^{\sigma} | \widetilde{\psi}_{i\sigma} \rangle &= \left(-\frac{1}{2} \nabla^2 + \tilde{V}_{loc}^{\sigma} \right) | \widetilde{\psi}_{i\sigma} \rangle \\ &+ \sum_{IJ} | \tilde{p}_I \rangle (\hat{D}_{IJ} [\tilde{V}_{loc}^{\sigma}] + D_{IJ}^1 - \tilde{D}_{IJ}^1) \langle \tilde{p}_J | \widetilde{\psi}_{i\sigma} \rangle \\ &+ \tilde{k}_{\sigma}^{\gamma} | \widetilde{\psi}_{i\sigma} \rangle \end{split}$$
(23)

Here, we have several additional PAW terms compared to eq 1. The PAW tensor in the Hamiltonian is $\hat{D}_{IJ}[\tilde{V}] = \sum_{LM} \int \tilde{V}(r)$ $\hat{Q}_{IJ}^{LM}(r) dr$ and for the definitions of the functions $\hat{Q}_{IJ}^{LM}(r)$, see, for example, Eq 27 of ref 51. The difference $(D_{IJ}^{I} - \tilde{D}_{IJ}^{I})$ is calculated as $\partial (E^1 - \tilde{E}^1) / \partial \rho_{IJ}^{\sigma}$, where E^1 and \tilde{E}^1 are parts of the total energy computed on the radial grid⁵¹ and $\rho_{IJ}^{\sigma} = \sum_i \langle \tilde{\psi}_{i\sigma} | \tilde{p}_I \rangle \langle \tilde{p}_J | \tilde{\psi}_{i\sigma} \rangle$ is the occupancy of each augmentation channel (I, J).

Within PAW, the range-separated exchange operator $\tilde{k}^{\prime}_{\sigma}$ acts on the PS orbital as

$$\begin{split} \tilde{k}_{\sigma}^{\gamma} | \widetilde{\psi}_{i\sigma} \rangle &= -\sum_{j} \tilde{V}_{\text{RSH}} [\tilde{n}_{ji\sigma} + \hat{n}_{ji\sigma}] | \widetilde{\psi}_{j\sigma} \rangle \\ &- \sum_{j,IJ} | \tilde{p}_{I} \rangle \hat{D}_{IJ} [\tilde{V}_{\text{RSH}}] \langle \tilde{p}_{J} | \widetilde{\psi}_{j\sigma} \rangle \\ &- \sum_{(I,K)(J,L)} (K^{1}_{IJLK} - \tilde{K}^{1}_{IJLK}) \rho_{LJ}^{\sigma} | \tilde{p}_{I} \rangle \langle \tilde{p}_{K} | \widetilde{\psi}_{i\sigma} \rangle \end{split}$$

$$(24)$$

Here, $\tilde{V}_{\rm RSH}$ is the range-separated exchange potential, expressed as

$$\tilde{V}_{\text{RSH}}[\tilde{n}_{ji\sigma} + \hat{n}_{ji\sigma}] = \int u_C^{\gamma} (|r - r'|) [\tilde{n}_{ji\sigma}(r') + \hat{n}_{ji\sigma}(r')] dr'$$
(25)

where $\tilde{n}_{ij\sigma} = \tilde{\psi}_{i\sigma}^* \tilde{\psi}_{j\sigma}$ is the PS charge density and \hat{n} is the compensation charge density

$$\hat{n}_{ij\sigma}(r) = \sum_{IJ,LM} \langle \widetilde{\psi}_{i\sigma} | \tilde{p}_I \rangle \langle \tilde{p}_J | \widetilde{\psi}_{j\sigma} \rangle \hat{Q}_{IJ}^{LM}(r)$$
(26)

Both \tilde{n} and \hat{n} are calculated on the uniform plane-wave grid. K_{IJLK}^1 (\tilde{K}_{IJLK}^1) is the two-electron four-AE (PS)-partial-wave integral⁵⁸ obtained using the range-separated exchange kernel $u_C^{r}(r)$.

