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Modified linear response for time-dependent density-functional theory: Application to Rydberg and charge-transfer excitations

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We present an improved *ab initio* time-dependent density-functional theory (TDDFT) approach to electronic excitations. A conventional TDDFT scheme within the local-density approximation (LDA) inaccurately predicts Rydberg and charge-transfer excitation energies, mainly because the electron-hole (*e*-*h*) interaction is inappropriately described in these excitations, as can be found by analyzing the linear response formula [M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996)]. When the formula is averaged over the electron occupation, the inappropriate *e*-*h* interaction within LDA is corrected to become explicitly similar to that of the exact exchange system. As anticipated from the similarity, our proposed scheme of modified linear response greatly improves the prediction of the problematic excitations, which are exemplified for typical molecules.

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I. INTRODUCTION

Electronic excitation is a fundamental process in spectroscopic experiments, and its accurate prediction has been a central topic of theoretical physics and chemistry. Many-body theories have long been developed toward this goal, but the alternative approach based on the density functional theory (DFT) [1] has recently attracted wide attention because of its efficiency: The time-dependent DFT (TDDFT) [2], mapping time evolution of interacting electrons into that of noninteracting particles, provides a compact and formally exact expression for electronic excitation [3]. With use of the simple adiabatic local-density approximation (ALDA), in which the static LDA functional is used for dynamic properties, the theory generally predicts reasonably accurate excitation energies, enabling application to larger systems [4,5]. It does not, however, yield a reliable result when high-lying Rydberg states [6] or charge-transfer excitations [7] are concerned. In such cases, the errors are often larger than 1 eV, which renders TDDFT predictions untrustworthy. Improved approaches, with the ability to overcome the problems of TDDFT on these types of excitations, are thus highly desired to stimulate further extensive application to materials research.

The salient difference between TDDFT-based density response scheme and the ground-state DFT is in the fact that the difference of one-particle eigenvalues is shifted in TDDFT by the Coulomb and exchange-correlation (xc) terms: *The Coulomb kernel* V_c *is responsible for the exchange interaction of the electron-hole* (*e*-*h*) *pair, and conversely, the exchange kernel*, f_x, *for its Coulomb interaction* [8]. Therefore the ALDA, with accurate V_c and approximate f_x optimized for the ground state, might be problematic for excited states. Introducing an asymptotic [9–11] or long-range [12] correction for f_x may be one way to semiempirically avoid the problem, and introducing exact-exchange [13] or accurate xc schemes [14] may be another way, but computationally demanding. Here we propose an *ab initio* ALDA-based scheme, which is simple and cheap but has the correct form for the *e*-*h* Coulomb interaction. Note that Wasserman and Burke [15] recently showed that Rydberg transition energies of atoms can be decoded accurately within LDA by extracting the limiting quantum defect of the Rydberg series from *static* Kohn-Sham (KS) equations. Our approach will show that the Rydberg and charge-transfer excitation energies of molecules can also be decoded from time-dependent KS equations without any correction to the LDA potential.

The basic idea of our approach is to take an average over the occupation number by examining the dependence of response over the electron occupancy, as detailed in the next section. In Sec. III, our approach is implemented to the real-time TDDFT method, and the practical calculation scheme is given. In Sec. IV, we have applied this scheme to typical diatomic molecular systems and compared valence, Rydberg, and charge-transfer excitations to test its applicability. In Sec. V, we conclude our work and give some view on the future applications.

II. BASIC IDEA

A. Approximate excitation energies from TDDFT within the linear response scheme (ALDA and the exact change system) and the change in self-consistent field theory

To show our approach, we first address the approximate expressions of excitation energies in TDDFT within the linear response (LR) scheme. Following Gonze and Scheffler [8], we assume that KS orbitals are real and do not explicitly consider spin. We will also use the notation $\nu=(j,k)$ for a single-particle transition from the occupied level k to the unoccupied level j, and $\{g_1|f|g_2\}$ for the integral

$\int g_1(\mathbf{r}_1)f(\mathbf{r}_1,\mathbf{r}_2)g_2(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$. In TDDFT LR scheme, the approximate excitation energy is deduced [3] as

$$\Omega \approx \omega_\nu + \{\Phi_\nu|V_c|\Phi_\nu\} + \{\Phi_\nu|f_{xc}|\Phi_\nu\}, \tag{1}$$

where $\omega_\nu=\epsilon_j^{KS}-\epsilon_k^{KS}$, the energy difference between corresponding KS eigenenergies. $\Phi_\nu(\mathbf{r})$ is the product of wave functions $\phi_k(\mathbf{r})\phi_j(\mathbf{r})$. V_c and f_{xc} are interaction kernels for the Coulomb and *xc* terms, respectively, i.e.,

$$V_c(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}, \tag{2}$$

$$f_{xc}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\delta V_{xc}[\rho(\mathbf{r}_1)]}{\delta\rho(\mathbf{r}_2)}, \tag{3}$$

where V_{xc} is the exchange-correlation potential and ρ is the electron density.

