Combining localized orbital scaling correction and Bethe–Salpeter equation for accurate excitation energies (EP)

(iD) **Jiachen Li**, (iD) **Ye Jin**, (iD) **Neil Qiang Su**, et al.

COLLECTIONS

(EP)   This paper was selected as an Editor's Pick

View Online   Export Citation   CrossMark

Combining localized orbital scaling correction and Bethe–Salpeter equation for accurate excitation energies (EP)

View Online   Export Citation   CrossMark

Jiachen Li, (iD) Ye Jin, (iD) Neil Qiang Su, (iD) and Weitao Yang[a] (iD)

AFFILIATIONS

Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

[a] Author to whom correspondence should be addressed: weitao.yang@duke.edu

ABSTRACT

We applied localized orbital scaling correction (LOSC) in Bethe–Salpeter equation (BSE) to predict accurate excitation energies for molecules. LOSC systematically eliminates the delocalization error in the density functional approximation and is capable of approximating quasiparticle (QP) energies with accuracy similar to or better than GW Green's function approach and with much less computational cost. The QP energies from LOSC, instead of commonly used G_0W_0 and evGW, are directly used in BSE. We show that the BSE/LOSC approach greatly outperforms the commonly used BSE/G_0W_0 approach for predicting excitations with different characters. For the calculations of Truhlar–Gagliardi test set containing valence, charge transfer, and Rydberg excitations, BSE/LOSC with the Tamm–Dancoff approximation provides a comparable accuracy to time-dependent density functional theory (TDDFT) and BSE/evGW. For the calculations of Stein CT test set and Rydberg excitations of atoms, BSE/LOSC considerably outperforms both BSE/G_0W_0 and TDDFT approaches with a reduced starting point dependence. BSE/LOSC is, thus, a promising and efficient approach to calculate excitation energies for molecular systems.

I. INTRODUCTION

Electronic excitation energy is one of the most important quantities for describing the electronic excited states. It can be compared with the 0–0 energy, which is measured by the optical spectroscopy. Computationally, determining the excitation energy from the electronic structure theory plays a critical role in obtaining insights about various phenomena and processes in chemistry, biochemistry, and materials science, such as molecular drug delivery[1,2] and solar cells.[3–5] In the past few decades, much effort has been devoted to develop accurate and efficient theoretical approaches to compute excitation energies. One of the most popular approaches is time-dependent density functional theory (TDDFT).[6–8] TDDFT has been widely implemented in modern quantum chemistry packages to calculate energies, structures, and other properties of excited states for molecular and periodic systems.[9–12] The success of TDDFT stems from the good compromise between the accuracy and the computational cost. However, TDDFT still suffers from several problems. For example, it is known that TDDFT with commonly used density functional approximations (DFAs)

fails to describe Rydberg excitations and charge transfer (CT) excitations.[12,13] This issue can be attributed to the incorrect description for the long-range behavior for the potential energy surface.[14,15] Efforts for correcting the long-range behavior includes using range-separated or Coulomb-attenuated functionals[16–18] and mixing the Hartree–Fock (HF)[19,20] exchange in DFAs.[21] In addition, the failures for describing CT and Rydberg excitations, TDDFT has an undesired dependence on the exchange–correlation (XC) kernel stemming from different choices of DFAs. The difference originating from using different DFAs can exceed 1.0 eV for valence excitation energies and even exceed 2.0 eV for Rydberg excitation energies.[12,13]

Recently, the Bethe–Salpeter equation (BSE)[22–27] in Green's function many-body perturbation theory[26,28] has gained increasing attention to compute optical spectroscopy for molecular systems. The BSE approach commonly takes the energy levels computed from the GW approximation as the input,[26,28–30] and this approach is denoted as the BSE/GW approach. In the BSE/GW approach, the screened interaction is used instead of the bare Coulomb interaction to describe the electron–hole interaction. The screened interaction

is formulated with the quasiparticle (QP) energies from the GW calculation. It is known that the QP energies from GW are more accurate for predicting the HOMO–LUMO gap (fundamental gap) than the conventional Kohn–Sham (KS) orbital energies. In addition to the improved gap prediction, energies also have more clear physical meanings that they are interpreted as the charged excitation energies, or excitation energies for electron removal and addition. It has been shown that the GW approximation substantially improves the accuracy of predicting energy levels over the KS density functional theory (KS-DFT) approach for both occupied and unoccupied states,[26,31,32] which are the key quantities to calculate the excitation energies. Because of the correct long-range behavior in the BSE/GW approach and the importance of the dynamical screening in real systems, BSE/GW has been applied to calculate excitation energies for systems of different sizes.[33–49] However, the BSE/GW approach still has several challenges. First, although BSE has the same scaling as TDDFT,[50,51] which is $\mathcal{O}(N^4)$ (N is the size of the system), the preceding GW calculation is computationally expensive. In the fully analytical treatment of GW, the scaling of solving the random phase approximation (RPA) equation is $\mathcal{O}(N^6)$, and the scaling of evaluating the self-energy is $\mathcal{O}(N^5)$.[29,52] Thus, the computational-demanding GW calculation is the bottleneck of the BSE/GW approach. To reduce the cost of GW calculations, different techniques can be used. For example, the cost of formulating the response function can be reduced to $\mathcal{O}(N^4)$ by using the plasmon-pole models[53] or the analytic continuation.[29,31,54] The cost of evaluating the self-energy can be reduced to $\mathcal{O}(N^5)$ in the contour deformation approach[55] and $\mathcal{O}(N^4)$ in the analytical continuation approach.[56] Recently, the cubic scaling implementations[57,58] of GW calculations have also gained increasing attention. Second, the performance of the most used BSE/G_0W_0 approach strongly depends on the choice of the DFA. Because of the perturbative nature of the one-shot G_0W_0 method, the accuracy of G_0W_0 strongly depends on the starting point.[59–61] This undesired dependence is inherited in the BSE/G_0W_0 approach. It has been shown that the accuracy of BSE/G_0W_0 for predicting excitation energies of molecular systems is largely affected by the starting point.[40] G_0W_0 based on range-separated functionals and tuned hybrid functionals provides more accurate QP energies,[55,62–65] which lead to better excitation energies in BSE/G_0W_0. It has been shown that BSE/G_0W_0 with optimally tuned hybrid functionals and range-separated functionals predicts accurate core electron excitation energies and low-lying excitation energies.[66,67] One path to improve the accuracy is to introduce the self-consistency into the GW calculations. BSE combining with the eigenvalue self-consistent GW [evGW] approach[32] is shown to predict accurate excitation energies for organic molecules and CT systems with the reduced starting point dependence.[36,38,40,68] It has been shown that BSE/evGW provides comparable accuracy to TDDFT with hybrid functionals and the difference of excitation energies originating from using different DFAs in BSE/evGW is only around 0.1 to 0.3 eV.[36,37,68] In practice, few iterations are necessary for evGW calculations to reach the convergence.[32] The additional computational cost in evGW is only prohibited for large systems.