By using PAW, the kernel in eq 6 becomes¹⁵

$$\begin{split} \langle \widetilde{\psi}_{j\sigma} | \widetilde{K}_{\sigma\tau} | \widetilde{\psi}_{k\tau} \widetilde{\psi}_{l\tau} \rangle &= \left\{ \widetilde{V}_{H} [\widetilde{n}_{kl\tau} + \widehat{n}_{kl\tau}] + \frac{\delta^{2} E_{xc}}{\delta n^{\sigma} \delta n^{\tau}} (\widetilde{n}_{kl\tau} + \widehat{n}_{kl\tau}) \right\} \\ & | \widetilde{\psi}_{j\sigma} \rangle + \sum_{IJ} | \widetilde{p}_{I} \rangle \widehat{D}_{IJ} \Big[\widetilde{V}_{H} [\widetilde{n}_{kl\tau} + \widehat{n}_{kl\tau}] \\ & + \frac{\delta^{2} E_{xc}}{\delta n^{\sigma} \delta n^{\tau}} (\widetilde{n}_{kl\tau} + \widehat{n}_{kl\tau}) \Big] \langle \widetilde{p}_{J} | \widetilde{\psi}_{j\sigma} \rangle \\ & + \sum_{IJ,I'J'} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{J} | \widetilde{\psi}_{j\sigma} \rangle \frac{\delta^{2} (E^{1} - E^{1})}{\delta \rho_{IJ}^{\sigma} \delta \rho_{IJ'}^{\tau}} \langle \widetilde{\psi}_{k\tau} | \widetilde{p}_{I'} \rangle \\ & \langle \widetilde{p}_{J'} | \widetilde{\psi}_{l\tau} \rangle + \delta_{\sigma\tau} \langle \widetilde{\psi}_{j\sigma} | \widetilde{K}_{RSH} | \widetilde{\psi}_{k\sigma} \widetilde{\psi}_{l\sigma} \rangle \tag{27} \end{split}$$

where $\tilde{V}_{\rm H}$ is the Hartree potential. The RSH part in the kernel functional is expressed by

$$\begin{split} \langle \widetilde{\psi}_{j\sigma} | \tilde{K}_{\text{RSH}} | \widetilde{\psi}_{k\sigma} \widetilde{\psi}_{l\sigma} \rangle &= -\tilde{V}_{\text{RSH}} [\tilde{n}_{kj\sigma} + \hat{n}_{kj\sigma}] | \widetilde{\psi}_{l\sigma} \rangle \\ &- \sum_{IJ} | \tilde{p}_{I} \rangle \hat{D} [\tilde{V}_{\text{RSH}}] \langle \tilde{p}_{J} | \widetilde{\psi}_{l\sigma} \rangle \\ &- \sum_{(I,K)(J,L)} (K^{1}_{IJLK} - \tilde{K}^{1}_{IJLK}) | \tilde{p}_{I} \rangle \langle \tilde{p}_{K} | \widetilde{\psi}_{j\sigma} \rangle \\ &\langle \widetilde{\psi}_{k\sigma} | \tilde{p}_{L} \rangle \langle \tilde{p}_{J} | \widetilde{\psi}_{l\sigma} \rangle \end{split}$$

$$(28)$$

The occupied-projected random orbital (eq 9) and random linear-response orbital (eq 16) in PAW are

$$|\widetilde{\eta}_{\sigma}\rangle = \sum_{i} |\widetilde{\psi}_{i\sigma}\rangle \langle \widetilde{\psi}_{i\sigma} | \widetilde{S}^{1/2} | \xi \rangle$$
⁽²⁹⁾

and

$$|\tilde{\eta}_{\sigma}^{\pm}\rangle = \sum_{i} |\tilde{\psi}_{i\sigma}^{\pm}\rangle \langle \tilde{\psi}_{i\sigma} |\tilde{\delta}^{1/2}|\xi\rangle$$
(30)

respectively. The stochastic orbital $|\tilde{\chi}_{\sigma}\rangle$ (eq 14) and the stochastic linear-response orbital $|\tilde{\chi}_{\sigma}^{\pm}\rangle$ (eq 18) are then

$$|\widetilde{\chi}_{\sigma}\rangle = \zeta(r)|\widetilde{\eta}_{\sigma}\rangle + \sum_{IJLM} |\widetilde{p}_{I}\rangle\langle \widetilde{p}_{J}|\widetilde{\eta}_{\sigma}\rangle \int \hat{Q}_{IJ}^{LM}(r')\zeta(r')dr'$$
(31)

and

$$|\widetilde{\chi}_{\sigma}^{\pm}\rangle = \zeta(r)|\widetilde{\eta}_{\sigma}^{\pm}\rangle + \sum_{IJLM} |\widetilde{p}_{I}\rangle\langle\widetilde{p}_{J}|\widetilde{\eta}_{\sigma}^{\pm}\rangle \int \hat{Q}_{IJ}^{LM}(r')\zeta(r')dr'$$
(32)