For the ALDA, V_c is accurate and gives the contribution as the exchange integral K_ν, $\int\frac{\Phi_\nu(\mathbf{r}_1)\Phi_\nu(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2$, but f_{xc} is only a local one, in the form

$$f_{xc}^{LDA}(\mathbf{r}_1,\mathbf{r}_2) = \delta(\mathbf{r}_1-\mathbf{r}_2)f_{xc}^{LDA}(\mathbf{r}_1). \tag{4}$$

Thus Eq. (1) becomes

$$\Omega^{ALDA} \approx \omega_\nu^{LDA} + K_\nu + \{\rho_k|f_{xc}^{LDA}|\rho_j\}, \tag{5}$$

where $\rho_i(\mathbf{r})=\phi_i^2(\mathbf{r})$.

To see how the local f_{xc} affects the result, we can see the approximate excitation energy expression for the exact exchange (EXX) system. The form is derived as [8]

$$\Omega^{EXX} \approx \tilde{\omega}_\nu^{EXX} + K_\nu - J_\nu, \tag{6}$$

where $\tilde{\omega}_\nu^{EXX}=(\epsilon_j^{KS,EXX}+\Delta_j)-(\epsilon_k^{KS,EXX}+\Delta_k)$, and Δ_i's are the difference in the expectation value for the Hartree-Fock exchange operator $\hat{v}_x^{HF}$ and that for the exchange potential v_x^{EXX}, i.e., $\Delta_i=\langle\phi_i|\hat{v}_x^{HF}-v_x^{EXX}|\phi_i\rangle$. Unlike in the ALDA case, Eq. (6) induces a shift of KS eigenenergies in the EXX system. The term J_ν is the Coulomb integral, $\int\frac{\rho_k(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2$. Most importantly, the Coulomb (exchange) kernel yields the exchange (Coulomb) integral, so that the electron-hole interaction is described by the Hartree-Fock interaction kernel. A comparison of Eqs. (1) and (6) illustrates this fact. The term $\{\rho_k|f_{xc}^{LDA}|\rho_j\}$, however, does not usually yield the term $-J_\nu$. These two terms differ greatly, especially when electrons in the *k*th and *j*th orbitals are separated spatially, as they are for Rydberg and charge-transfer excitations. Therefore, Eq. (5) does not have the similar form of Eq. (6). The fact that conventional TDDFT schemes within the ALDA inaccurately predict Rydberg and charge-transfer excitation energies can be understood from such a comparison.

In contrast to the performance of the TDDFT ALDA, the ΔSCF method, in which the excitation energy is computed from the total energy difference between the ground state and the excited state in self-consistent-field (SCF) calculations, can sometimes give a relatively better estimation on Rydberg and charge-transfer excitation energies [16]. When orbital relaxation is neglected, the approximate excitation energy from the ΔSCF method can be derived (see Appendix A) as

$$\Omega^{\Delta SCF,LDA} \approx \tilde{\omega}_\nu^{LDA} - \{\rho_k|f_{xc}^{LDA}|\rho_j\} - J_\nu, \tag{7}$$

where $\tilde{\omega}_\nu^{LDA}=(\epsilon_j^{KS,LDA}+U_j)-(\epsilon_k^{KS,LDA}+U_k)$. As detailed in Appendix A, U_i's are the self-interaction (SI) energies, which vanish for SI-free theories, such as the Hartree-Fock theory. From the comparison of Eq. (6) and Eq. (7), it might be important to include this correction term as the shift to the eigenenergy. Another important term, the Coulomb attraction of the electron-hole pair ($-J_\nu$), is also explicitly included in Eq. (7). These two features in the ΔSCF method might give an explanation for its relatively good performance in some cases. On the other hand, the term $-\{\rho_k|f_{xc}^{LDA}|\rho_j\}$ does not generally yield K_ν, which might be responsible for the inadequacy of the ΔSCF method in other cases.