While Green's function theory provides QP energies by construction, there is parallel development in DFT. Within DFT, the physical meaning of the one-electron orbital energies of the frontier orbitals, namely HOMO and LUMO, has been established based on the three key theoretical results. First, the Janak theorem links Kohn–Sham orbital energies to the derivatives of the total energy with respect to the orbital occupation numbers, which are, however, not related to any physical observables directly.[69] Second, the derivatives of the total energy with respect to the total electron number and chemical potentials are, respectively, the negative of the first ionization potential (IP) and the first electron affinity (EA) for the exact functional based on the linear condition on the behavior of energy for fractional charges.[70–72] Third, chemical potentials were established to be equal to the derivatives of the total energy with respect to the HOMO/LUMO orbital occupation numbers in the Kohn–Sham calculation with XC energy being functionals of the density, or the generalized Kohn–Sham calculation with XC energy being functionals of the noninteracting one-electron density matrix.[73] Combining these theoretical results, the HOMO and LUMO energies are, thus, the approximation to the negative of the first IP and the first EA, respectively, as first established by Cohen et al.[73] This interpretation of the frontier orbital energies has been further extended for other orbitals: Kohn–Sham or generalized Kohn–Sham orbital energies are corresponding QP energies from the DFA used.[74] This extension was based on the extensive observation for a large set of molecules that DFAs, which were designed with minimal delocalization error and provide accurate prediction of IP and EA from the HOMO and LUMO energies, also predict other QP energies from the corresponding generalized Kohn–Sham orbital energies with similar excellent accuracy as HOMO and LUMO orbitals. Therefore, accurate QP energies can be provided from the ground state calculations of DFT.[74]

We want to leverage these recent developments of DFT within the BSE formalism for electronic excitations to achieve and improve the accuracy of the BSE/G_0W_0 approach at more affordable computational cost based on the localized orbital scaling correction (LOSC).[75] Let us briefly review the development of LOSC and other DFAs. Over past decades, DFT[76–78] has become the most popular tool in the electronic structure theory. In DFT, the complicated electron correlation effect can be properly and efficiently described by DFAs, including local density approximations (LDAs),[79,80] generalized gradient approximations (GGAs),[81–83] and hybrid functionals.[81,84] However, the predictive power of DFT is impaired by some intrinsic deficiencies. It has been shown that the delocalization error[85,86] is responsible for many failures in DFT, such as the bandgap prediction.[86] The delocalization error in mainstream DFAs is manifested in small molecules as the violation of the Perdew–Parr–Levy–Balduz (PPLB) condition[70–72] showing that the total energy of a system as a function of the electron number should be piecewise linear between energies at integer points. In 2011, global scaling correction (GSC)[87] was developed to impose the PPLB condition by using canonical occupations and curvatures that are constructed from canonical orbitals. It has shown that GSC largely restores the linearity behavior and predicts accurate bandgaps for systems of all sizes. However, GSC offers zero corrections to total energies at integers, which implies the correction is not size-consistent. To provide a size-consistent correction, local scaling correction (LSC)[88,89] was developed by using local fractional information. However, LSC has numerical difficulties for capturing tiny fractions.[75,88] To combine merits of describing global fractions in GSC and local fractions in LSC, LOSC was developed to systematically eliminate the delocalization error in a size-consistent

manner by utilizing orbitalets.[75] Orbitalets are defined as a set of orbitals localized in both physical and energy spaces that are obtained by the restrained Boys localization.[75] By using orbitalets, LOSC can be applied to the global and local regions of the system in a dynamical way. It has been shown that LOSC successfully describes dissociation of cationic species, bandgaps, and photoemission spectrum.[74,75] As shown in the recent work from our group, accurate QP energies can be approximated from LOSC.[74] LOSC provides very similar or better photoemission spectra and fundamental gaps to those obtained from the fully self-consistent GW (scGW) approach.[74] As shown in Sec. 5 in the supplementary material, G_0W_0 with conventional DFAs gives underestimated fundamental gaps compared with evGW. LOSC provides larger fundamental gaps, which are similar to the evGW level. In addition, fundamental gaps obtained from LOSC with hybrid functionals are closer to those obtained from evGW than LOSC with GGA functionals. Furthermore, there is further development of LOSC approach[90] and a open-source software.[91] Because LOSC is computationally favorable,[75] it is a promising alternative to the GW methods in BSE/GW. In this work, we introduced the BSE/LOSC approach, which directly uses LOSC orbital energies in BSE to calculate excitation energies. Applying LOSC in BSE to bypass the GW calculation shares a similar thinking as combining Koopmans-compliant functionals with BSE in Ref. 92. In the KI-BSE approach, the QP energies are derived from Koopmans-compliant functionals and the screened interaction is obtained via a direct minimization on top of a maximally localized Wannier function basis.[92] It is shown that KI-BSE provides similar accuracy to BSE/G_0W_0.[92] We show that the BSE/LOSC approach considerably outperforms BSE/G_0W_0 for predicting valence, Rydberg, and CT excitation energies with lower computational cost.