The stochastic RSH (eq 15) is thus reformulated within PAW as

$$\begin{split} \tilde{k}_{\sigma}^{\gamma} | \widetilde{\psi}_{i\sigma} \rangle &= -[l \widetilde{\chi}_{\sigma} \rangle \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{i\sigma} \rangle]_{\xi,\varphi} - \sum_{(I,K)(J,L)} \left(K_{IJLK}^{1} - \tilde{K}_{IJLK}^{1} \right) | \tilde{p}_{I} \rangle \\ & \langle \tilde{p}_{K}^{} | \widetilde{\psi}_{i\sigma} \rangle [\tilde{p}_{J}^{} | \widetilde{\eta}_{\sigma} \rangle \langle \widetilde{\eta}_{\sigma}^{} | \tilde{p}_{L}^{} \rangle]_{\xi} \end{split}$$

$$(33)$$

Similarly, eqs 19 and 20 are re-expressed as

$$\begin{split} \sum_{j} \langle \widetilde{\psi}_{i\sigma} | \widetilde{K}_{\text{RSH}} | \widetilde{\psi}_{j\sigma} \widetilde{\psi}_{j\sigma}^{\pm} \rangle \\ &= - [| \widetilde{\chi}_{\sigma}^{\pm} \rangle \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{i\sigma} \rangle]_{\xi,\varphi} - \sum_{(I,K)(J,L)} (K_{IJLK}^{1} - \widetilde{K}_{IJLK}^{1}) | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} | \\ & \widetilde{\psi}_{i\sigma} \rangle [\widetilde{p}_{J} | \widetilde{\eta}_{\sigma}^{\pm} \rangle \langle \widetilde{\eta}_{\sigma} | \widetilde{p}_{L} \rangle_{\xi} \end{split}$$
(34)

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Figure 1. Energy difference between the stochastic and deterministic results of the lowest-energy singlet excited state as a function of the number of stochastic orbitals N_{χ} for the N₂ molecule with (a) $\gamma = 0.2$ Å⁻¹ and (b) $\gamma = 0.62$ Å⁻¹ and the CO molecule with (c) $\gamma = 0.2$ Å⁻¹ and (d) $\gamma = 0.62$ Å⁻¹. The error bars scale the statistical errors. The red-dashed lines indicate the zero difference.

and

$$\sum_{j} \langle \widetilde{\psi}_{i\sigma} | \widetilde{K}_{\text{RSH}} | \widetilde{\psi}_{j\sigma}^{\pm} \widetilde{\psi}_{j\sigma} \rangle$$

= $-[|\widetilde{\chi}_{\sigma} \rangle \langle \widetilde{\chi}_{\sigma}^{\pm} | \widetilde{\psi}_{i\sigma} \rangle]_{\xi,\varphi} - \sum_{(I,K)(J,L)} (K^{1}_{IJLK} - \widetilde{K}^{1}_{IJLK}) | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} |$
 $\widetilde{\psi}_{i\sigma} \rangle [\widetilde{p}_{J} | \widetilde{\eta}_{\sigma} \rangle \langle \widetilde{\eta}_{\sigma}^{\pm} | \widetilde{p}_{L} \rangle_{\xi}$ (35)

The ionic force in the excited state is obtained as the negative derivative of the Lagrangian $\hat{\mathcal{L}}_{\alpha}$ at its stationary point. Because $\hat{\mathcal{L}}_{\alpha}$ is fully variational, the first-order derivative with respect to an ionic coordinate *x* does not involve any chain-rule derivatives of its variables, that is, KS orbitals, linear-response orbitals, and stochastic orbitals. Thus, the partial derivatives of the RSH elements in $\hat{\mathcal{L}}_{\alpha}$ are entirely because of the explicit dependence of the PAW projector functions $|\tilde{p}_I\rangle$ and the function \hat{Q}_{IJ}^{LM} on *x*. The partial derivatives of the stochastic RSH elements in the GKS Hamiltonian is

$$\left\langle \widetilde{\psi}_{i\sigma} \left| \frac{\partial \widetilde{k}_{\sigma}^{\gamma}}{\partial x} \right| \widetilde{\psi}_{j\sigma} \right\rangle$$