B. Occupation number averaging: Going beyond ordinary LR

Comparing Eqs. (5)–(7), we have an idea to go beyond the ordinary linear response. If averaged (integrated) over the occupation number for *j*th and *k*th orbitals, denoted as q and p $(=1-q)$, respectively, Eq. (5) becomes

$$\begin{aligned}\langle\Omega^{ALDA}\rangle = \int_0^1 \Omega^{ALDA}dq &\approx \Omega^{\Delta SCF,LDA} + K_\nu + \{\rho_k|f_{xc}^{LDA}|\rho_j\}\\ &\approx \tilde{\omega}_\nu^{LDA} + K_\nu - J_\nu.\end{aligned} \tag{8}$$

In this derivation, the Janak's theorem [17],

$$\frac{\partial E_{tot}}{\partial f_i} = \epsilon_i, \tag{9}$$

which states that the derivative of the total energy (E_{tot}) with respect to the occupation number of the *i*th orbital (f_i) is equal to the eigenenergy of the *i*th level, has been used to connect the eigenenergy difference with the ΔSCF method. Meanwhile, other terms in Eq. (5) are assumed to have a negligible dependence on the occupation number. It is highly appealing that Eq. (8) has a form similar to that of Eq. (6). One similarity is the shift in the KS eigenenergies. The other is the same Hartree-Fock kernel in describing the electron-hole interaction. For exchange-dominant systems, therefore, Eq. (8) indicates that the occupation number averaging scheme has the potential to obtain same-level performance as EXX, and might correct the ALDA [18]. Casida *et al.* [16] suggested a "charge-transfer correction" (CTC) scheme that relies on the analysis of the two-level model. In this model, their direct addition of a term $\Delta\omega^{CTC}$ to Ω^{ALDA} creates a similar expression to Eq. (8). Our analysis therefore provides some basis for this method and shows that the general scheme in DFT is to average over the occupation number.

We now examine this idea from a different point of view. In the true KS theory with the exact *xc*, information of the excited state Ψ_{ex} can be extracted from the perturbed state through use of the orthogonality condition $\langle\Psi_{ex}|\Psi_{gr}\rangle=0$, where Ψ_{gr} denotes the ground state. However, when adiabatic approximations are used, this condition is not strictly satisfied, and the perturbation yields, instead, an ensemble of mixed ground- and excited-state densities. This problem is known to originate from the lack of derivative discontinuity

(DD, or integer discontinuity) [19]. In the true KS theory, the derivative of the total energy with respect to the number of electrons, namely, the chemical potential $\mu(N)$, should show a stepwise jump at each integer N. The significance of this DD feature can be understood from a simple image: For a system consisting of isolated subsystems, the stepwise behavior of μ means that the energy required to transfer one electron from a subsystem to the other can be obtained by examining the transference of an infinitesimal fraction of electron, which is sufficient to get the difference of μ between the two subsystems. However, if DD is not satisfied, as in the ALDA, it is not sufficient to do so, because of the dependence of μ on the transferred fraction of electron. Instead, the technique of the ΔSCF method, in which the energy change is obtained by transferring a whole electron, should be taken into consideration.

The discussion is analogous when a perturbative electric field is applied to induce the infinitesimal electron transfer from the ground state. The time-dependent perturbation accounts for the rate at which the component of the final state mixes with the initial state. The true resonance frequency, which corresponds to the photon energy, is not dependent on the amount of the mixing, but constant until transferring one electron. However, in the case of the ALDA, the photon energy depends on the transferred fraction of electron, as may be understood from Eq. (5), and the occupation dependence of the KS eigenenergy within the ALDA. Therefore, only perturbing the initial state would lead to an incorrect prediction of the photon energy. The key to correct the ALDA error is expected to be the way of examining how the energy depends on the transferred fraction of electron. In this context, we consider a path to transfer one electron by repeatedly applying the perturbation, and take an average of the photon energy. The occupation number averaging scheme corresponds to this idea. Even though only intuitively driven, this idea leads to the form of Eq. (8), which is explicitly similar to that of the exact exchange that has the integer discontinuity, suggesting that our idea is one of the ways to better decode the excitation energy from the ALDA. Below, we will demonstrate how this procedure works. In doing so, we can simply average over the occupation number q, but it is preferable to adopt a weighted average, e.g., using the amplitude of the dipole response, $\alpha(\omega)$, at peak $\omega = \Omega^{ALDA}$ for each q to obtain

$$\langle\Omega\rangle = \frac{\int_0^1 \Omega^{ALDA}(q)|\alpha[\Omega^{ALDA}(q)]|dq}{\int_0^1 |\alpha[\Omega^{ALDA}(q)]|dq}. \tag{10}$$

Following the basic idea of this modified linear response scheme, we have applied it to typical diatomic molecular systems and compared valence, Rydberg, and charge-transfer excitations. We have used the real-time evolution scheme with a plane-wave basis set to take full account of the orbital relaxation effect. The results of our modified linear-response scheme are almost identical to those of ordinary linear-response theory for valence excitations, but show great improvement on Rydberg and charge-transfer excitations, achieving the EXX-level accuracy for the prediction of excitation energies.

