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Extension of the Core-Valence-Rydberg B3LYP Functional to Core-Excited-State Calculations of Third-Row Atoms

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Abstract: A modified core-valence-Rydberg Becke's three-parameter exchange (B3) + Lee−Yang−Parr (LYP) correlation (CVR-B3LYP) functional is proposed in order to calculate core-excitation energies of third-row atoms with reasonable accuracy. The assessment of conventional exchange-correlation functionals shows that the appropriate portions of Hartree−Fock (HF) exchange for core-excited-state calculations depend on shells: 70% and 50% for K-shell and L-shell excitations, respectively. Therefore, the modified CVR-B3LYP functional is designed to use the appropriate portions of HF exchange, 70%, 50%, and 20%, for K-shell, L-shell, and valence regions separately. Time-dependent density functional theory calculations with the modified CVR-B3LYP functional yield both K-shell and L-shell excitation energies with reasonable accuracy. The modified CVR-B3LYP also provides valence-excitation energies and standard enthalpies of formation accurately. Thus, the modified CVR-B3LYP describes all of the K-shell, L-shell, and valence electrons appropriately.

1. Introduction

Time-dependent density functional theory (TDDFT)[1−8] has been one of the most widely used tools for excited-state calculations. TDDFT provides quantitative results for low-lying valence-excited states with low computational costs because electron correlations are included through exchange-correlation functionals. However, the disadvantages of TD-DFT have been reported: TDDFT calculations with conventional exchange-correlation functionals tend to largely underestimate the core- and Rydberg-excitation energies.[9−14] The underestimation is considered to occur because of the inappropriate behavior of exchange-correlation functionals in core and Rydberg regions.[11,15] Several methods for improving TDDFT accuracy for core and Rydberg excitations have been advocated.[9,12,16−20]

For core excitations, core-valence Becke's three-parameter exchange (B3)[21] + Lee−Yang−Parr (LYP)[22] correlation (CV-B3LYP)[9] hybrid functional has been proposed. CV-

B3LYP yields both core- and valence-excitation energies with high accuracy by using appropriate portions of Hartree−Fock (HF) exchange for core and valence regions separately. Density functional theory (DFT) with the transition state approach and the delta-Kohn−Sham (ΔE_{KS}) method,[23,24] which are based on DFT but not on TDDFT, also reproduce core excitation energies with high accuracy. For Rydberg excitations, the van Leeuwen−Baerends' 94 (LB94) functional,[16] the statistical average of different orbital model potential (SAOP) functional,[17] the asymptotically corrected (AC) Kohn−Sham (KS) equation of Tozer and Handy,[18] and the long-range correction (LC) scheme for the exchange functional[19] have been proposed. The modified LB94 and the Becke's 1988 exchange (B88)[25] + LYP correlation (BLYP) pure functional, BmLBLYP,[12] and the core-valence-Rydberg B3LYP (CVR-B3LYP)[20] hybrid functional have been reported as the methods for improving the descriptions of both core and Rydberg excitations. By taking advantage of the appropriate portions of HF exchange not only for core and occupied-valence orbitals but also for the unoccupied-valence and Rydberg orbitals separately, TDDFT calculations

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Table 1. 1s Core-Excitation Energies of SiH₄, PH₃, H₂S, SO₂, HCl, and Cl₂ Molecules by TDHF and TDDFT with the BLYP, B3LYP, and BHHLYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	assignment	BLYP			B3LYP			BHHLYP			TDHF			exptl
		NR[b]	R[c]	Δ_{R−NR}[d]	NR[b]	R[c]	Δ_{R−NR}[d]	NR[b]	R[c]	Δ_{R−NR}[d]	NR[b]	R[c]	Δ_{R−NR}[d]	
SiH₄	Si 1s → σ*	1781.0 (−61.5)	1784.7 (−57.8)	3.7	1797.7 (−44.8)	1801.1 (−41.4)	3.4	1823.7 (−18.8)	1827.6 (−14.9)	3.9	1864.9 (+22.4)	1869.1 (+26.6)	4.2	1842.5[e]
PH₃	P 1s → σ*(e)	2077.5 (−68.4)	2082.4 (−63.4)	4.9	2095.1 (−50.8)	2100.1 (−45.7)	5.1	2122.8 (−23.0)	2128.1 (−17.8)	5.2	2166.9 (+21.1)	2172.5 (+26.6)	5.6	2145.8[f]
H₂S	S 1s → 3b₂(σ*)	2397.2 (−75.9)	2403.7 (−69.4)	6.5	2415.9 (−57.2)	2422.6 (−50.5)	6.7	2445.6 (−27.5)	2452.5 (−20.6)	6.9	2492.9 (+19.8)	2500.1 (+27.0)	7.3	2473.1[g]
SO₂	S 1s → 3b₁(π*)	2397.7 (−76.1)	2404.3 (−69.5)	6.5	2416.3 (−57.5)	2423.0 (−50.8)	6.7	2445.8 (−28.0)	2452.7 (−21.1)	6.9	2492.3 (+18.5)	2499.6 (+25.8)	7.3	2473.8[g]
HCl	Cl 1s → 3pσ*	2739.9 (−84.0)	2748.4 (−75.5)	8.5	2760.4 (−63.5)	2769.0 (−54.9)	8.7	2792.4 (−31.5)	2801.3 (−22.6)	8.9	2843.3 (+19.4)	2852.6 (+28.7)	9.4	2823.9[h]
Cl₂	Cl 1s → 3pσ_u*	2738.0 (−83.3)	2746.5 (−74.8)	8.5	2757.9 (−63.4)	2766.5 (−54.8)	8.7	2789.4 (−31.9)	2798.3 (−23.0)	8.9	2839.7 (+18.4)	2849.1 (+27.8)	9.4	2821.3[h]
ME[i]		−64.2	−58.6		−48.2	−42.6		−23.0	−17.1		17.1	23.2		

[a] Differences from experimental data are shown in parentheses. [b] Excitation energies by nonrelativistic calculations. [c] Excitation energies by relativistic calculations. [d] Differences between NR and R. [e] Reference 36. [f] Reference 37. [g] Reference 38. [h] Reference 39. [i] Mean errors from experimental data.

with CVR-B3LYP have succeeded in describing Rydberg excitations with reasonable accuracy.

In the previous CV- and CVR-B3LYP studies, the calculations have been performed on the small molecules containing second-row atoms. In this study, we extend the CVR-B3LYP functional to core-excited-state calculations of third-row atoms. The assessment of time-dependent HF (TDHF) and TDDFT calculations with conventional exchange-correlation functionals on the molecules containing third-row atoms are shown in the next section. Based on the assessment, the CVR-B3LYP functional is modified in the third section in order to improve the descriptions of core excitations from third-row atoms. The last section gives the conclusions of the present study.

2. Assessment of Conventional Exchange-Correlation Functionals for Core-Excited-State Calculations on Third-Row Atoms

In this section, the appropriate portions of HF exchange for describing K-shell and L-shell core excitations have been investigated by performing TDDFT calculations with conventional exchange-correlation functionals: BLYP, B3LYP, and Becke's half-and-half exchange + LYP correlation (BHHLYP).[26] TDHF calculations were carried out for comparison. The correlation consistent polarized core-valence triple-ζ (cc-pCVTZ) basis set[27−30] was used. Single (s, p) Rydberg basis functions were added for describing (3s, 3p) orbitals of second-row atoms and (4s, 4p) orbitals of third-row atoms.[31−33] All molecular structures were optimized at the B3LYP/cc-pVTZ[27] level. The scalar relativistic effect is included by using the relativistic scheme by eliminating small-components (RESC) method.[34,35] Spin−orbit interactions are not included in the present calculations.