II. THEORY

A. Localized orbital scaling correction

LOSC to the total energy is expressed as[75]

$$\Delta E^{\text{LOSC}} = \sum_{pq} \frac{1}{2} \kappa_{pq} \lambda_{pq} (\delta_{pq} - \lambda_{pq}), \tag{1}$$

where λ is the local occupation matrix and κ is the curvature matrix. In Eq. (1) and the following equations, we use i and j for occupied orbitals, a and b for virtual orbitals, and p and q for general orbitals.

The local occupation matrix λ in Eq. (1) is defined as[75]

$$\lambda_{pq} = \langle \phi_p | \rho_s | \phi_q \rangle, \tag{2}$$

where ρ_s is the KS density matrix and $\{\phi_p\}$ is the set of orbitalets. The diagonal elements of λ contain the information of the fractional electron distribution and the off-diagonal elements bring corrections to the unphysical interaction between the local fractions centered at different positions.[75]

The curvature matrix κ in Eq. (1) is defined as[75]

$$\frac{1}{2} \kappa_{pq} = \frac{1}{2} \iint \frac{\rho_p(r)\rho_q(r')}{|r - r'|} dr dr' - \frac{\tau C_x}{3} \int [\rho_p(r)]^{\frac{2}{3}} [\rho_q(r)]^{\frac{2}{3}} dr, \tag{3}$$

where $\rho_p(r) = |\phi_q(r)|^2$ is the density of the orbitalet, $C_x = \frac{3}{4}(\frac{6}{\pi})^{1/3}$, and $\tau = 1.2378$.[75,87] Equation (3) exactly compensates the deviation from the linearity condition under the frozen-orbital assumption.[75]

Orbitalets $\{\phi_p\}$ used in λ and κ are obtained from the restrained Boys localization, which minimizes the following spread function:[75]

$$F = \sum_p \left[\langle \phi_p | r^2 | \phi_p \rangle - \langle \phi_p | r | \phi_p \rangle^2 \right] + \sum_{pq} w_{pq} |U_{pq}|^2, \tag{4}$$

where w is the penalty function defined in Ref. 75 and U is the unitary transformation matrix from canonical orbitals to orbitalets. This restrained Boys localization mixes both occupied and virtual orbitals, which is different from the original Boys localization that only mixes occupied orbitals.[93] In Eq. (4), the first term that has the similar form as the spread function in the original Boys localization ensures orbitals localized in the physical space, and the second term forbids mixing between canonical orbitals that are far apart in the energy space by using the penalty function w. More recently, a modified localization function was developed, which leads to similar accuracy, but preserving the degeneracy of orbitals.[90] We have used the localization function of Eq. (4) in this work.

With LOSC defined in Eq. (1), the total energy is expressed as

$$E = E^{\text{DFA}} + \Delta E^{\text{LOSC}}. \tag{5}$$

LOSC to the Hamiltonian is

$$H = H^{\text{DFA}} + \Delta h^{\text{LOSC}}, \tag{6}$$

where

$$\Delta h^{\text{LOSC}} = \sum_p \kappa_{pp} \left(\frac{1}{2} - \lambda_{pp} \right) |\phi_p\rangle\langle\phi_p| - \sum_{p \neq q} \kappa_{pq} \lambda_{pq} |\phi_p\rangle\langle\phi_q|. \tag{7}$$

The LOSC orbital energies are obtained by diagonalizing H in Eq. (6).

LOSC can be applied in either the self-consistent manner (SCF LOSC) or the post-SCF manner (post-SCF LOSC). As shown in Ref. 75, SCF LOSC provides improved orbitals and corrects the wrong electron density caused by the delocalization error. As shown in Table S18 in Sec. 6 in the supplementary material, dipole moments of tested molecules obtained from SCF LOSC are similar to those obtained from quasiparticle-self-consistent GW (qsGW) and scGW. This indicates that the electron density from LOSC is similar to those from qsGW and scGW, which are also more localized compared with the electron density from KS-DFT.[32,94] SCF LOSC with hybrid functionals provides better agreement with GW results, which is similar to fundamental gaps. However, as discussed in Ref. 32 and shown in numerical results in Tables S2 and S7 in the supplementary material, orbital updates have a minor effect on QP energies for the systems studied in this work. Therefore, we do not expect SCF to change the results. In addition to the minor effects from using SCF LOSC orbitals, as shown in numerical results of Tables S2 and S7 in the supplementary material, SCF LOSC has convergence problems in previous implementation[75] when using the augmented basis sets or calculating large systems, although the convergence problem can be overcome with the recently developed SCF method for LOSC.[74] Thus, we

focus on the simplest BSE/post-SCF LOSC approach, denoted as BSE/LOSC.

B. The Bethe–Salpeter equation

The key idea of this work is to use LOSC orbital energies $\{\varepsilon_p^{\text{LOSC}}\}$ as the input in BSE. With the static approximation for the screened interaction,[25,50,51] the working equation of BSE is a generalized eigenvalue equation,[25,50,51] which is similar to the Casida equation in TDDFT[7,8]

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \omega \begin{bmatrix} I & \mathbf{0} \\ \mathbf{0} & -I \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}, \tag{8}$$

where ω is the excitation energies. The **A** and **B** matrices in Eq. (8) are defined as

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + v_{ia,jb} - W_{ij,ab}, \tag{9}$$

$$B_{ia,jb} = v_{ia,bj} - W_{ib,aj}, \tag{10}$$

where $\{\varepsilon_p\}$ are input orbital energies. In Eq. (8), v is the Coulomb interaction defined as

$$v_{pq,rs} = \int dx_1 dx_2 \frac{\varphi_p^*(x_1)\varphi_r^*(x_2)\varphi_q(x_1)\varphi_s(x_2)}{|r_1 - r_2|}, \tag{11}$$

where $\{\varphi_p\}$ is the set of input orbitals. W is the screened interaction defined as

$$W_{pq,rs} = \sum_{tu}(\varepsilon^{-1})_{pq,tu}v_{tu,rs}, \tag{12}$$

where the dielectric function is calculated by the static response function χ,[50,51]

$$\varepsilon_{pq,rs} = \delta_{pr}\delta_{qs} - v_{pq,rs}\chi_{rs,rs}, \tag{13}$$

$$\chi_{ia,ia} = \chi_{ai,ai} = (\varepsilon_i - \varepsilon_a)^{-1}. \tag{14}$$

The Tamm–Dancoff approximation (TDA) in BSE is obtained by neglecting the **B** matrix in Eq. (8), which is denoted as BSE-TDA. TDA has been used in TDHF and TDDFT to overcome the triplet instability problem.[95,96] A recent work[97] has shown that BSE-TDA also provides an improved accuracy over BSE.