III. METHOD AND COMPUTATIONAL DETAILS

A. Real-time propagation technique

For TDDFT calculation of excitation energies, two main types of techniques exist in the literature. One is the real-time propagation method [4,20,21]. First the initial wave function (ground state) is given a weak perturbation, which causes a dipole moment to develop as the system evolves with time. Then we solve the time-dependent Kohn-Sham equations, propagate the wave function, and keep track of the dipole moment. The Fourier transform of the dipole moment is the response we seek. Excitation energies can thus be determined from the peak positions of the dipole response. The other type of technique is rather different, which is implemented in the frequency space and does not explicitly propagate the wave function or electron density. As a popular method in quantum chemistry, the calculation of excitation energies is recast into a pseudoeigenvalue problem, known as the Casida equation in the matrix form [22]. The eigenvalues are corresponding to the square of the excitation energies. The real-time propagation scheme, when approximated to first order in the initial perturbation, provides us with a formula explicitly equivalent to the Casida equation.

The basic idea of our modified linear-response scheme is to examine the dependence of linear response on the occupation number, i.e., not only the response from the ground state, but also the response from excited states, which are constructed by promoting a fraction of electron from the occupied orbital to the unoccupied orbital, as usually done in constrained DFT. The excitation energy is then estimated by taking the average over the occupation number. For our purpose, therefore, both schemes can be equally applied. We note, however, that the real-time propagation can describe more easily the response far beyond the first order, and considering a future extension of the scheme, we will adopt the real-time propagation scheme, which is available in the existing program package of our group, the FPSEID code [23]. This is a plane-wave pseudopotential code, developed by Sugino and Miyamoto to study electron-ion dynamics. The Suzuki-Trotter-type split-operator method is used to integrate the time-dependent KS equations. Troullier-Martins norm-conserving pseudopotentials [24] with s nonlocality are used for all atomic species (except the local one for H). The xc potential is approximated by the LDA functional from Perdew and Zunger [25]. Before real-time simulation, initial wave functions are prepared by performing a self-consistent calculation of the static KS equations. Then, the wave functions are perturbed by the replacement

$$\phi_n(\mathbf{r},0_+) = e^{ik_0 r_v}\phi_n(\mathbf{r},0), \tag{11}$$

using the scheme proposed by Yabana and Bertsch [20]. In the phase factor, k_0 is a small constant, and r_v is the electron coordinate in the direction of the perturbation ($v = x$, y, or z). The system is propagated until some finite time T, during which the time-dependent induced dipole moment $\alpha(t)$ is calculated. The dipole response $\alpha(\omega)$ is essentially equal to the dynamic polarizability.

In our modified linear-response scheme, nearly all calculation procedures are kept the same. Only minor modifications for changing the occupation number of orbitals are required, thus the effort to modify the source code is little and quite easily done.

B. TDDFT orbital analysis scheme

Since the excitation energies can be obtained from the dipole response, the assignment of excitation energy peaks should also be achieved by analyzing the orbital contributions to the dipole moment. During time evolution, we perform a TDDFT orbital analysis by decomposing the time-dependent KS orbital into all eigenstates at $t=0$,

$$\phi_n(t)=\sum_m a_m^n(t)\phi_m(0), \quad a_m^n(t)=\langle\phi_m(0)|\phi_n(t)\rangle. \tag{12}$$

Therefore, the real-time dipole moment can be written as the following:

$$\begin{aligned}\alpha(t)&=\sum_n\langle\phi_n(t)|r_v|\phi_n(t)\rangle\\&=\sum_n\sum_{m,m'}d_{mm'}a_m^n(t)a_{m'}^{n*}(t)f_n\\&\simeq\sum_n\sum_m d_{nm}a_n^n(t)a_m^{n*}(t)f_n+\text{c.c.}\end{aligned} \tag{13}$$

Therein, f_n is the occupation number for the nth orbital, and $d_{mm'}$ is the initial transition dipole moment, $\langle\phi_m(0)|r_v|\phi_{m'}(0)\rangle$. The approximation in Eq. (13) is made because the initial eigenstate gives the dominant contribution over the others. Define the transition coefficient as

$$A_m^n(t)=a_n^n(t)a_m^{n*}(t), \tag{14}$$

and evaluate it in the real-time evolution. Thereby, the Fourier transform $A_m^n(\omega)$ gives the peak positions of the $n\rightarrow m$ transition.