The 1s and 2p core-excitation energies of SiH₄, PH₃, H₂S, SO₂, HCl, and Cl₂ molecules calculated with TD-BLYP, TD-B3LYP, TD-BHHLYP, and TDHF are shown in Tables 1 and 2. Si, P, S, and Cl in boldface correspond to the atoms whose 1s or 2p electrons are excited. The results of relativistic (R) and nonrelativistic (NR) calculations and their differences are shown in the tables. The differences from the experimental values are shown in parentheses. For the 2p excitation energies of SiH₄, PH₃, and Cl₂, the weighted averaged values between P₁/₂ and P₃/₂ states, which are obtained by the procedure mentioned in ref 44, are adopted as the experimental data. As for the 1s core-excitation energies in Table 1, the relativistic effect becomes larger as the atomic number increases: The differences between the results with and without relativistic corrections are 3.4−4.2, 4.9−5.6, 6.5−7.3, and 8.5−9.4 eV for Si, P, S, and Cl, respectively. It is also shown that the relativistic correction becomes larger in the order BLYP < B3LYP < BHHLYP < TDHF, which is consistent with the portions of HF exchange in the functionals. The mean errors (MEs) of TD-BLYP, TD-B3LYP, TD-BHHLYP, and TDHF with relativistic corrections for third-row atoms are −58.6, −42.6, −17.1, and 23.2 eV, respectively, which are significantly larger than −17.9, −12.0, −2.8, and 11.1 eV for the second-row atoms obtained in the previous study.[20] 1s core-excitation

Table 2. 2p Core-Excitation Energies of SiH$_4$, PH$_3$, H$_2$S, SO$_2$, HCl, and Cl$_2$ Molecules by TDHF and TDDFT with the BLYP, B3LYP, and BHHLYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	assignment	BLYP			B3LYP			BHHLYP			TDHF			exptl
		NR[b]	R[c]	Δ_{R-NR}[d]	NR[b]	R[c]	Δ_{R-NR}[d]	NR[b]	R[c]	Δ_{R-NR}[d]	NR[b]	R[c]	Δ_{R-NR}[d]	
SiH$_4$	Si 2p → σ*	94.4	94.4	0.0	97.8	97.8	0.0	102.4	102.4	0.0	109.4	109.4	0.0	102.8[e,i]
		(−8.4)	(−8.4)		(−5.0)	(−5.0)		(−0.4)	(−0.4)		(+6.6)	(+6.6)		
PH$_3$	P 2p → σ*(a$_1$)	122.4	122.4	0.0	126.5	126.5	0.0	132.2	131.4	−0.8	139.0	140.9	1.9	132.3[e,i]
		(−9.9)	(−9.9)		(−5.8)	(−5.9)		(−0.1)	(−0.9)		(+6.7)	(+8.6)		
H$_2$S	S 2p → 3b$_2$(σ*)	154.8	154.8	0.0	158.6	158.5	0.0	164.4	164.4	0.0	172.9	172.9	0.0	164.5[e]
		(−9.7)	(−9.7)		(−5.9)	(−6.0)		(−0.1)	(−0.1)		(+8.4)	(+8.4)		
SO$_2$	S 2p → 3b$_1$(π*)	154.7	154.7	0.0	158.4	158.4	0.0	163.6	163.6	0.0	171.6	171.7	0.0	164.4[f]
		(−9.6)	(−9.7)		(−6.0)	(−6.0)		(−0.7)	(−0.7)		(+7.3)	(+7.3)		
HCl	Cl 2pπ → 3pσ*	189.5	189.5	0.0	194.0	194.0	0.0	200.4	200.4	0.0	210.1	210.1	0.0	201.0[g]
		(−11.5)	(−11.5)		(−7.0)	(−7.0)		(−0.6)	(−0.6)		(+9.1)	(+9.1)		
Cl$_2$	Cl 2pπ → 3pσ$_u$*	187.3	187.3	0.0	191.4	191.4	0.0	197.4	197.4	0.0	206.8	206.8	0.0	198.7[h,i]
		(−11.5)	(−11.5)		(−7.3)	(−7.3)		(−1.4)	(−1.3)		(+8.1)	(+8.1)		
ME[j]		−8.7	−8.7		−5.3	−5.3		−0.5	−0.6		6.6	6.9		

[a] Differences from experimental data are shown in parentheses. [b] Excitation energies by relativistic calculations. [c] Excitation energies by nonrelativistic calculations. [d] Differences between NR and R. [e] Reference 40. [f] Reference 41. [g] Reference 42. [h] Reference 43. [i] Weighted average value calculated with the method in ref 44. [j] Mean errors from experimental data.

energies are underestimated by pure TDDFT, while those are overestimated by TDHF. Using hybrid functionals such as B3LYP and BHHLYP improves the descriptions of 1s core-excitations in comparison with a pure functional, which shows that HF exchange reduces the underestimation of the pure TDDFT method. The behavior of 1s core-excitation energies of third-row atoms discussed above is analogous to that of second-row atoms in ref 20.

With regards to the 2p core-excitation energies in Table 2, the relativistic corrections are at most 1.9 eV, which are smaller than those for the 1s excitation energies. The MEs of TD-BLYP, TD-B3LYP, TD-BHHLYP, and TDHF with relativistic corrections are −8.5, −5.2, −0.5, and 7.0 eV, respectively. The underestimation by TDDFT, the overestimation by TDHF, and the improvement of the results by using hybrid functionals instead of pure functionals are also observed for 2p core-excitations. BHHLYP, which have the smallest mean absolute error (MAE) of 0.5 eV, gives the excitation energies accurately enough to discuss 2p core excitations.

In order to investigate the effect of HF exchange more precisely, we performed the additional TDDFT calculations with the following exchange-correlation functionals

$$E_{xc} = a \sum_{ij} (-K_{ij}) + (1-a)E_x^{B88}[\rho] + E_c^{LYP}[\rho] \quad (1)$$

where K_{ij}, E_x^{B88}, and E_c^{LYP} represent HF exchange, B88 exchange, and LYP correlation energies. Suffixes i and j denote the indexes of occupied orbitals. ρ is the total electron density. The portion of HF exchange is changed to 60%, 70%, 80%, 90%, or 100% by setting the coefficient a to 0.6, 0.7, 0.8, 0.9, or 1.0, respectively. We denote the functional in eq 1 with $X\%$ portions of HF exchange "HF+B88+LYP ($X\%$)" in the present study. The scalar relativistic effects are considered by the RESC method.

Tables 3 and 4 show the 1s and 2p core-excitation energies calculated with nine kinds of methods: BLYP, B3LYP, BHHLYP, HF+B88+LYP ($X\%$) (X = 60, 70, 80, 90, and
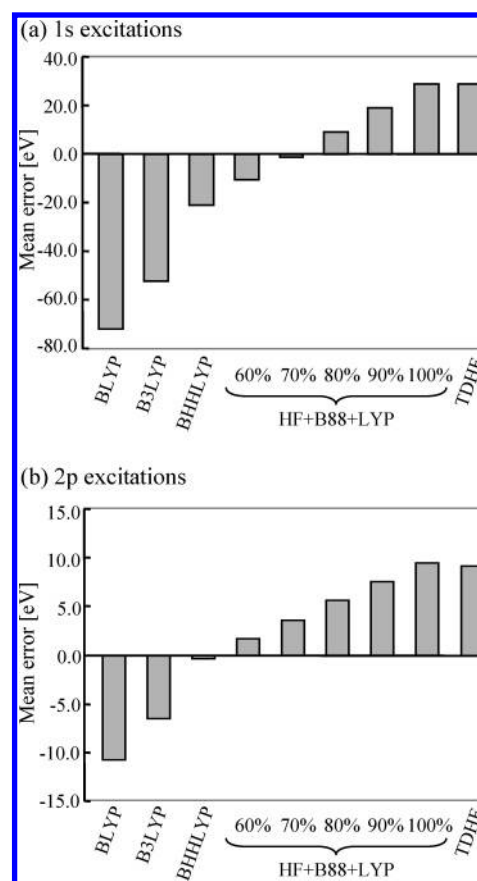
Figure 1. Mean errors of 1s and 2p core-excitation energies by TDHF and TDDFT with the BLYP, B3LYP, BHHLYP, and HF+B88+LYP functionals with cc-pCVTZ plus Rydberg basis functions.