Equation (8) is analogous to the Casida equation[7,8] in TDDFT. The only difference is that the BSE kernel replaces the XC kernel. Thus, Eq. (8) can be solved by the canonical Davidson algorithm[98,99] with a $\mathscr{O}(N^4)$ scaling.

In the BSE/GW approach, the input orbital energies in Eq. (9) are QP energies from a GW calculation. In our BSE/LOSC approach, LOSC orbital energies are directly used as the input orbital energies for BSE.

As shown in Sec. 1 of the supplementary material, the scaling of adding the LOSC correction is only $\mathscr{O}(N^4)$, which is the same as the scaling of solving the BSE equation in Eq. (8). Therefore, the overall scaling of the BSE/LOSC approach is only $\mathscr{O}(N^4)$ and is computationally much more favorable than BSE/G_0W_0. This opens the new possibility of the BSE formalism for describing excited states of larger systems.

III. COMPUTATIONAL DETAILS

We implemented the BSE/LOSC approach in the QM4D quantum chemistry package[100] and applied it to calculate excitation energies of different systems. For the Truhlar–Gagliardi test set,[101] the aug-cc-pVTZ basis set[102,103] was used, except that the aug-cc-pVDZ basis set[102,103] was used for naphthalene, pNA, and DMABN. B-TCNE was excluded because of the computational cost. For Stein CT test set,[104] the cc-pVDZ[102] basis set was used. The experiment values in the gas phase[104] were taken as references. For the test of Rydberg excitation energies of B$^+$, Be, Mg, and Al$^+$, the aug-cc-pVQZ basis set[102,103] was used. Reference values were taken from Ref. 105. BSE/LOSC and BSE/G_0W_0 calculations were performed with QM4D, and TDDFT calculations were performed with GAUSSIAN16 A.03 software.[106] QM4D uses Cartesian basis sets and the resolution of identity (RI) technique[107–109] to compute two-electron integrals. All basis sets and corresponding fitting basis sets were taken from the Basis Set Exchange.[110–112]

IV. RESULTS

A. Truhlar–Gagliardi test set

We first examine the performance of the BSE/LOSC approach for predicting excitation energies of systems in the Truhlar–Gagliardi test set. This test set contains 18 valence excitations as well as two Rydberg excitations and two CT excitations. The mean absolute errors (MAEs) and mean signed errors (MSEs) of excitation energies obtained from BSE/LOSC, BSE/G_0W_0, TDDFT, BSE/evGW, BSE-TDA/LOSC, BSE-TDA/G_0W_0, TDDFT-TDA, and BSE-TDA/evGW with HF, BLYP, PBE, B3LYP, and PBE0 are listed in Table I. It shows that BSE/G_0W_0 has relatively large errors. The MAEs of BSE/G_0W_0 with hybrid functionals are around 0.9 eV and of BSE/G_0W_0 with GGA functionals can even exceed 1.3 eV. The BSE/LOSC approach significantly outperforms BSE/G_0W_0 with both GGA and hybrid functionals. The MAEs of BSE/LOSC are reduced by around 0.4 eV compared with BSE/G_0W_0. TDDFT@PBE0 provides a small MAE of 0.28 eV, which agrees with results from Ref. 101. BSE/evGW provides the largely reduced starting point dependence and only slightly larger MAEs than TDDFT with hybrid functionals. We also find that using TDA greatly improves the accuracy of BSE/LOSC in the calculation for this test set. MAEs of BSE-TDA/LOSC are reduced by 0.1 to 0.2 eV compared with BSE/LOSC. As can be seen in Table I, using TDA leads to increased excitation energies and improves the accuracy for triplet excitations in BSE/LOSC and BSE/G_0W_0, which largely underestimate triplet excitation energies. However, one should be careful when using TDA in the BSE/GW approach. As shown in the present work and Ref. 37, using TDA in BSE/evGW leads to similar or worse results and provides minor effects for singlet calculations. In addition, as shown in recent studies, using TDA in BSE/GW can lead to blue-shifts in nanosized systems[115–117] and worse estimations for singlet-triplet energy gaps in organic molecules.[36] As shown in detail in Sec. 2 in the supplementary material, BSE/LOSC and BSE/G_0W_0 largely underestimate valence excitation energies. Excitation energies obtained from BSE-TDA/LOSC and BSE-TDA/G_0W_0 are always higher than BSE/LOSC and BSE/G_0W_0 by 0.1 to 0.7 eV, which lead to smaller errors. In BSE/LOSC,

TABLE I. Mean absolute errors (MAEs) and mean signed errors (MSEs) of excitation energies in Truhlar–Gagliardi test set obtained from BSE/LOSC, BSE/G_0W_0, TDDFT, BSE/evGW, BSE-TDA/LOSC, BSE-TDA/G_0W_0, TDDFT-TDA, and BSE-TDA/evGW based on HF, BLYP, PBE, B3LYP, and PBE0, all values in eV. Geometries were taken from Ref. 101. Reference values for pNA and DMABN were taken from Ref. 113 and for remaining molecules were taken from Ref. 114. The aug-cc-pVDZ basis set was used for naphthalene, pNA, and DMABN, and the aug-cc-pVTZ basis set was used for the remaining systems. B-TCNE was excluded considering the computational cost. Total MAEs and total MSEs were calculated by averaging all systems with equal weights. MAEs and MSEs for valence, Rydberg, and CT excitations can be found in Table S6 in the supplementary material.