C. Excitation energies from the modified linear response scheme

The excitation energy of the transition from the occupied orbital k to the unoccupied orbital j, as discussed previously [Eq. (10)], is calculated using

$$\omega_a=\langle\Omega\rangle\simeq\frac{\int_0^1\omega_t(q)A_t(q)|d_{jk}(q)|f(q)dq}{\int_0^1 A_t(q)|d_{jk}(q)|f(q)dq}, \tag{15}$$

where ω_t and A_t are the position and height of the peak of $A_j^k(\omega)$. q is the occupation number of the jth orbital, i.e., the fraction of the excited electron. Assuming that the change of the transition dipole d_{jk} is negligible during excitation, we can make the approximation of

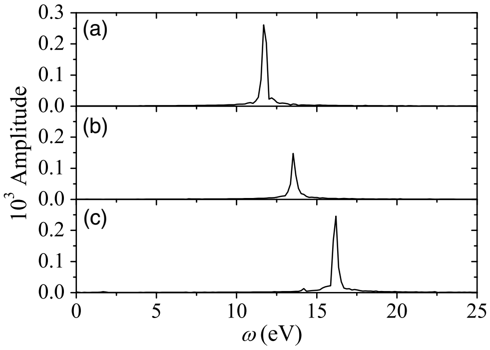

FIG. 1. The Fourier transform of transition coefficients A_{10}^5 ($\sigma_g\rightarrow 3p\pi_u$ Rydberg transition) for (a) ground state, (b) half-electron excited state, and (c) one-electron excited state of N_2. The sharp peaks give the transition energies and amplitudes.

$$\omega_a\simeq\frac{\int_0^1\omega_t(q)A_t(q)f(q)dq}{\int_0^1 A_t(q)f(q)dq}\simeq\frac{\sum_{q_i}\omega_tA_tf}{\sum_{q_i}A_tf}, \tag{16}$$

where the integral is replaced by a sum. We suggest that a three-point formula using $q=0$, 0.5, and 1 is appropriate for this purpose, as discussed later.

IV. RESULTS AND DISCUSSIONS

To demonstrate the performance of our scheme, we next apply it to calculate excitation energies of typical diatomic molecules, including N_2, CO, HCl, and HBr. Perturbations are applied in the x direction, so we can only consider the dipole transition between σ-type and π-type orbitals; there is no change of spin multiplicity during the transition. We keep the atomic positions fixed at the optimized ground-state geometry and calculate the vertical excitation energies ΔE_e, evaluated as ω_a in Eq. (16).

Assignment of peaks in the dipole response is done using the TDDFT orbital analysis approach. For N_2, the dipole response shows a nearly flat continuum preceding the first sharp peak. This peak is assigned to the $\sigma_g\rightarrow 3p\pi_u$ Rydberg transition. The $\sigma_g\rightarrow\pi_g$ valence excitation is located in the continuum region. In comparison, the first two sharp peaks in the dipole response of CO are assigned to the $\sigma\rightarrow\pi^*$ (valence) and $\sigma\rightarrow 3p\pi$ (Rydberg) transitions. For HCl and HBr, the first two peaks are determined as a charge-transfer excitation and a Rydberg transition, respectively, both from π type to σ type. Understanding the transition between certain orbitals facilitates subsequent calculations, in which a fractional number (q) of electron is promoted to the corresponding orbital. Figure 1 shows the Fourier transform of transition coefficients for the $c\ {}^1\Pi_u$ Rydberg state of N_2, when the initial wave function is at the ground state, half-electron excited state, and one-electron excited state. The excitation is mimicked by promoting a fraction of the electron from the fifth orbital (σ_g) equally to the ninth and tenth orbitals ($3p\pi_u$). Apparently, the transition peak is very sharp and the peak position has a considerable shift for different states.