100), and TDHF. In Table 3, the MAEs of BLYP with no HF exchange and HF+B88+LYP (100%) and TDHF only with HF exchange are significantly large: 70.8, 28.8, and 28.4 eV, respectively. The difference of the MAEs between HF+B88+LYP (100%) and TDHF is 0.4 eV, which indicates that the effect of the correlation functional on calculated

Table 3. 1s Core-Excitation Energies of SiH$_4$, PH$_3$, H$_2$S, SO$_2$, HCl, and Cl$_2$ Molecules by TDHF and TDDFT with the BLYP, B3LYP, BHHLYP, and HF+B88+LYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	assignment	BLYP 0%	B3LYP 20%	BHHLYP 50%	HF+B88+LYP 60%	70%	80%	90%	100%	TDHF 100%	exptl
SiH$_4$	Si 1s → σ*	1784.7 (−57.8)	1801.1 (−41.4)	1827.6 (−14.9)	1836.0 (−6.5)	1844.4 (+1.9)	1852.8 (+10.3)	1861.1 (+18.6)	1869.3 (+26.8)	1869.1 (+26.6)	1842.5[b]
PH$_3$	P 1s → σ*(e)	2082.4 (−63.4)	2100.1 (−45.7)	2128.1 (−17.8)	2137.1 (−8.8)	2146.0 (+0.2)	2155.0 (+9.1)	2163.8 (+18.0)	2172.7 (+26.8)	2172.5 (+26.6)	2145.8[c]
H$_2$S	S 1s → 3b$_2$(σ*)	2403.7 (−69.4)	2422.6 (−50.5)	2452.5 (−20.6)	2462.2 (−10.9)	2471.8 (−1.3)	2481.3 (+8.2)	2490.9 (+17.8)	2500.3 (+27.2)	2500.1 (+27.0)	2473.1[d]
	S 1s → 4pb$_2$	2404.4 (−71.9)	2424.4 (−51.9)	2456.1 (−20.2)	2466.4 (−9.9)	2476.7 (+0.4)	2486.9 (+10.6)	2497.2 (+20.9)	2507.4 (+31.1)	2506.8 (+30.5)	2476.3[d]
SO$_2$	S 1s → 3b$_1$(π*)	2404.3 (−69.5)	2423.0 (−50.8)	2452.7 (−21.1)	2462.2 (−11.6)	2471.7 (−2.1)	2481.1 (+7.3)	2490.4 (+16.6)	2499.7 (+25.9)	2499.6 (+25.8)	2473.8[d]
	S 1s → 9a$_1$(γ*)	2408.0 (−70.4)	2427.5 (−50.9)	2457.9 (−20.5)	2467.6 (−10.8)	2477.3 (−1.1)	2486.9 (+8.5)	2496.5 (+18.1)	2506.1 (+27.7)	2505.9 (+27.5)	2478.4[d]
HCl	Cl 1s → 3pσ*	2748.4 (−75.5)	2769.0 (−54.9)	2801.3 (−22.6)	2811.7 (−12.2)	2822.1 (−1.8)	2832.4 (+8.5)	2842.6 (+18.7)	2852.8 (+28.9)	2852.6 (+28.7)	2823.9[e]
	Cl 1s → 4pπ	2750.0 (−77.8)	2771.4 (−56.4)	2805.2 (−22.6)	2816.2 (−11.6)	2827.2 (−0.6)	2838.2 (+10.4)	2849.1 (+21.3)	2860.0 (+32.2)	2859.3 (+31.5)	2827.8[e]
Cl$_2$	Cl 1s → 3pσ$_u$*	2746.5 (−74.8)	2766.5 (−54.8)	2798.3 (−23.0)	2808.6 (−12.7)	2818.8 (−2.5)	2829.0 (+7.7)	2839.1 (+17.8)	2849.2 (+27.9)	2849.1 (+27.8)	2821.3[e]
	Cl 1s → 4p	2751.1 (−77.4)	2772.6 (−55.9)	2806.6 (−21.9)	2817.7 (−10.8)	2828.7 (+0.2)	2839.7 (+11.2)	2850.7 (+22.2)	2861.6 (+33.1)	2860.9 (+32.4)	2828.5[e]
MAE[f]		70.8	51.3	20.5	10.6	1.2	9.2	19.0	28.8	28.4	

[a] The portion of HF exchange in the exchange-correlation functional is shown for each method. Differences from experimental data are shown in parentheses. [b] Reference 36. [c] Reference 37. [d] Reference 38. [e] Reference 39. [f] Mean absolute errors from experimental data.

Table 4. 2p Core-Excitation Energies of SiH$_4$, PH$_3$, H$_2$S, SO$_2$, HCl, and Cl$_2$ Molecules by TDHF and TDDFT with the BLYP, B3LYP, BHHLYP, and HF+B88+LYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	assignment	BLYP 0%	B3LYP 20%	BHHLYP 50%	HF+B88+LYP 60%	70%	80%	90%	100%	TDHF 100%	exptl
SiH$_4$	Si 2p → σ*	94.4 (−8.4)	97.8 (−5.0)	102.4 (−0.4)	103.9 (+1.1)	105.4 (+2.6)	106.8 (+4.0)	108.3 (+5.5)	109.6 (+6.8)	109.4 (+6.6)	102.8[b,f]
PH$_3$	P 2p → σ*	122.4 (−9.9)	126.5 (−5.9)	131.4 (−0.9)	134.1 (+1.8)	134.6 (+2.3)	137.8 (+5.5)	139.5 (+7.2)	141.3 (+8.9)	140.9 (+8.6)	132.3[b,f]
H$_2$S	S 2p → σ*	154.8 (−9.7)	158.5 (−6.0)	164.4 (−0.1)	166.2 (+1.7)	167.9 (+3.4)	169.7 (+5.2)	171.4 (+6.9)	173.2 (+8.7)	172.9 (+8.4)	164.5[b]
	S 2p → 4s	155.5 (−11.0)	160.3 (−6.2)	167.3 (+0.8)	169.5 (+3.0)	171.7 (+5.2)	173.9 (+7.4)	176.0 (+9.5)	178.1 (+11.6)	177.6 (+11.1)	166.5[b]
SO$_2$	S 2p → 3b$_1$(π*)	154.7 (−9.7)	158.4 (−6.0)	163.6 (−0.7)	165.3 (+1.0)	167.0 (+2.6)	168.7 (+4.3)	170.3 (+5.9)	171.9 (+7.5)	171.7 (+7.3)	164.4[c]
	S 2p → 4s	159.0 (−12.3)	163.8 (−7.5)	170.9 (−0.4)	173.2 (+1.9)	175.6 (+4.3)	177.9 (+6.6)	180.1 (+8.8)	182.4 (+11.1)	181.7 (+10.4)	171.3[c]
HCl	Cl 2pπ → 3pσ*	189.5 (−11.5)	194.0 (−7.0)	200.4 (−0.6)	202.4 (+1.4)	204.5 (+3.5)	206.5 (+5.5)	208.4 (+7.4)	210.4 (+9.4)	210.1 (+9.1)	201.0[d]
	Cl 2pπ → 4pπ	191.1 (−13.5)	196.4 (−8.2)	204.0 (−0.6)	206.6 (+2.0)	209.1 (+4.5)	211.7 (+7.1)	214.2 (+9.6)	216.7 (+12.1)	215.9 (+11.3)	204.6[d]
Cl$_2$	Cl 2pπ → 3pσ$_u$*	187.3 (−11.5)	191.4 (−7.3)	197.4 (−1.3)	199.4 (+0.6)	201.3 (+2.6)	203.2 (+4.5)	205.1 (+6.4)	207.0 (+8.3)	206.8 (+8.1)	198.7[e,f]
MAE[g]		10.8	6.6	0.7	1.6	3.4	5.5	7.5	9.4	9.0	

[a] The portion of HF exchange in the exchange-correlation functional is shown for each method. Differences from experimental data are shown in parentheses. [b] Reference 40. [c] Reference 41. [d] Reference 42. [e] Reference 43. [f] Weighted average value calculated with the method in ref 44. [g] Mean absolute errors from experimental data.