$$= - \left[\frac{\partial \langle \widetilde{\psi}_{i\sigma} | \widetilde{\chi}_{\sigma} \rangle}{\partial x} \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{j\sigma} \rangle + \langle \widetilde{\psi}_{i\sigma} | \widetilde{\chi}_{\sigma} \rangle \frac{\partial \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{j\sigma} \rangle}{\partial x} \right]_{\xi,\varphi}$$

$$- \sum_{(I,K)(I,L)} K^{1}_{IJLK} - \widetilde{K}^{1}_{IJLK}$$

$$\left\{ \frac{\partial \langle \widetilde{\psi}_{i\sigma} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} | \widetilde{\psi}_{j\sigma} \rangle}{\partial x} [\langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma} \rangle \langle \widetilde{\eta}_{\sigma} | \widetilde{p}_{L} \rangle]_{\xi}$$

$$+ \langle \widetilde{\psi}_{i\sigma} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} | \widetilde{\psi}_{j\sigma} \rangle \left[\frac{\partial \langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma} \rangle \langle \widetilde{\eta}_{\sigma} | \widetilde{p}_{L} \rangle}{\partial x} \right]_{\xi} \right\}$$

$$(36)$$

where the partial derivative of an inner product between a KS orbital and a stochastic orbital is calculated by

$$\frac{\partial \langle \widetilde{\psi}_{i\sigma} | \widetilde{\chi}_{\sigma} \rangle}{\partial x} = \sum_{IJLM} \frac{\partial \langle \widetilde{\psi}_{i\sigma} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma} \rangle}{\partial x} \int \hat{Q}_{IJ}^{LM}(\vec{r}') \zeta(\vec{r}') d\vec{r}'
+ \sum_{IJLM} \langle \widetilde{\psi}_{i\sigma} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma} \rangle \int \frac{\partial \hat{Q}_{IJ}^{LM}(\vec{r}')}{\partial x} \zeta(\vec{r}') d\vec{r}'$$
(37)

The partial derivative of stochastic RSH elements in the kernel functional is similarly calculated. For example,

$$\begin{split} \frac{\partial \sum_{ij\sigma} \langle \widetilde{\psi}_{i\sigma}^{\pm} \widetilde{\psi}_{i\sigma}^{i} | \widetilde{K}_{\text{RSH}} | \widetilde{\psi}_{j\sigma}^{i} \widetilde{\psi}_{j\sigma}^{\pm} \rangle}{\partial x} \\ &= -\sum_{i\sigma} \left[\frac{\partial \langle \widetilde{\psi}_{i\sigma}^{\pm} | \widetilde{\chi}_{\sigma}^{\pm} \rangle}{\partial x} \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{j\sigma} \rangle + \langle \widetilde{\psi}_{i\sigma}^{\pm} | \widetilde{\chi}_{\sigma}^{\pm} \rangle \frac{\partial \langle \widetilde{\chi}_{\sigma} | \widetilde{\psi}_{i\sigma} \rangle}{\partial x} \right]_{\xi,\varphi} \\ &- \sum_{i\sigma(I,K)(J,L)} (K_{IJLK}^{1} - \widetilde{K}_{IJLK}^{1}) \\ &\left\{ \frac{\partial \langle \widetilde{\psi}_{i\sigma}^{i} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} | \widetilde{\psi}_{i\sigma} \rangle}{\partial x} [\langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma}^{\pm} \rangle \langle \widetilde{\eta}_{\sigma}^{i} | \widetilde{p}_{L} \rangle]_{\xi} \right. \\ &\left. + \langle \widetilde{\psi}_{i\sigma}^{\pm} | \widetilde{p}_{I} \rangle \langle \widetilde{p}_{K} | \widetilde{\psi}_{i\sigma} \rangle \left[\frac{\partial \langle \widetilde{p}_{J} | \widetilde{\eta}_{\sigma}^{\pm} \rangle \langle \widetilde{\eta}_{\sigma}^{i} | \widetilde{p}_{L} \rangle}{\partial x} \right]_{\xi} \right\}$$
(38)

III. NUMERICAL EXAMPLES

The approach presented here is general and can be implemented in any plane-wave PAW software package as a plug-and-compute module. In the present work, the groundstate calculations are carried out with the Vienna Ab Initio Simulation Package (VASP).^{59,60} To expedite the selfconsistent convergence, the fully self-consistent ground-state GKS-DFT calculations are performed following a few non-selfconsistent DFT iterations without the stochastic RSH potential. The ground-state charge density and KS orbitals are then taken as the input for GKS-TDDFT which is used to compute the excited-state properties, including excitation energy, exciton charge density, and ionic force.