		Total		Singlet		Triplet	
		MAE	MSE	MAE	MSE	MAE	MSE
BLYP	BSE/LOSC	1.02	−1.02	0.90	−0.90	1.42	−1.38
	BSE-TDA/LOSC	0.82	−0.80	0.75	−0.74	1.03	−0.98
PBE	BSE/LOSC	1.04	−1.03	0.94	−0.93	1.35	−1.29
	BSE-TDA/LOSC	0.83	−0.80	0.79	−0.76	0.96	−0.90
B3LYP	BSE/LOSC	0.62	−0.56	0.51	−0.44	0.96	−0.89
	BSE-TDA/LOSC	0.46	−0.38	0.41	−0.30	0.63	−0.56
PBE0	BSE/LOSC	0.54	−0.45	0.46	−0.34	0.82	−0.73
	BSE-TDA/LOSC	0.39	−0.27	0.35	−0.20	0.50	−0.41
HF	BSE/G_0W_0	0.89	0.87	0.88	0.85	0.93	1.05
	BSE-TDA/G_0W_0	0.95	0.93	0.92	0.89	1.06	1.17
BLYP	BSE/G_0W_0	1.53	−1.48	1.42	−1.36	1.88	−1.92
	BSE-TDA/G_0W_0	1.34	−1.19	1.32	−1.26	1.42	−0.83
PBE	BSE/G_0W_0	1.48	−1.32	1.39	−1.34	1.76	−1.17
	BSE-TDA/G_0W_0	1.32	−1.16	1.29	−1.23	1.41	−0.81
B3LYP	BSE/G_0W_0	1.11	−0.90	1.01	−0.92	1.43	−0.68
	BSE-TDA/G_0W_0	0.97	−0.76	0.92	−0.83	1.16	−0.43
PBE0	BSE/G_0W_0	1.00	−0.78	0.90	−0.80	1.35	−0.57
	BSE-TDA/G_0W_0	0.88	−0.66	0.82	−0.71	1.09	−0.33
HF	TDDFT	1.55	−0.56	0.69	0.51	4.48	−4.14
	TDDFT-TDA	0.78	0.46	0.82	0.69	0.63	−0.21
BLYP	TDDFT	0.62	−0.59	0.68	−0.65	0.40	−0.46
	TDDFT-TDA	0.57	−0.52	0.64	−0.59	0.32	−0.34
PBE	TDDFT	0.59	−0.56	0.65	−0.61	0.40	−0.46
	TDDFT-TDA	0.54	−0.48	0.60	−0.54	0.30	−0.32
B3LYP	TDDFT	0.40	−0.33	0.40	−0.31	0.41	−0.43
	TDDFT-TDA	0.32	−0.23	0.36	−0.25	0.18	−0.19
PBE0	TDDFT	0.36	−0.27	0.32	−0.21	0.51	−0.52
	TDDFT-TDA	0.25	−0.15	0.28	−0.14	0.16	−0.17
HF	BSE/evGW	0.65	0.62	0.71	0.68	0.43	0.43
	BSE-TDA/evGW	0.87	0.85	0.83	0.80	1.00	1.10
BLYP	BSE/evGW	0.58	−0.55	0.46	−0.42	0.98	−0.97
	BSE-TDA/evGW	0.53	−0.24	0.43	−0.26	0.88	−0.04
PBE	BSE/evGW	0.57	−0.54	0.45	−0.42	0.98	−0.97
	BSE-TDA/evGW	0.52	−0.24	0.42	−0.26	0.87	−0.05
B3LYP	BSE/evGW	0.54	−0.52	0.44	−0.40	0.90	−0.88
	BSE-TDA/evGW	0.51	−0.21	0.42	−0.24	0.83	0.03
PBE0	BSE/evGW	0.52	−0.49	0.42	−0.37	0.87	−0.84
	BSE-TDA/evGW	0.49	−0.19	0.39	−0.22	0.81	0.06

BSE-TDA/LOSC@PBE0 provides the smallest MAE of 0.36 eV, which is close to the accuracy of TDDFT-TDA with hybrid functionals and BSE/evGW. In addition to the improved accuracy, BSE/LOSC and BSE-TDA/LOSC approaches also reduce the starting point dependence compared with BSE/G_0W_0 and BSE-TDA/G_0W_0. However, there is still a large difference between using GGA and hybrid functionals for predicting excitation energies in this test set.

TABLE II. Mean absolute errors (MAEs) and mean signed errors (MSEs) of CT excitation energies in the Stein CT test set obtained from BSE/LOSC, BSE/G_0W_0, TDDFT, BSE-TDA/LOSC, BSE-TDA/G_0W_0, and TDDFT-TDA with HF, BLYP, PBE, B3LYP, and PBE0, all values in eV. References and geometries were taken from Ref. 104. Gas phase references were used. The cc-pVDZ basis set was used for all systems.

	HF		BLYP		PBE		B3LYP		PBE0	
	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE
BSE/LOSC			0.50	−0.36	0.50	−0.38	0.45	−0.39	0.42	−0.37
BSE/G_0W_0	0.10	−0.06	1.28	−1.28	1.31	−1.31	0.74	−0.74	0.65	−0.65
TDDFT	0.78	0.78	1.44	−1.44	1.45	−1.45	1.16	−1.16	1.08	−1.08
BSE-TDA/LOSC			0.56	−0.27	0.57	−0.29	0.46	−0.32	0.43	−0.31
BSE-TDA/G_0W_0	0.11	−0.04	1.13	−1.13	1.16	−1.16	0.66	−0.66	0.59	−0.59
TDDFT-TDA	0.80	0.80	1.34	−1.30	1.35	−1.32	1.10	−1.07	1.03	−1.00