1s core-excitation energies is small. HF+B88+LYP (70%) with a MAE of 1.2 eV shows the best performance among the nine methods. In Table 4, BHHLYP gives the smallest MAE, 0.6 eV. HF+B88+LYP (60%) with a MAE of 1.7 eV shows high performance. The effect of the correlation functional is small on 2p core excitations: The difference of the MAEs between HF+B88+LYP (100%) and TDHF is 0.4 eV.

The MEs of 1s and 2p excitation energies calculated with the nine methods are illustrated in Figure 1. Figure 1

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clearly demonstrates that both calculated 1s and 2p core-excitation energies increase as the portion of HF exchange in the employed functional increases. The appropriate portion of HF exchange for 1s core excitations is different from that for 2p core excitations: about 70% and 50% for 1s and 2p excitations, respectively. This fact is thought to be due to the large self-interaction errors of 1s electrons because K-shell electrons in a third-row atom are attracted to the nucleus more strongly than L-shell electrons in a third-row atom and K-shell electrons in a second-row atom are.[11,15]

3. Extension of CVR-B3LYP to Core-Excited-State Calculations of Third-Row Atoms

3.1. Modified CVR-B3LYP Equations for Core Excitations from Third-Row Atoms. As mentioned in section 2, 70% and 50% portions of HF exchange are appropriate for describing K-shell and L-shell electrons, while B3LYP with 20% portion of HF exchange is well-known to perform well for valence properties. Therefore, CVR-B3LYP is modified to use appropriate portions of HF exchange for K-shell, L-shell, and valence regions separately. In the previous CVR-B3LYP, the occupied orbitals are distinguished into core (C) and occupied-valence (OV) orbitals. In the present modified CVR-B3LYP, the occupied orbitals are distinguished into three groups, namely, K-shell (C1), L-shell (C2), and occupied-valence (OV) orbitals. Thus, the electronic energy is decomposed into C1−C1, C1−C2, C1−OV, C2−C2, C2−OV, and OV−OV interactions

$$
\begin{aligned}
E = {} & 2\sum_k^{C1} H_k + 2\sum_m^{C2} H_m + 2\sum_p^{OV} H_p + \sum_{kl}^{C1} 2J_{kl} + \\
& \sum_k^{C1}\sum_m^{C2} 2J_{km} + \sum_k^{C1}\sum_p^{OV} 2J_{kp} + \sum_m^{C2}\sum_k^{C1} 2J_{mk} + \sum_{mn}^{C2} 2J_{mn} + \\
& \sum_m^{C2}\sum_p^{OV} 2J_{mp} + \sum_p^{OV}\sum_k^{C1} 2J_{pk} + \sum_p^{OV}\sum_m^{C2} 2J_{pm} + \sum_{pq}^{OV} 2J_{pq} + \\
& a_{C1C1}\sum_{kl}^{C1} (-K_{kl}) + a_{C1C2}\sum_k^{C1}\sum_m^{C2} (-K_{km}) + \\
& a_{C1OV}\sum_k^{C1}\sum_p^{OV} (-K_{kp}) + a_{C1C2}\sum_m^{C2}\sum_k^{C1} (-K_{mk}) + \\
& a_{C2C2}\sum_{mn}^{C2} (-K_{mn}) + a_{C2OV}\sum_m^{C2}\sum_p^{OV} (-K_{mp}) + \\
& a_{C1OV}\sum_p^{OV}\sum_k^{C1} (-K_{pk}) + a_{C2OV}\sum_p^{OV}\sum_m^{C2} (-K_{pm}) + \\
& a_{OVOV}\sum_{pq}^{OV} (-K_{pq}) + b_{C1C1}E_{xc}[\rho_{C1}] + b_{C2C2}E_{xc}[\rho_{C2}] + \\
& b_{OVOV}E_{xc}[\rho_{OV}] + b_{C1C2}(E_{xc}[\rho_{C1+C2}] - E_{xc}[\rho_{C1}] - \\
& E_{xc}[\rho_{C2}]) + b_{C1OV}(E_{xc}[\rho_{C1+OV}] - E_{xc}[\rho_{C1}] - E_{xc}[\rho_{OV}]) + \\
& b_{C2OV}(E_{xc}[\rho_{C2+OV}] - E_{xc}[\rho_{C2}] - E_{xc}[\rho_{OV}]) \quad (2)
\end{aligned}
$$

Table 5. Coefficients of Exchange-Correlation Functionals in the Modified CVR-B3LYP Functional

	C1C1	C1C2	C1OV	C2C2	C2OV	OVOV
a (HF exchange)	0.7	0.6	0.45	0.5	0.35	0.2
b (Slater exchange)	0	0	0.04	0	0.04	0.08
(B88 exchange)	0.3	0.4	0.51	0.5	0.61	0.72
(VWN5 correlation)	0	0	0.095	0	0.095	0.19
(LYP correlation)	1	1	0.905	1	0.905	0.81

where H and J are 1-electron and Coulomb integrals, and a and b are the coefficients of HF exchange and DFT exchange-correlation functionals. The "C1", "C2", and "OV" on the Σ mean that the summation runs over the K-shell, L-shell, and occupied-valence orbitals, respectively; therefore, suffixes (k, l), (m, n), and (p, q) correspond to K-shell, L-shell, and occupied-valence orbitals. The definitions of the electron densities are as follows

$$
\rho_{C1} = \sum_k^{C1} |\varphi_k|^2, \ \rho_{C2} = \sum_m^{C2} |\varphi_m|^2, \ \rho_{OV} = \sum_p^{OV} |\varphi_p|^2
$$

$$
\rho_{C1+C2} = \sum_i^{\neq OV} |\varphi_i|^2, \ \rho_{C1+OV} = \sum_i^{\neq C2} |\varphi_i|^2,
$$

$$
\rho_{C2+OV} = \sum_i^{\neq C1} |\varphi_i|^2 \quad (3)
$$

where φ is the KS orbital, and the "$\neq$C1", "$\neq$C2", and "$\neq$OV" on the Σ mean that the summation runs over all occupied orbitals without the K-shell, L-shell, and occupied-valence orbitals, respectively. The C1−C2 interaction is represented as the subtraction of $E_{xc}[\rho_{C1}]$ and $E_{xc}[\rho_{C2}]$ from $E_{xc}[\rho_{C1+C2}]$, and the same applies to C1−OV and C2−OV interactions. In eq 2, the three- and higher-body interactions in DFT exchange-correlation energies are neglected. However, our preliminary calculations have shown that the energy differences due to the truncation are small enough to be negligible. For more details, see ref 45. The exchange-correlation functional in CVR-B3LYP consists of Slater exchange,[46] B88 exchange,[25] Vosko−Wilk−Nusair (VWN5) correlation,[47] and LYP correlation[22] functionals. The coefficients a_Y and b_Y (Y = C1C1, C1C2, C1OV, C2C2, C2OV, and OVOV) used in the present calculations are listed in Table 5. The coefficients of C1C1, C2C2, and OVOV are set to those of HF+B88+LYP (70%), BHHLYP, and B3LYP. The coefficients of C1C2, C1OV, and C2OV are set to the mean values of {C1C1 and C2C2}, {C1C1 and OVOV}, and {C2C2 and OVOV}, respectively. The sum of the coefficients in each group Y becomes one.