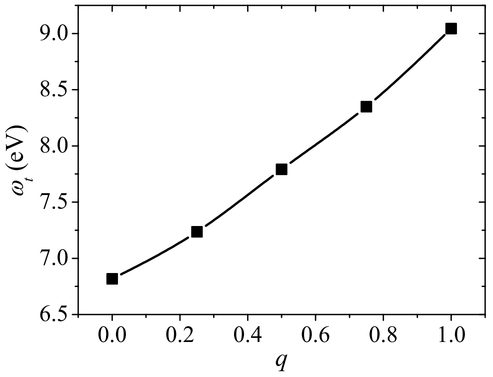

FIG. 2. Transition energy ω_t for the $A\ ^1\Pi$ charge-transfer state of HCl, evaluated by the peak position of $A_5^3(\omega)$, is calculated as a function of the fraction q of the excited electron. Five equally spaced points, i.e., $q=0$, 0.25, 0.5, 0.75, and 1, are given to show the smoothness of the curve.

Figure 2 shows the dependence of the transition energy on the fraction of excited electron, for the $A\ ^1\Pi$ charge-transfer state of HCl. Five equally-spaced points as q changes are calculated from 0 to 1. Smoothness of the curve indicates that it is reasonable to use several points to represent the whole profile. For that reason, we calculate the excitation energy using the three-point formula of Eq. (16) for $q=0$, 0.5, and 1.

The calculated results, along with comparisons to experiments and other calculations, are summarized in Table I. The error, whether taking into account the initial dipole moment d_{jk} or not, is rather small (a mean absolute error of about 0.06 eV), supporting our assumption that d_{jk} can be negligible to simplify the calculations. It is apparent that an ordinary TDDFT LR scheme gives considerably underestimated predictions for the Rydberg and charge-transfer excitation energies. The results for such excitations are greatly improved in our present work. They also retain good accuracy for valence excitations. In comparison to the TDDFT approaches with EXX [13] or accurate xc [14] potentials, our work predicts ΔE_e of two Rydberg transitions, $\sigma \rightarrow 3p\pi$ of N_2 and CO, to be 13.05 eV and 12.01 eV, close to their reported 13.04 eV and 11.91 eV, respectively. This suggests that similarly good accuracy can be achieved within the ALDA in our work. For the $A\ ^1\Pi$ state of HCl, we also use a sum of five points, as shown in Fig. 2, and obtain a value of 7.75 eV, which is similar to that of the three-point result of 7.74 eV. This result indicates that it is reasonable to use a simpler three-point formula for general purposes. The ΔSCF result also shows good performance for Rydberg and charge-transfer excitations, but exhibits large errors for the two valence excitations. It is noteworthy that, for N_2 and HCl, the calculated results in the present work closely resemble those of experiments and of CI. For HBr, the differences among them are larger. This is not surprising because we do not consider relativistic effects, which may yield substantial errors for heavy atoms such as Br; moreover, perfect CI calculations are not easy for HBr. The ΔE_e of $A\ ^1\Pi$ and $C\ ^1\Pi$ states of HBr are calculated as 6.53 and 8.64 eV in Ref. [32], which uses an asymptotically correct xc potential and a large set of augmented STO basis within the TDDFT. Therefore, we infer that our result can be reasonable for HBr.

V. CONCLUSION AND FUTURE WORK

In summary, we have shown an improved TDDFT approach to electronic excitations. The conventional scheme is

TABLE I. Vertical excitation energies ΔE_e for several diatomic molecules. Calculated values by different methods (LR: ordinary TDDFT linear response, CI: configuration interaction), as well as experimental results, are listed. Each transition is labeled as valence (V), Rydberg (R), or charge-transfer (C) in character. Note that T_e is the energy gap between the ground state and excited state at the equilibrium geometry of each, while ΔE_e is the gap at the fixed geometry.

	State	Transition	LR	Present	CI	ΔSCF	Experimental
N_2	$a\ ^1\Pi_g$	$V: \sigma_g \rightarrow \pi_g$	9.18	9.18	9.69[a]	8.62	9.31[b]
	$c\ ^1\Pi_u$	$R: \sigma_g \rightarrow 3p\pi_u$	11.69	13.05	13.14[a]	13.28	12.90[b]
CO	$A\ ^1\Pi$	$V: \sigma \rightarrow \pi^*$	8.20	8.19	8.54[c]	7.36	8.51[d]
	$E\ ^1\Pi$	$R: \sigma \rightarrow 3p\pi$	10.44	12.01	11.83[a]	12.20	11.53[d]
HCl	$A\ ^1\Pi$	$C: \pi \rightarrow \sigma^*$	6.78	7.74	7.84[e]	7.70	8.0[f]
	$C\ ^1\Pi$	$R: \pi \rightarrow \sigma$	8.35	9.65	9.67[e]	9.76	9.61[g]
HBr	$A\ ^1\Pi$	$C: \pi \rightarrow \sigma^*$	6.09	6.64	7.08[h]	6.58	7.01[i]
	$C\ ^1\Pi$	$R: \pi \rightarrow \sigma$	7.30	8.41	9.29[h]	8.57	8.74[i]

[a] MRD-CI results from Ref. [12]. The coupled-cluster method [26] gives a value of 9.27 eV for $a\ ^1\Pi_g$ of N_2.