B. Stein CT test set

We further investigate the performance of our BSE/LOSC approach on predicting CT excitation energies by testing 12 CT systems in Stein' set. The MAEs of predicting CT excitation energies obtained from BSE/LOSC, BSE/G_0W_0, TDDFT, BSE-TDA/LOSC, BSE-TDA/G_0W_0, and TDDFT-TDA with HF, BLYP, PBE, B3LYP, and PBE0 are listed in Table II. It can be seen that TDDFT with both GGA and hybrid functionals fails to predict CT excitation energies due to the wrong description for the long-range behavior. The MAEs are around 1.4 eV for TDDFT with GGA functionals and 1.1 eV for TDDFT with hybrid functionals. Because of the correct long-range behavior, BSE/G_0W_0 shows smaller MAEs compared with TDDFT. BSE/G_0W_0 has MAEs around 1.3 eV with GGA functionals and only around 0.7 eV with hybrid functionals. BSE/G_0W_0@HF gives a very small MAE of 0.10 eV. Our BSE/LOSC approach provides further improvements over BSE/G_0W_0. BSE/LOSC with both GGA functionals and hybrid functionals has a small MAE of 0.5 eV. However, the MAEs obtained from BSE/LOSC are larger than the MAE of 0.10 eV obtained from BSE/evGW reported in Ref. 38. In addition to the improved accuracy over BSE/G_0W_0, the starting point dependence is largely eliminated in the BSE/LOSC approach. We also find that BSE-TDA/LOSC gives very close results to BSE/LOSC for predicting CT excitation energies. This observation is different from the results of Truhlar–Gagliardi test set, where BSE-TDA/LOSC results are always better.

C. Rydberg excitations

We further study the performance of our BSE/LOSC approach on predicting Rydberg excitation energies by testing B$^+$, Be, and Mg. The MAEs of predicting Rydberg excitation energies obtained from BSE/LOSC, BSE/G_0W_0, TDDFT, BSE/evGW, BSE-TDA/LOSC, BSE-TDA/G_0W_0, TDDFT-TDA, and BSE-TDA/evGW with HF, BLYP, PBE, B3LYP, and PBE0 are listed in Table III. Similar to the CT excitation energies, TDDFT also fails to predict Rydberg excitation energies. The MAEs of TDDFT with GGA functionals or hybrid functionals are relatively large. BSE/G_0W_0 provides improvements over TDDFT for both GGA and hybrid functionals, where MAEs are reduced by 0.1 to 0.2 eV. BSE/evGW provides accurate Rydberg excitation energies with the minimal starting point dependence. Our BSE/LOSC approach provides the best accuracy

TABLE III. Mean absolute errors of Rydberg excitation energies of B$^+$, Be, and Mg, all values in eV. References were taken from Ref. 105. The aug-cc-pVQZ basis set was used.

	HF	BLYP	PBE	B3LYP	PBE0
BSE/LOSC		0.88	0.69	0.74	0.56
BSE/G_0W_0	0.16	1.00	0.97	0.73	0.64
BSE/evGW	0.15	0.65	0.65	0.59	0.44
TDDFT	0.92	1.17	1.03	0.89	0.80
BSE-TDA/LOSC		0.84	0.65	0.71	0.54
BSE-TDA/G_0W_0	0.15	1.00	0.97	0.70	0.61
TDDFT-TDA	0.90	1.16	1.02	0.88	0.79
BSE-TDA/evGW	0.14	0.61	0.61	0.55	0.51

for Rydberg excitation energies. The MAEs of BSE/LOSC are further reduced by 0.1 to 0.2 eV compared with BSE/G_0W_0. The accuracy of BSE/LOSC with hybrid functionals is comparable to the BSE/evGW level. BSE-TDA/LOSC yields very close results to BSE/LOSC for Rydberg excitations, which is similar to the case of CT excitations.

V. CONCLUSIONS

In summary, we applied LOSC in BSE to calculate excitation energies of molecular systems. In the BSE/LOSC approach, the LOSC correction is added in the post-SCF manner to correct the KS orbital energies. Then, the LOSC orbital energies are directly used in BSE. The BSE-TDA/LOSC can be obtained by neglecting the **B** matrix in the BSE calculation. BSE/LOSC was first examined by predicting excitation energies in the Truhlar–Gagliardi test set. We showed that BSE/LOSC significantly outperforms BSE/G_0W_{0z} and BSE-TDA/LOSC provides further improvements. BSE-TDA/LOSC with hybrid functionals provides the comparable accuracy to TDDFT for predicting excitation energies in this set. Then, we showed that BSE/LOSC predicts accurate CT excitation energies in the Stein CT test set. BSE/LOSC provides considerable improvements over BSE/G_0W_0 and largely eliminates the starting point dependence. We also showed that the BSE/LOSC approach describes Rydberg excitations well by testing atomic Rydberg

excitation energies. Therefore, the BSE/LOSC approach greatly outperforms BSE/G_0W_0 for predicting valence, CT, and Rydberg excitation energies. In addition to the improved accuracy, our BSE/LOSC approach only scales as $\mathcal{O}(N^4)$, which is much more computationally favorable than BSE/G_0W_0. The BSE/LOSC approach is expected to extend the applicability of the BSE formalism for large systems.

SUPPLEMENTARY MATERIAL

See the supplementary material for the scaling analysis of LOSC and the numerical results of excitation energies for Truhlar–Gagliardi test set, Stein charge transfer test set, and Rydberg excitations of atoms.

ACKNOWLEDGMENTS

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

[1] W. A. Velema, J. P. van der Berg, M. J. Hansen, W. Szymanski, A. J. M. Driessen, and B. L. Feringa, Nat. Chem. 5, 924 (2013).

[2] A. A. Beharry, O. Sadovski, and G. A. Woolley, J. Am. Chem. Soc. 133, 19684 (2011).

[3] B. A. Gregg, J. Phys. Chem. B 107, 4688 (2003).

[4] P. Peumans, S. Uchida, and S. R. Forrest, Materials for Sustainable Energy (Co-Published with Macmillan Publishers Ltd, UK, 2010), pp. 94–98.

[5] A. Hagfeldt and M. Grätzel, Acc. Chem. Res. 33, 269 (2000).

[6] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[7] M. E. Casida, Recent Advances in Density Functional Methods, Recent Advances in Computational Chemistry (World Scientific, 1995), Vol. 1, pp. 155–192.

[8] C. A. Ullrich, Time-Dependent Density-Functional Theory: Concepts and Applications (Oxford University Press, Oxford, 2011).