Using the variational principle to eq 2 leads to three kinds of Fock operators

$$
\begin{aligned}
F_{C1} = {} & h + 2J - (a_{C1C1}K_{C1} + a_{C1C2}K_{C2} + a_{C1OV}K_{OV}) + \\
& (b_{C1C1} - b_{C1C2} - b_{C1OV})V_{xc}[\rho_{C1}] + b_{C1C2}V_{xc}[\rho_{C1+C2}] + \\
& b_{C1OV}V_{xc}[\rho_{C1+OV}] \quad (4)
\end{aligned}
$$

$$F_{C2} = h + 2J - (a_{C1C2}K_{C1} + a_{C2C2}K_{C2} + a_{C2OV}K_{OV}) + (b_{C2C2} - b_{C1C2} - b_{C2OV})V_{xc}[\rho_{C2}] + b_{C1C2}V_{xc}[\rho_{C1+C2}] + b_{C2OV}V_{xc}[\rho_{C2+OV}] \quad (5)$$

$$F_{OV} = h + 2J - (a_{C1OV}K_{C1} + a_{C2OV}K_{C2} + a_{OVOV}K_{OV}) + (b_{OVOV} - b_{C1OV} - b_{C2OV})V_{xc}[\rho_{OV}] + b_{C1OV}V_{xc}[\rho_{C1+OV}] + b_{C2OV}V_{xc}[\rho_{C2+OV}] \quad (6)$$

where h is 1-electron operator, and J and K in and after eq 4 are Coulomb and HF-exchange operators. HF-exchange operators and the first derivatives of E_{xc} are as follows:

$$K_{C1} = \sum_{k}^{C1} K_k, \quad K_{C2} = \sum_{m}^{C2} K_m, \quad K_{OV} = \sum_{p}^{OV} K_p,$$

$$V_{xc}[\rho_{C1}] = \frac{\delta E_{xc}[\rho_{C1}]}{\delta \rho_{C1}}, \quad V_{xc}[\rho_{C2}] = \frac{\delta E_{xc}[\rho_{C2}]}{\delta \rho_{C2}},$$

$$V_{xc}[\rho_{OV}] = \frac{\delta E_{xc}[\rho_{OV}]}{\delta \rho_{OV}}, \quad V_{xc}[\rho_{C1+C2}] = \frac{\delta E_{xc}[\rho_{C1+C2}]}{\delta \rho_{C1+C2}},$$

$$V_{xc}[\rho_{C1+OV}] = \frac{\delta E_{xc}[\rho_{C1+OV}]}{\delta \rho_{C1+OV}},$$

$$V_{xc}[\rho_{C2+OV}] = \frac{\delta E_{xc}[\rho_{C2+OV}]}{\delta \rho_{C2+OV}} \quad (7)$$

In order to guarantee the invariance under the unitary transformation, the coupling-operator technique of Roothaan[48−50] is adopted. Introducing the operators R

$$R_{C1} = -\sum_{m}^{C2} \{|\varphi_m\rangle\langle\varphi_m|\Theta_{C1C2}) + (\Theta_{C1C2}|\varphi_m\rangle\langle\varphi_m|\} - \sum_{p}^{OV} \{|\varphi_p\rangle\langle\varphi_p|\Theta_{C1OV}) + (\Theta_{C1OV}|\varphi_p\rangle\langle\varphi_p|\} \quad (8)$$

$$R_{C2} = -\sum_{k}^{C1} \{|\varphi_k\rangle\langle\varphi_k|\Theta_{C2C1}) + (\Theta_{C2C1}|\varphi_k\rangle\langle\varphi_k|\} - \sum_{p}^{OV} \{|\varphi_p\rangle\langle\varphi_p|\Theta_{C2OV}) + (\Theta_{C2OV}|\varphi_p\rangle\langle\varphi_p|\} \quad (9)$$

$$R_{OV} = -\sum_{k}^{C1} \{|\varphi_k\rangle\langle\varphi_k|\Theta_{OVC1}) + (\Theta_{OVC1}|\varphi_k\rangle\langle\varphi_k|\} - \sum_{m}^{C2} \{|\varphi_m\rangle\langle\varphi_m|\Theta_{OVC2}) + (\Theta_{OVC2}|\varphi_m\rangle\langle\varphi_m|\} \quad (10)$$

we obtain the coupling operators as

$$F_{C1}' = F_{C1} + R_{C1} \quad (11)$$

$$F_{C2}' = F_{C2} + R_{C2} \quad (12)$$

$$F_{OV}' = F_{OV} + R_{OV} \quad (13)$$

where Θs are

$$\Theta_{C1C2} = (1 - \lambda)F_{C1} + \lambda F_{C2} \quad (14)$$

$$\Theta_{C2C1} = -\lambda F_{C1} + (1 + \lambda)F_{C2} \quad (15)$$

$$\Theta_{C1OV} = (1 - \mu)F_{C1} + \mu F_{OV} \quad (16)$$

$$\Theta_{OVC1} = -\mu F_{C1} + (1 + \mu)F_{OV} \quad (17)$$

$$\Theta_{C2OV} = (1 - \sigma)F_{C2} + \sigma F_{OV} \quad (18)$$

$$\Theta_{OVC2} = -\sigma F_{C2} + (1 + \sigma)F_{OV} \quad (19)$$

and λ, μ, and σ are arbitrary nonzero numbers and are set to 0.1 in the present study. Thus, the Fock operator for occupied orbitals is rewritten as follows:

$$F = \sum_{k}^{C1} F_{C1}'|\varphi_k\rangle\langle\varphi_k| + \sum_{m}^{C2} F_{C2}'|\varphi_m\rangle\langle\varphi_m| + \sum_{p}^{OV} F_{OV}'|\varphi_p\rangle\langle\varphi_p| \quad (20)$$

The virtual orbitals are treated in a similar way as the previous CVR-B3LYP,[20] in which the Rydberg orbitals are distinguished by using second moments of the orbitals. F_{OV} and the Fock operator form in the HF method were adopted as the Fock operator forms of unoccupied-valence and Rydberg orbitals, respectively. In the TDDFT calculations, we adopted an approximation similar to that for the previous study,[20] in which we used the **A** and **B** matrix forms of B3LYP,[1−8] while using the orbital energies and coefficients of CVR-B3LYP.

3.2. Assessment of Modified CVR-B3LYP Functional. The descriptions of K-shell, L-shell, and valence electrons by the modified CVR-B3LYP functional are assessed in this section by calculating core- and valence-excitation energies and standard enthalpies of formations. In the CVR-B3LYP calculations, the portions of HF exchange for K-shell, L-shell, and occupied-valence orbitals were determined to be 70%, 50%, and 20% by using the coefficients given in Table 5. The scalar relativistic effects were included by using the RESC method. The basis sets and geometries of molecules used in CVR-B3LYP calculations are the same as those used in section 2.