[b] Experimental ΔE_e are calculated from spectroscopic constants. See Ref. [26].

[c] Quasidegenerate perturbation theory (QDPT) CI result from Ref. [27].

[d] Fitted values of experimental ΔE_e from Ref. [28].

[e] *Ab initio* CI results from Ref. [29].

[f] Experimental broad absorption band with a maximum near 8.0 eV [30].

[g] Experimental value of the (0,0) band origin, ΔE_{00} [30].

[h] Relativistic CI results of ΔE_e from Ref. [31]. The calculated T_e is 9.17 eV for $C\ ^1\Pi$ of HBr.

[i] Experimental ΔE_e not available. T_e values are used instead [31,32].

not rigorous for describing the electron-hole interaction because of the local approximation in *xc*. By averaging over the occupation number within a linear response, the approximate excitation energy of a system within an adiabatic LDA is found to have a form that is explicitly similar to that of the EXX system, i.e., the difference of shifted KS eigenenergies plus the Hartree-Fock interaction of the electron-hole pair. Implemented in the real-time propagation method, our scheme of modified linear response greatly improves a prediction for the problematic Rydberg and charge-transfer excitations. Its simplicity and efficiency has been exemplified for typical diatomic molecules.

The application of a modified linear response to a complex system is expected to be straightforward. This approach requires the states to be localized in the real space so as for the response to be dependent on the occupation number. Besides molecular systems, there are circumstances where electrons and/or holes are constructed with discrete states in some extended systems, such as in the excitations of semiconductor defects or localized surface adsorbate states. Our approach might be useful in these studies, and needs to be verified in future work.

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APPENDIX: APPROXIMATE EXCITATION ENERGIES FROM THE ΔSCF METHOD

Here, we do not rely on the two-level model as one usually does, and would give a general derivation for the approximate excitation energies from the ΔSCF calculations. First, the total energy of an *N*-electron system within LDA can be expressed as

$$E_{tot}^{LDA} = \sum_{i=1}^{N} \int \phi_i(\mathbf{r})\left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r})\right)\phi_i(\mathbf{r})d\mathbf{r} + \frac{1}{2}\sum_{i,j=1}^{N} \int\int \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}^{LDA}[\rho], \tag{A1}$$

where $\phi_i(\mathbf{r})$ is the one-electron Kohn-Sham orbital, which is assumed to be real, $\rho_i(\mathbf{r})$ stands for $\phi_i^2(\mathbf{r})$, and $v_{ext}(\mathbf{r})$ is the external potential. We will use the notation J_{ij} for the Coulomb integral, and t_i for the kinetic and external potential energy integral, i.e.,

$$J_{ij} = \int\int \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{A2}$$

$$t_i = \int \phi_i(\mathbf{r})\left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r})\right)\phi_i(\mathbf{r})d\mathbf{r}. \tag{A3}$$

The total energy in the ground state is then expressed as

$$E_{tot}^{gr,LDA} = \sum_{i=1}^{N} t_i + \frac{1}{2}\sum_{i,j=1}^{N} J_{ij} + E_{xc}^{LDA}[\rho^{gr}], \tag{A4}$$

where ρ_{gr} is the ground-state electron density, simply calculated as $\rho^{gr}(\mathbf{r}) = \Sigma_{i=1}^{N}\rho_i(\mathbf{r})$. When an excited state is constructed by promoting an electron from the occupied orbital *k* to the unoccupied orbital *j*, and the orbital relaxation effect is neglected, the self-consistent calculation gives the total energy difference between the excited state and the ground state as

$$\Omega^{\Delta SCF,LDA} \approx t_j - t_k + \sum_{i=1}^{N}(J_{ij} - J_{ik}) + \frac{1}{2}(J_{jj} + J_{kk}) - J_{kj} + E_{xc}^{LDA}[\rho^{gr} + \rho_j - \rho_k] - E_{xc}^{LDA}[\rho^{gr}]. \tag{A5}$$