[9] M. E. Casida, J. Mol. Struct.: THEOCHEM 914, 3 (2009).

[10] M. E. Casida, A. Ipatov, and F. Cordova, in Time-Dependent Density Functional Theory, Lecture Notes in Physics, edited by M. A. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer, Berlin, Heidelberg, 2006), pp. 243–257.

[11] Z. Yuan and S. Gao, Comput. Phys. Commun. 180, 466 (2009).

[12] A. D. Laurent and D. Jacquemin, Int. J. Quantum Chem. 113, 2019 (2013).

[13] J. Kaur, E. Ospadov, and V. N. Staroverov, J. Chem. Theory Comput. 15, 4956 (2019).

[14] A. Dreuw, J. L. Weisman, and M. Head-Gordon, J. Chem. Phys. 119, 2943 (2003).

[15] D. J. Tozer, J. Chem. Phys. 119, 12697 (2003).

[16] T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, Chem. Phys. Lett. 275, 151 (1997).

[17] N. A. Besley, M. J. G. Peach, and D. J. Tozer, Phys. Chem. Chem. Phys. 11, 10350 (2009).

[18] M. J. G. Peach, P. Benfield, T. Helgaker, and D. J. Tozer, J. Chem. Phys. 128, 044118 (2008).

[19] J. C. Slater, Phys. Rev. 35, 210 (1930).

[20] A. Szabo and N. S. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory (Courier Corporation, 2012).

[21] Y. Zhao and D. G. Truhlar, J. Phys. Chem. A 110, 13126 (2006).

[22] L. J. Sham and T. M. Rice, Phys. Rev. 144, 708 (1966).

[23] E. E. Salpeter and H. A. Bethe, Phys. Rev. 84, 1232 (1951).

[24] W. Hanke and L. J. Sham, Phys. Rev. Lett. 43, 387 (1979).

[25] X. Blase, I. Duchemin, D. Jacquemin, and P.-F. Loos, J. Phys. Chem. Lett. 11, 7371 (2020).

[26] R. M. Martin, L. Reining, and D. M. Ceperley, Interacting Electrons (Cambridge University Press, 2016).

[27] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).

[28] L. Hedin, Phys. Rev. 139, A796 (1965).

[29] D. Golze, M. Dvorak, and P. Rinke, Front. Chem. 7 (2019).

[30] L. Reining, Wiley Interdiscip. Rev.: Comput. Mol. Sci 8, e1344 (2018).

[31] M. J. van Setten, F. Caruso, S. Sharifzadeh, X. Ren, M. Scheffler, F. Liu, J. Lischner, L. Lin, J. R. Deslippe, S. G. Louie et al., J. Chem. Theory Comput. 11, 5665 (2015).

[32] F. Kaplan, M. E. Harding, C. Seiler, F. Weigend, F. Evers, and M. J. van Setten, J. Chem. Theory Comput. 12, 2528 (2016).

[33] C. Azarias, I. Duchemin, X. Blase, and D. Jacquemin, J. Chem. Phys. 146, 034301 (2017).

[34] C. Azarias, C. Habert, Š. Budzák, X. Blase, I. Duchemin, and D. Jacquemin, J. Phys. Chem. A 121, 6122 (2017).

[35] D. Escudero, I. Duchemin, X. Blase, and D. Jacquemin, J. Phys. Chem. Lett. 8, 936 (2017).

[36] D. Jacquemin, I. Duchemin, A. Blondel, and X. Blase, J. Chem. Theory Comput. 13, 767 (2017).

[37] D. Jacquemin, I. Duchemin, and X. Blase, J. Phys. Chem. Lett. 8, 1524 (2017).

[38] X. Blase and C. Attaccalite, Appl. Phys. Lett. 99, 171909 (2011).

[39] V. Ziaei and T. Bredow, J. Chem. Phys. 145, 174305 (2016).

[40] D. Jacquemin, I. Duchemin, and X. Blase, J. Chem. Theory Comput. 11, 3290 (2015).

[41] C. Faber, P. Boulanger, C. Attaccalite, I. Duchemin, and X. Blase, Philos. Trans. R. Soc., A 372, 20130271 (2014).

[42] X. Jiang, Q. Zheng, Z. Lan, W. A. Saidi, X. Ren, and J. Zhao, Sci. Adv. 7, eabf3759 (2021).

[43] C. Liu, J. Kloppenburg, Y. Yao, X. Ren, H. Appel, Y. Kanai, and V. Blum, J. Chem. Phys. 152, 044105 (2020).

[44] P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012).

[45] M. Dvorak, D. Golze, and P. Rinke, Phys. Rev. Mater. 3, 070801 (2019).

[46] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Phys. Rev. Lett. 80, 4510 (1998).

[47] P. Cudazzo, L. Sponza, C. Giorgetti, L. Reining, F. Sottile, and M. Gatti, Phys. Rev. Lett. 116, 066803 (2016).

[48] P. Romaniello, D. Sangalli, J. A. Berger, F. Sottile, L. G. Molinari, L. Reining, and G. Onida, J. Chem. Phys. 130, 044108 (2009).

[49] S. Di Sabatino, P.-F. Loos, and P. Romaniello, Front. Chem. 9 (2021).

[50] K. Krause and W. Klopper, J. Comput. Chem. 38, 383 (2017).

[51] S. K. Ghosh and P. K. Chattaraj, Concepts and Methods in Modern Theoretical Chemistry: Electronic Structure and Reactivity (CRC Press, 2016).

[52] M. J. van Setten, F. Weigend, and F. Evers, J. Chem. Theory Comput. 9, 232 (2013).

[53] J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Comput. Phys. Commun. 183, 1269 (2012).

[54] E. L. Shirley, X. Zhu, and S. G. Louie, Phys. Rev. Lett. 69, 2955 (1992).

[55] D. Golze, J. Wilhelm, M. J. van Setten, and P. Rinke, J. Chem. Theory Comput. **14**, 4856 (2018).