Table 6 shows the core excitation energies and oscillator strengths of the HCl molecule calculated by TDDFT with B3LYP, BHHLYP, the modified CVR-B3LYP, and TDHF. The errors from experimental values are shown in parentheses. The 1s → 4pπ and 1s → 4pσ excitations are assigned to the same peak experimentally. As for the 1s core-excitation energies, the modified CVR-B3LYP shows a significantly higher performance than conventional functionals: the errors of the modified CVR-B3LYP are about 1 eV, while those of B3LYP, BHHLYP, and TDHF are about 55, 22, and 30 eV, respectively. TD-B3LYP and TD-BHHLYP fail to reproduce the order of 1s excitations because 4s and 4pσ excitations are calculated to be strongly mixed with each other. Only the modified CVR-B3LYP represents the correct order of the four 1s-excited states. With regards to 2p excitations, the accuracy of the modified CVR-B3LYP is comparable to that of BHHLYP. TDHF overestimates 2p excitation energies by about 10 eV, while B3LYP underestimates those by about 10 eV. The MAE of the modified CVR-B3LYP, 0.8 eV, is significantly smaller than those of

CVR-B3LYP for Core Excitations of Third-Row Atoms

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Table 6. 1s and 2p Core-Excitation Energies and Oscillator Strengths of HCl by TDHF and TDDFT with B3LYP, BHHLYP, and the Modified CVR-B3LYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

	excitation energy					oscillator strength			
	B3LYP	BHHLYP	TDHF	CVR-B3LYP	exptl	B3LYP	BHHLYP	TDHF	CVR-B3LYP
	1s Excitation								
Cl 1s → 3pσ*	2769.0 (−54.9)	2801.3 (−22.6)	2852.6 (+28.7)	2824.8 (+0.9)	2823.9[b]	0.0023	0.0045	0.0085	0.0015
Cl 1s → 4s	2771.3 (−55.7)	2805.2 (−21.8)	2859.5 (+32.5)	2827.8 (+0.8)	2827.0[b]	0.0010	0.0004	0.0000	0.0003
Cl 1s → 4pπ	2771.4 (−56.4)	2805.2 (−22.6)	2859.3 (+31.5)	2827.9 (+0.1)	2827.8[b]	0.0000	0.0003	0.0023	0.0001
Cl 1s → 4pσ	2771.0 (−56.8)	2804.4 (−23.4)	2858.2 (+30.4)	2829.4 (+1.6)	2827.8[b]	0.0010	0.0007	0.0004	0.0025
	2p Excitation								
Cl 2pπ → 3pσ*	194.0 (−7.0)	200.4 (−0.6)	210.1 (+9.1)	202.0 (+1.0)	201.0[c]	0.0080	0.0112	0.0162	0.0071
Cl 2pπ → 4s	196.3 (−7.6)	204.0 (+0.1)	215.9 (+12.0)	204.9 (+1.0)	203.9[c]	0.0014	0.0015	0.0025	0.0009
Cl 2pπ → 4pπ	196.4 (−8.2)	204.0 (−0.6)	215.9 (+11.3)	205.0 (+0.4)	204.6[c]	0.0000	0.0000	0.0000	0.0000
Cl 2pπ → 4pσ	196.0 (−8.7)	203.2 (−1.5)	214.7 (+10.0)	206.6 (+1.9)	204.7[c]	0.0002	0.0000	0.0009	0.0016
MAE[d]	24.8	8.7	16.9	0.8					

[a] Differences from experimental data are shown in parentheses. [b] Reference 39. [c] Reference 42. [d] Mean absolute errors from experimental data.

Table 7. C-1s, F-1s, Cl-1s, and 2p Excitation Energies of CF₃Cl by TDDFT with B3LYP, BHHLYP, and the Modified CVR-B3LYP Functionals with cc-pCVTZ (in eV)[a]

assignment		B3LYP	BHHLYP	CVR-B3LYP	exptl[b]
C 1s	→ σ* (C−Cl)	283.0 (−11.2)	291.2 (−2.9)	293.9 (−0.3)	294.2
	→ σ* (C−F)	286.0 (−10.7)	293.8 (−2.9)	296.9 (+0.2)	296.7
F 1s	→ σ* (C−Cl)	672.0 (−18.5)	687.5 (−3.0)	688.8 (−1.7)	690.5
	→ σ* (C−F)	674.9 (−17.7)	691.0 (−1.6)	691.7 (−0.9)	692.6
Cl 1s	→ σ* (C−Cl)	2769.1 (−54.4)	2801.0 (−22.5)	2824.9 (+1.4)	2823.5
	→ σ* (C−F)	2773.5 (−53.9)	2807.1 (−20.3)	2829.3 (+1.9)	2827.4
Cl 2p	→ σ* (C−Cl)	194.9 (−6.8)	200.9 (−0.8)	202.7 (+1.0)	201.7[c]
	→ σ* (C−F)	198.8 (−6.0)	206.1 (+1.4)	206.7 (+1.9)	204.8[c]
MAE[d]		22.4	6.9	1.2	

[a] Differences from experimental data are shown in parentheses. [b] Reference 51. [c] Weighted average value calculated with the method in ref 44. [d] Mean absolute errors from experimental data.

B3LYP, BHHLYP, and TDHF, which are calculated to be 24.8, 8.7, and 16.9 eV, respectively. It indicates that the modified CVR-B3LYP provides quite well-balanced results for 1s and 2p excitations. The values of the oscillator strengths of CVR-B3LYP are close to those of the other three methods. In particular, the oscillator strengths of core → unoccupied-valence excitations calculated by CVR-B3LYP are close to those by B3LYP. The oscillator strengths of 4pσ excitations are slightly overestimated by CVR-B3LYP.

In order to investigate the accuracy of core-excited-state calculations on the molecules containing both second- and third-row atoms, TDDFT calculations on CF₃Cl were performed with B3LYP, BHHLYP, and the modified CVR-B3LYP functionals. No Rydberg-basis functions were used in the calculations of CF₃Cl. In order to set HF portions of core and occupied-valence orbitals of second-row atoms to 50% and 20%, which are the same values used in the previous CVR-B3LYP study on core excitations of second-row atoms,[20] 1s orbitals of the second-row atoms are treated as C2 orbitals in eq 2. The calculated 1s and 2p core-excitation energies of CF₃Cl are shown in Table 7. As for the core-excitation energies from 1s orbitals of the second-row atoms (C and F), CVR-B3LYP shows higher performance than B3LYP and BHHLYP do. The errors of C1s-excitation energies calculated with the modified CVR-B3LYP are less than 0.5 eV, while those of B3LYP and BHHLYP are about 11 and 3 eV, respectively. The errors

of F1s-excitation energies are underestimated more largely than C1s ones. As for the third-row atom (Cl), CVR-B3LYP gives both 1s and 2p core-excitation energies within the errors of 2 eV. The errors of 1s-excitation energies of B3LYP and BHHLYP, which are about 55 and 20 eV, are significantly larger than those of CVR-B3LYP. The accuracy of BHHLYP for Cl2p excitations are comparable to that of CVR-B3LYP. B3LYP has large errors of about 6 eV. Only CVR-B3LYP reproduces core excitation energies of both second- and third-row atoms with reasonable accuracy.