To validate the stochastic formulation, we calculate the excitation energy of the lowest-energy singlet excited state for two small molecules, N₂ and CO. The spin-restricted ground-state calculations are performed with supercell dimensions of 20 Å × 20 Å × 20 Å. The energy cutoff of the plane-wave basis is 400 eV. Here, the local adiabatic XC functional is the Perdew–Burke–Ernzerhof (PBE) GGA.⁶¹ The short-range exchange interaction is incorporated by modifying the conventional GGA exchange.⁴⁶

We use $\gamma = 0.62 \text{ Å}^{-1}$ for the range-separation parameter, a value that has been successfully used for these two molecules.⁶² To examine the effect of γ on the statistical errors, we have also considered a smaller range-separation parameter $\gamma = 0.2$ Å⁻¹. Figure 1 depicts the energy difference between the stochastic and deterministic values of the excitation energy as a function of the number of stochastic orbitals N_{γ} . The expectation values are estimated from 10 samples of independent stochastic TDDFT simulations, each with a different set of random functions $|\xi\rangle$. The statistical errors are estimated from the standard deviation of these 10 samples. Clearly, the excitation energies converge as N_{γ} increases. In addition, the stochastic fluctuations become smaller as the range-separation parameter decreases. Thus, a smaller value of N_{γ} is sufficient for convergence when γ is smaller. For example, with $N_{\gamma} = 40$, the energy fluctuation of N₂ is within 0.05 eV for $\gamma = 0.2$ Å⁻¹, while it is about 0.5 eV for $\gamma = 0.62$ Å⁻¹. Similarly, for the smaller γ , N_{γ} = 200 converges the excitation energy with a statistical error less than 0.02 eV. However, for the larger γ , N_{γ} > 800 is necessary for a statistical error of less than 0.1 eV.

Similar results have been observed previously in the calculation of the GKS-DFT orbital energy for hydrogenpassivated silicon nanocrystals.⁴⁰ The reduction of stochastic fluctuations is due to a smaller contribution of the nonlocal exchange to the one-body Hamiltonian for smaller γ . The fact that the number of stochastic orbitals decreases with the system size makes the current method very appealing for solids, where explicit exchange is needed only at long distances, that is, the range-separation parameter is usually much smaller than that in molecules.⁶³ Further, while the reduction in γ (and therefore the reduction in N_{χ}) was only studied here for excitonic states, we expect that an even smaller γ (and therefore a smaller N_{χ}) would be required for charge transfer excitations where the charge is more separated.

As shown in Figure 1, the convergence of the GKS-TDDFT energy is always from below, that is, at a finite N_{χ} , the results will have a slight bias toward smaller excitations. A finite N_{χ} simulation yields excitations that have a statistical deviation (decreasing by $1/\sqrt{N_{\chi}}$) around an average value which is slightly different from the infinite- N_{χ} limit (i.e., the deterministic) by an amount-labeled "bias". The bias decreases by $1/N_{\chi}$ and is a general phenomenon in stochastic simulations that involve self-consistency or more general iterations. Such bias appears, for example, in stochastic DFT^{42,64} and GF2.⁶⁵

Next, we apply the method to an extended system of 2D MoS_2 . The pristine 2D MoS_2 is modeled by (9 × 9) units with 81 Mo atoms and 162 S atoms. There are 1458 valence electrons in this system. In the GKS-TDDFT calculations, 80 occupied orbitals are included. We confirmed that this number yields converged results for both energy and ionic force of the lowest-energy excited state. The GKS-TDDFT calculations are

performed without the spin—orbit coupling. The optimal value of the range-separation parameter is found to be $\gamma = 0.07$ Å⁻¹ for 2D MoS₂. $N_{\chi} = 80$ stochastic orbitals are sufficient for converging both the fundamental and optical band gaps with a statistical error of less than 0.01 eV. Furthermore, because of the small value of γ , the bias is tiny (less than 5 meV) and the statistical error is also tiny, less than 0.01 eV.