[56] I. Duchemin and X. Blase, J. Chem. Theory Comput. **16**, 1742 (2020).

[57] J. Wilhelm, D. Golze, L. Talirz, J. Hutter, and C. A. Pignedoli, J. Phys. Chem. Lett. **9**, 306 (2018).

[58] I. Duchemin and X. Blase, J. Chem. Theory Comput. **17**, 2383 (2021).

[59] S.-H. Ke, Phys. Rev. B **84**, 205415 (2011).

[60] N. Marom, F. Caruso, X. Ren, O. T. Hofmann, T. Körzdörfer, J. R. Chelikowsky, A. Rubio, M. Scheffler, and P. Rinke, Phys. Rev. B **86**, 245127 (2012).

[61] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Phys. Rev. B **76**, 115109 (2007).

[62] M. Dauth, F. Caruso, S. Kümmel, and P. Rinke, Phys. Rev. B **93**, 121115 (2016).

[63] T. Körzdörfer, R. M. Parrish, N. Marom, J. S. Sears, C. D. Sherrill, and J.-L. Brédas, Phys. Rev. B **86**, 205110 (2012).

[64] D. Hollas, E. Muchová, and P. Slavíček, J. Chem. Theory Comput. **12**, 5009 (2016).

[65] F. Bruneval, S. M. Hamed, and J. B. Neaton, J. Chem. Phys. **142**, 244101 (2015).

[66] E. Monino and P.-F. Loos, J. Chem. Theory Comput. **17**, 2852 (2021).

[67] Y. Yao, D. Golze, P. Rinke, V. Blum, and Y. Kanai, J. Chem. Theory Comput. **18**, 1569 (2022).

[68] D. Jacquemin, I. Duchemin, and X. Blase, Mol. Phys. **114**, 957 (2016).

[69] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[70] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[71] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, V. N. Staroverov, and J. Tao, Phys. Rev. A **76**, 040501 (2007).

[72] W. Yang, Y. Zhang, and P. W. Ayers, Phys. Rev. Lett. **84**, 5172 (2000).

[73] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Phys. Rev. B **77**, 115123 (2008).

[74] Y. Mei, C. Li, N. Q. Su, and W. Yang, J. Phys. Chem. A **123**, 666 (2019).

[75] C. Li, X. Zheng, N. Q. Su, and W. Yang, Natl. Sci. Rev. **5**, 203 (2018).

[76] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[77] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[78] R. G. Parr and Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).

[79] U. v. Barth and L. Hedin, J. Phys. C: Solid State Phys. **5**, 1629 (1972).

[80] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[81] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[82] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[83] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[84] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

[85] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008).

[86] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **100**, 146401 (2008).

[87] X. Zheng, A. J. Cohen, P. Mori-Sánchez, X. Hu, and W. Yang, Phys. Rev. Lett. **107**, 026403 (2011).

[88] X. Zheng, C. Li, D. Zhang, and W. Yang, Sci. China: Chem. **58**, 1825 (2015).

[89] C. Li, X. Zheng, A. J. Cohen, P. Mori-Sánchez, and W. Yang, Phys. Rev. Lett. **114**, 053001 (2015).

[90] N. Q. Su, A. Mahler, and W. Yang, J. Phys. Chem. Lett. **11**, 1528 (2020).

[91] Y. Mei, J. Yu, Z. Chen, N. Q. Su, and W. Yang, J. Chem. Theory Comput. **18**, 840 (2022).

[92] J. D. Elliott, N. Colonna, M. Marsili, N. Marzari, and P. Umari, J. Chem. Theory Comput. **15**, 3710 (2019).

[93] J. M. Foster and S. F. Boys, Rev. Mod. Phys. **32**, 300 (1960).

[94] F. Caruso, V. Atalla, X. Ren, A. Rubio, M. Scheffler, and P. Rinke, Phys. Rev. B **90**, 085141 (2014).

[95] M. J. G. Peach and D. J. Tozer, J. Phys. Chem. A **116**, 9783 (2012).

[96] M. J. G. Peach, N. Warner, and D. J. Tozer, Mol. Phys. **111**, 1271 (2013).

[97] T. Rangel, S. M. Hamed, F. Bruneval, and J. B. Neaton, J. Chem. Phys. **146**, 194108 (2017).

[98] R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **109**, 8218 (1998).

[99] E. R. Davidson, J. Comput. Phys. **17**, 87 (1975).

[100] See http://www.qm4d.info for an in-house program for qm/mm simulations.

[101] C. E. Hoyer, S. Ghosh, D. G. Truhlar, and L. Gagliardi, J. Phys. Chem. Lett. **7**, 586 (2016).

[102] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).

[103] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[104] T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. **131**, 2818 (2009).

[105] X. Xu, K. R. Yang, and D. G. Truhlar, J. Chem. Theory Comput. **10**, 2070 (2014).

[106] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji *et al.*, Gaussian16 Revision a.03, Gaussian Inc., Wallingford CT, 2016.

[107] F. Weigend, Phys. Chem. Chem. Phys. **8**, 1057 (2006).

[108] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, and M. Scheffler, New J. Phys. **14**, 053020 (2012).

[109] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, Chem. Phys. Lett. **240**, 283 (1995).

[110] D. Feller, J. Comput. Chem. **17**, 1571 (1996).

[111] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, J. Chem. Inf. Model. **47**, 1045 (2007).

[112] B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, and T. L. Windus, J. Chem. Inf. Model. **59**, 4814 (2019).

[113] X. Gui, C. Holzer, and W. Klopper, J. Chem. Theory Comput. **14**, 2127 (2018).

[114] M. Véril, A. Scemama, M. Caffarel, F. Lipparini, M. Boggio-Pasqua, D. Jacquemin, and P.-F. Loos, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **11**, e1517 (2021).

[115] C. Faber, P. Boulanger, I. Duchemin, C. Attaccalite, and X. Blase, J. Chem. Phys. **139**, 194308 (2013).

[116] D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. **133**, 164109 (2010).

[117] I. Duchemin, T. Deutsch, and X. Blase, Phys. Rev. Lett. **109**, 167801 (2012).