Table 8 shows the 1s and 2p core-excitation energies of SiH₄, PH₃, H₂S, HCl, and Cl₂ molecules calculated with the modified CVR-B3LYP functional. The comparison of the MAEs of CVR-B3LYP in Table 8, (1.5, 1.1) eV for (1s, 2p) core-excitation energies, with those of HF+B88+LYP (70%) and BHHLYP in Table 3 and 4 (1.2, 3.5) and (20.5, 0.6) eV, clarifies that the modified CVR-B3LYP provides well-balanced results for any third-row atoms. As for 1s excitations, the accuracy of the modified CVR-B3LYP is comparable to that of HF+B88+LYP (70%) and significantly higher than that of BHHLYP. On the other hand, the MAE of CVR-B3LYP for 2p core excitations is closer to that of BHHLYP than that of HF+B88+LYP (70%). The modified CVR-B3LYP gives more accurate results than HF+B88+LYP (70%) does for 2p excitations. Thus, it is demonstrated that the modified CVR-B3LYP shows high performance both for K-shell and L-shell core excitations, whereas the conven-

Table 8. 1s and 2p Core-Excitation Energies of SiH_4, PH_3, H_2S, HCl, and Cl_2 Molecules by TDDFT with the Modified CVR-B3LYP Functional with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

	1s excitation			2p excitation		
molecule	assignment	CVR-B3LYP	exptl	assignment	CVR-B3LYP	exptl
SiH_4	Si 1s → σ*	1846.6 (+4.1)	1842.5[b]	Si 2p → σ*	103.7 (+0.9)	102.8[g,i]
PH_3	P 1s → σ*(e)	2148.9 (+3.1)	2145.8[c]	P 2p → σ*	133.1 (+0.8)	132.3[g,i]
H_2S	S 1s → $3b_2$(σ*)	2474.7 (+1.6)	2473.1[d]	S 2p → σ*	166.1 (+1.6)	164.5[f]
	S 1s → $4pb_2$	2477.4 (+1.1)	2476.3[d]	S 2p → 4s	168.3 (+1.8)	166.5[f]
HCl	Cl 1s → 3pσ*	2824.8 (+0.9)	2823.9[e]	Cl 2pπ → 3pσ*	202.0 (+1.0)	201.0[g]
	Cl 1s → 4pπ	2827.9 (+0.1)	2827.8[e]	Cl 2pπ → 4pπ	205.0 (+0.4)	204.6[g]
Cl_2	Cl 1s → $3pσ_u$*	2822.1 (+0.8)	2821.3[e]	Cl 2pπ → $3pσ_u$*	199.1 (+0.4)	198.7[h,i]
	Cl 1s → 4p	2829.2 (+0.7)	2828.5[e]	Cl 2pπ → 4s	205.8 (+1.0)	204.8[h,i]
MAE[j]			1.5			1.0

[a] Differences from experimental data are shown in parentheses. [b] Reference 36. [c] Reference 37. [d] Reference 38. [e] Reference 39. [f] Reference 40. [g] Reference 41. [h] Reference 43. [i] Weighted average value calculated with the method in ref 44. [j] Mean absolute errors from experimental data.
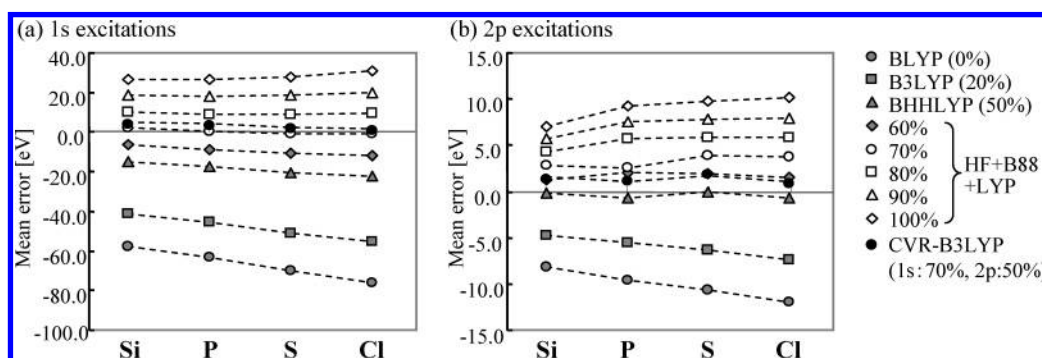
Figure 2. Atom-dependent mean errors of 1s and 2p excitation energies by TDHF and TDDFT with the BLYP, B3LYP, BHHLYP, HF+B88+LYP, and CVR-B3LYP functionals with cc-pCVTZ plus Rydberg basis functions.

tional functionals can describe either K-shell or L-shell excitation with high accuracy. Figure 2 shows the atom-dependent MEs of Z1s and Z2p core-excitation energies (Z = Si, P, S, and Cl) calculated with BLYP, B3LYP, BHHLYP, HF+B88+LYP (X%) (X = 60, 70, 80, 90, and 100), and the modified CVR-B3LYP, which are tabulated in Tables 3, 4, and 8. Both the underestimation with a small portion of HF exchange in the functional and the overestimation with a large portion of HF exchange becomes larger in the order, Si < P < S < Cl, which means that the errors become larger for heavier atom species, i.e., deeper K-shell and L-shell orbitals. In Figure 2(a) for 1s core-excitation energies, the errors of HF+B88+LYP (80%) and HF+B88+LYP (90%) are less atom-dependent, while those of BLYP, B3LYP, and BHHLYP largely depend on the kind of atom: The range of errors for Si, P, S, and Cl atoms are 18.5, 14.1, 7.6, 5.4, 3.1, 1.6, 2.0, 3.7, and 3.5 eV for BLYP, B3LYP, BHHLYP, HF+B88+LYP (X%) (X = 60, 70, 80, 90, and 100), and CVR-B3LYP, respectively. The atom-dependency of CVR-B3LYP is comparable to that of HF+B88+LYP (70%). For 2p core-excitation energies in Figure 2(b), the range of errors for Si, P, S, and Cl atoms are 8.3, 2.5, 0.6, 0.7, 1.3, 1.6, 2.3, 3.1, 2.9, and 0.9 eV for BLYP, B3LYP, BHHLYP, HF+B88+LYP (X%) (X = 60, 70, 80, 90, and 100), and CVR-B3LYP. CVR-B3LYP, BHHLYP, and HF+B88+LYP (60%) have significantly less atom-dependency.

In order to assess the accuracy of the description of occupied-valence electrons, excitation energies from oc-

cupied-valence orbitals of SiH_4, PH_3, H_2S, HCl, and Cl_2 molecules were calculated by TDHF and TDDFT with B3LYP, BHHLYP, and the modified CVR-B3LYP. Table 9 lists the calculated excitation energies. In Table 9, BHHLYP shows high performance, and the accuracy of BLYP, B3LYP, and TDHF are slightly worse than BHH-LYP: The MAEs of BLYP, B3LYP, BHHLYP, and TDHF are 0.8, 0.5, 0.3, and 0.7 eV, respectively. The excitation energies of CVR-B3LYP are close to and higher than those of B3LYP for occupied-valence → unoccupied-valence and occupied-valence → Rydberg excitations, respectively. This is because the valence and Rydberg orbitals of CVR-B3LYP are designed to be similar to those of B3LYP and HF. The MAE of CVR-B3LYP is 0.6 eV, which is comparable to that of B3LYP. Therefore, CVR-B3LYP describes valence-excitation energies with reasonable accuracy as like conventional DFT methods.

The standard enthalpies of formation of SiH_4, PH_3, H_2S, HCl, and Cl_2 molecules, which is one of the valence-electron properties in the ground states, were calculated by the procedure mentioned in ref 55. The results of HF and DFT calculations with the BLYP, B3LYP, BHHLYP, HF+B88+LYP (X%) (X = 60, 70, 80, 90, and 100), and CVR-B3LYP functionals are shown in Table 10. The DFT method gives more accurate results than the HF method does: The MAE of the HF method is 52.0 kcal/mol, while all of the MAEs of the DFT methods are less than 10 kcal/mol. The accuracy of BLYP and B3LYP are significantly high among the DFT methods, whose MAEs are 2.0 and 1.5 kcal/mol. The MAE