The fundamental band gap (E_g) is found to be 2.78 eV, and the optical band gap (E_{opt}) is found to be 1.71 eV. The exciton binding energy, defined as $E_b = E_g - E_{opt}$, is thus 1.07 eV. These values are in very good agreement with previous GW-BSE results ($E_g = 2.84 \text{ eV}$, $E_{opt} = 1.88 \text{ eV}$, and $E_b = 0.96 \text{ eV}$)⁶⁶ and ($E_g = 2.82 \text{ eV}$, $E_{opt} = 1.78 \text{ eV}$, and $E_b = 1.04 \text{ eV}$)⁶⁷ for the infinite 2D MoS₂ sheet. In Figure 2a, we show the charge



Figure 2. Charge densities of lowest-energy singlet excitons in (a) pristine MoS₂ and (b) MoS₂ with a single S vacancy. The charge density of the electron and the hole is colored green and blue, respectively. The isosurface levels are set at 9×10^{-5} e/Å³ in (a) and 3×10^{-4} e/Å³ in (b). The purple and yellow spheres represent Mo and S atoms, respectively.

density of the lowest-energy singlet exciton in pristine MoS_2 . The electron (green) and hole (blue) projections are delocalized over the 2D plane, characteristic of a Mott–Wannier exciton. The Bohr radius of the exciton cannot be extracted from the exciton charge density. Instead, it can be estimated based on the two-particle wave function and this is left open for future study. We note that despite the underestimation of the fundamental band gap $E_g = 1.68 \text{ eV}$ and the neglection of excitonic binding, the PBE functional provides a good estimate of the optical band gap, $E_{opt} = 1.69 \text{ eV}$, due to cancellation of errors.

We also examine a point defect in MoS_2 , an S vacancy, which is abundant because of its low formation energy.⁶⁸ This vacancy is modeled by removing an S atom in the middle of the supercell. The local minimum of the ground state (m_0) and first excited state (m_1) potential energy surfaces are obtained through geometric relaxation using GKS-DFT and GKS-TDDFT, respectively, in the presence of the S vacancy. The force convergence criterion for geometric relaxation is 0.03 eV/Å.

We find that the exciton induces a local lattice distortion and is trapped around the S vacancy as manifested by the localized electron and hole, as shown in Figure 2b. This polaronic effect is quantitatively characterized by the polaronic binding energy, $E_{\rm pol}$, the difference in the total energy (ground-state energy plus excitation energy) between the m_0 and m_1 geometries. The polaronic binding energy obtained using the stochastic RSH functional is $E_{\rm pol} = 0.1$ eV. We also performed a geometric relaxation of the excited state with the PBE functional that yields a polaronic binding energy of $E_{\rm pol} =$ 0.08 eV, comparing very well with the RSH result. Thus, PBE could also provide reliable ionic forces of the excited state in addition to the good estimation of the excitation energy in the MoS₂ system. The S vacancy induces two unoccupied defect levels within the gap, reducing the fundamental gap from $E_{\rm g} = 2.78~{\rm eV}$ in pristine MoS₂ to $E_{\rm g} = 2.16~{\rm eV}$ in the m_1 geometry. The optical gap is also decreased from $E_{\rm g} = 1.71~{\rm eV}$ in pristine MoS₂ to $E_{\rm g}$ = 1.09 eV in m_1 . Despite the significant difference in exciton charge density between the pristine and defective MoS₂, that is, delocalization versus localization in real space, the exciton binding energies of the two systems are the same, $E_{\rm b} = 1.07~{\rm eV}$. Therefore, the S vacancy does not affect the electron-hole interaction but could drastically influence their mobility in MoS₂. Previous GW-BSE calculations of MoSe₂ also found that the exciton binding energy remained essentially the same in the presence of the chalcogen vacancy.⁶⁹

IV. CONCLUSIONS

In summary, we have reformulated plane-wave based GKS-TDDFT using a stochastic representation of the optimally tuned RSH functional. The computational cost associated with the exchange operator is significantly reduced by treating the zero-order and first-order KS density matrix with stochastic orbitals and a stochastic decomposition of the Coulomb convolution. For large systems, the method is almost as efficient as a local-potential KS-TDDFT.

Applications to small molecules, N_2 and CO, show that the statistical error induced by the stochastic formulation is controlled by increasing the number of stochastic orbitals and is significantly reduced by using a smaller range-separation parameter. This makes the current method very appealing for extended systems, as demonstrated here by simulating a 2D MoS_2 sheet with ~1500 valence electrons. The fundamental gap, optical gap, and exciton binding energy of pristine MoS_2 obtained with an optimally tuned range-separation parameter compare very well with previous GW-BSE results. The fundamental gap and optical gap are reduced in the presence of S vacancy because of the defect-induced gap states, while the exciton binding energy is not changed. The S vacancy could trap the exciton where both the electron and hole are localized around the defect with a polaronic binding energy of 0.1 eV.

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Notes

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