The difference in the exchange-correlation energy can be expanded around ρ^{gr} to become

$$E_{xc}^{LDA}[\rho^{gr} + \rho_j - \rho_k] - E_{xc}^{LDA}[\rho^{gr}] \approx \int v_{xc}^{LDA}(\mathbf{r})\{\rho_j(\mathbf{r}) - \rho_k(\mathbf{r})\}d\mathbf{r} + \frac{1}{2}\int \{\rho_j(\mathbf{r}) - \rho_k(\mathbf{r})\}f_{xc}^{LDA}(\mathbf{r})\{\rho_j(\mathbf{r}) - \rho_k(\mathbf{r})\}d\mathbf{r}, \tag{A6}$$

where $v_{xc}^{LDA}(\mathbf{r})$ and $f_{xc}^{LDA}(\mathbf{r})$ are the LDA exchange-correlation potential and kernel at the ground state, respectively.

On the other hand, the eigenenergy of the *k*th orbital at the ground state can be computed from the Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \int \frac{\rho^{gr}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}^{LDA}(\mathbf{r})\right]\phi_k(\mathbf{r}) = \epsilon_k^{KS,LDA}\phi_k(\mathbf{r}). \tag{A7}$$

Multiplying both sides by $\phi_k(\mathbf{r})$ and integrating over the whole space, we obtain

$$\epsilon_k^{KS,LDA} = t_k + \sum_{i=1}^{N} J_{ik} + \int v_{xc}^{LDA}(\mathbf{r})\rho_k(\mathbf{r})d\mathbf{r}. \tag{A8}$$

In the same way, we can obtain the Kohn-Sham eigenenergy of the *j*th orbital at the ground state as

$$\epsilon_j^{KS,LDA} = t_j + \sum_{i=1}^{N} J_{ij} + \int v_{xc}^{LDA}(\mathbf{r})\rho_j(\mathbf{r})d\mathbf{r}. \tag{A9}$$

Therefore, Eq. (A5) can be expressed as

$$\Omega^{\Delta SCF,LDA} \approx \epsilon_j^{KS,LDA} - \epsilon_k^{KS,LDA} + \frac{1}{2}(J_{jj} + J_{kk}) - J_{kj} + \frac{1}{2}\int \{\rho_j(\mathbf{r}) - \rho_k(\mathbf{r})\}f_{xc}^{LDA}(\mathbf{r})\{\rho_j(\mathbf{r}) - \rho_k(\mathbf{r})\}d\mathbf{r}. \tag{A10}$$

This expression can be further transformed into

$$\Omega^{\Delta SCF,LDA} \approx \{\epsilon_j^{KS,LDA} + U_j\} - \{\epsilon_k^{KS,LDA} + U_k\} - \int \rho_j(\mathbf{r}) f_{xc}^{LDA}(\mathbf{r}) \rho_k(\mathbf{r}) d\mathbf{r} - J_{kj}. \quad \text{(A11)}$$

Here, U_i is the self-interaction energy, i.e.,

$$U_j = \frac{1}{2}\left[J_{jj} + \int \rho_j(\mathbf{r}) f_{xc}^{LDA}(\mathbf{r}) \rho_j(\mathbf{r}) d\mathbf{r} \right], \quad \text{(A12)}$$

which is the positive correction for the acceptor orbital, and

$$U_k = -\frac{1}{2}\left[J_{kk} + \int \rho_k(\mathbf{r}) f_{xc}^{LDA}(\mathbf{r}) \rho_k(\mathbf{r}) d\mathbf{r} \right], \quad \text{(A13)}$$

which is the negative correction for the donor orbital.

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[18] An illustrative example is the charge-transfer excitations in which the overlap of $\phi_k(\mathbf{r})$ and $\phi_j(\mathbf{r})$ is zero. Since K_ν and $\{\rho_k|f_{xc}^{LDA}|\rho_j\}$ both become zero, we can conclude that $\Omega^{ALDA} \approx \omega_\nu$. In comparison, our occupation number averaging scheme gives $\langle\Omega^{ALDA}\rangle \approx \tilde{\omega}_\nu^{LDA} - J_\nu$. It incorprates the shift by self-interaction energy and the electron-hole Coulomb attraction. Consistent behavior is observed when *xc* functionals containing derivative discontinuities are used, which yield a nonzero correction because of singularities in f_{xc} [A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. **126**, 4007 (2004)]. Meanwhile, the ΔSCF method gives the same expression as $\langle\Omega^{ALDA}\rangle$ in such cases, so it would also give results in good accuracy. For usual conditions (e.g., partial overlap or K_ν is nontrivial), our scheme is more rigorous and would give a better performance.

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