Table 9. Valence- and Rydberg-Excitation Energies of SiH$_4$, PH$_3$, H$_2$S, HCl, and Cl$_2$ Molecules by TDHF and TDDFT with BLYP, B3LYP, BHHLYP, and the Modified CVR-B3LYP Functional with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	assignment	BLYP	B3LYP	BHHLYP	TDHF	CVR-B3LYP	exptl
SiH$_4$	$t_2 \rightarrow$ 4s	8.0 (-0.8)	8.5 (-0.3)	9.2 ($+0.4$)	9.9 ($+1.1$)	9.4 ($+0.6$)	8.8[b]
PH$_3$	n $\rightarrow$ 4p	6.8 (-1.0)	7.2 (-0.6)	8.0 ($+0.2$)	8.4 ($+0.6$)	8.8 ($+1.0$)	7.8[c]
H$_2$S	$2b_1 \rightarrow \sigma^*$	5.8 ($+0.4$)	6.0 ($+0.5$)	6.1 ($+0.6$)	6.2 ($+0.8$)	6.0 ($+0.6$)	5.5[c]
HCl	$3p\pi \rightarrow$ 4s	8.3 (-1.3)	8.9 (-0.7)	9.8 ($+0.2$)	10.5 ($+0.9$)	9.8 ($+0.2$)	9.6[d]
Cl$_2$	$\pi_g \rightarrow \sigma_u$	3.2 (-0.6)	3.3 (-0.4)	3.6 (-0.2)	4.0 ($+0.2$)	3.3 (-0.5)	3.8[d]
MAE[e]		0.8	0.5	0.3	0.7	0.6	

[a] Differences from experimental data are shown in parentheses. [b] Reference 52. [c] Reference 53. [d] Reference 54. [e] Mean absolute errors from experimental data.

Table 10. Standard Enthalpies of Formation of SiH$_4$, PH$_3$, H$_2$S, HCl, and Cl$_2$ Molecules by HF and DFT with the BLYP, B3LYP, BHHLYP, HF+B88+LYP, and Modified CVR-B3LYP Functionals with cc-pCVTZ Plus Rydberg Basis Functions (in eV)[a]

molecule	BLYP	B3LYP	BHHLYP	HF+B88+LYP					HF	CVR-B3LYP	exptl[b]
				60%	70%	80%	90%	100%			
SiH$_4$	13.3	7.9	7.9	6.5	5.1	3.7	2.1	0.5	75.0	5.9	8.2
	($+5.1$)	(-0.3)	(-0.3)	(-1.7)	(-3.1)	(-4.5)	(-6.1)	(-7.7)	($+66.8$)	(-2.3)	
PH$_3$	1.2	-0.4	3.4	3.5	3.6	3.7	3.6	3.5	71.7	-2.5	1.3
	(-0.1)	(-1.7)	($+2.1$)	($+2.2$)	($+2.3$)	($+2.4$)	($+2.3$)	($+2.2$)	($+70.4$)	(-3.8)	
H$_2$S	-2.8	-3.7	0.5	1.0	1.5	2.0	2.4	2.8	48.7	-5.4	-4.9
	($+2.1$)	($+1.2$)	($+5.4$)	($+5.9$)	($+6.4$)	($+6.9$)	($+7.3$)	($+7.7$)	($+53.6$)	(-0.5)	
HCl	-19.9	-20.3	-17.5	-17.0	-16.6	-16.1	-15.7	-15.3	7.7	-21.5	-22.1
	($+2.2$)	($+1.8$)	($+4.6$)	($+5.1$)	($+5.5$)	($+6.0$)	($+6.4$)	($+6.8$)	($+29.8$)	($+0.6$)	
Cl$_2$	-0.5	2.7	10.3	12.2	14.1	15.9	17.6	19.3	39.4	2.1	0.0
	(-0.5)	($+2.7$)	($+10.3$)	($+12.2$)	($+14.1$)	($+15.9$)	($+17.6$)	($+19.3$)	($+39.4$)	($+2.1$)	
MAE[c]	2.0	1.5	4.5	5.4	6.3	7.1	7.9	8.7	52.0	1.9	

[a] Differences from experimental data are shown in parentheses. [b] Reference 55. [c] Mean absolute errors from experimental data.

becomes larger as the portion of HF exchange increases. Therefore, the appropriate portion of HF exchange for describing valence electrons is suggested to be 0%$-$20%. The accuracy of CVR-B3LYP with a MAE of 1.9 kcal/mol is comparable to BLYP and B3LYP. Thus, we confirm that CVR-B3LYP is capable of describing the behaviors of not only K-shell and L-shell electrons but also valence ones with reasonable accuracy, while HF+B88+LYP (70%) and BHHLYP are appropriate only for K-shell and L-shell excitations, respectively.

4. Conclusions

The CVR-B3LYP functional is extended to core-excited-state calculations of the molecules containing third-row atoms. The assessment of TDDFT calculations with conventional exchange-correlation functionals demonstrates that 70% and 50% portions of HF exchange are appropriate for calculating K-shell and L-shell core-excitation energies, respectively. Therefore, the CVR-B3LYP functional is modified to possess the appropriate portions of HF exchange for K-shell, L-shell, and occupied-valence regions separately. TDDFT calculations on HCl, CF3Cl, and several molecules containing third-row atoms show that the modified CVR-B3LYP functional reproduces the K-shell and L-shell core-excitation energies with reasonable accuracy. For valence properties, the calculations of valence-excitation energies and standard enthalpies of formation confirm that CVR-B3LYP describes valence electrons accurately as well as B3LYP does. The numerical assessments have revealed the

high accuracy of CVR-B3LYP for the descriptions of all of the K-shell, L-shell, and valence electrons.

Appendix

Size-Consistency and Size-Extensivity. CVR-B3LYP does not satisfy size-consistency rigorously: In the case that electrons transfer between two categories in the dissociation process, CVR-B3LYP is size-inconsistent. However, the orbitals are categorized into three groups, K-shell-, L-shell- and valence-orbital groups in the present study, and electrons hardly transfer between two different categories in the process of the dissociation in most realistic cases. Figure 3 shows the dissociation curves of HCl, which are obtained by performing unrestricted DFT calculations with BHHLYP, B3LYP, and CVR-B3LYP. The energies at the largest H$-$Cl distance in the calculations are set to zero in Figure 3. The electrons transferred in the dissociation are valence ones in most cases. CVR-B3LYP well reproduces the curve of B3LYP, because the valence orbitals of CVR-B3LYP are designed to reproduce those of B3LYP. Thus, CVR-B3LYP is size-consistent in practical cases.

On the other hand, CVR-B3LYP satisfies size-extensivity. We have numerically examined size-extensive nature by performing CVR-B3LYP calculations of a Cl$_2$ monomer and (Cl$_2$)$_2$ dimer separated at 50 Å. The energy difference between two Cl$_2$ monomers and the largely separated (Cl$_2$)$_2$ dimer is only 6.3×10^{-08} hartree, which indicates that CVR-B3LYP is size-extensive.
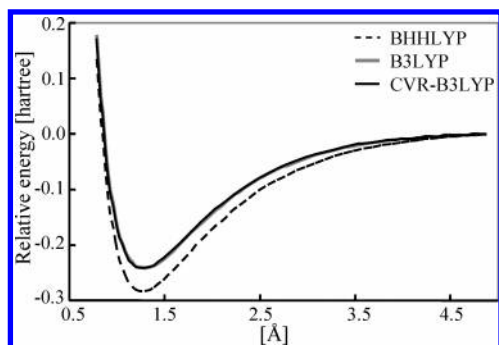
Figure 3. Potential energy curves for the dissociation of HCl calculated by DFT with the B3LYP, BHHLYP, and CVR-B3LYP functionals with cc-pCVTZ plus Rydberg basis functions.

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(45) The three- and higher-body interactions are neglected in eq 2. The energy differences due to the truncation are about 0.02% of the total energies for HCl, Cl_2, H_2S, PH_3, and SiH_4 molecules. Furthermore, the excitation energies and the standard enthalpies of formation, which correspond to the energy differences between two or more states, have been calculated accurately under the truncation. Therefore, the effect of the truncation seems negligible in the present study.

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