Supplemental Material to: Asymptotic Correction Schemes for Semilocal Exchange-Correlation Functionals

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I. PROOF OF THE SIZE-CONSISTENCY OF THE LFA SCHEME

The LFA scheme, which contains the sum of E_x^{LFA} and E_{DC}, can be shown to be size-consistent for systems composed of atoms (e.g, atoms, molecules, and solids). Consider a system composed of two well-separated subsystems, S_1 and S_2, and each subsystem contains a number of atoms. Assume that $\rho_\sigma^{S_1}(\mathbf{r})$ and $\rho_\sigma^{S_2}(\mathbf{r})$ are the σ-spin densities of S_1 and S_2, respectively. Since $\rho_\sigma^{S_1}(\mathbf{r})$ and $\rho_\sigma^{S_2}(\mathbf{r})$ are not overlapped, their product should vanish. Similarly, $\{w_A(\mathbf{r})\rho_\sigma^{S_1}(\mathbf{r})\}$ should vanish if the atom A belongs to S_2, and $\{w_A(\mathbf{r})\rho_\sigma^{S_2}(\mathbf{r})\}$ should vanish if the atom A belongs to S_1.

The LFA exchange energy of the system can be shown to be equal to the sum of the LFA exchange energies of the two separate subsystems as follows:

$$
\begin{aligned}
\sum_{\sigma=\alpha,\beta} E_{x,\sigma}^{\mathrm{LFA}}[\rho_\sigma^{S_1}+\rho_\sigma^{S_2}] &= -\sum_{\sigma=\alpha,\beta}\sum_{A}\frac{1}{2N_{A,\sigma}}\iint \rho_{A,\sigma}(\mathbf{r})\rho_{A,\sigma}(\mathbf{r}')\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= -\sum_{\sigma=\alpha,\beta}\sum_{A}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})\rho_\sigma(\mathbf{r})\}\{w_A(\mathbf{r}')\rho_\sigma(\mathbf{r}')\}\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= -\sum_{\sigma=\alpha,\beta}\sum_{A}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})[\rho_\sigma^{S_1}(\mathbf{r})+\rho_\sigma^{S_2}(\mathbf{r})]\}\{w_A(\mathbf{r}')[\rho_\sigma^{S_1}(\mathbf{r}')+\rho_\sigma^{S_2}(\mathbf{r}')]\} \\
&\quad\times\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= -\sum_{\sigma=\alpha,\beta}\sum_{A}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})\rho_\sigma^{S_1}(\mathbf{r})\}\{w_A(\mathbf{r}')\rho_\sigma^{S_1}(\mathbf{r}')\}\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&\quad -\sum_{\sigma=\alpha,\beta}\sum_{A}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})\rho_\sigma^{S_2}(\mathbf{r})\}\{w_A(\mathbf{r}')\rho_\sigma^{S_2}(\mathbf{r}')\}\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= -\sum_{\sigma=\alpha,\beta}\sum_{A\in S_1}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})\rho_\sigma^{S_1}(\mathbf{r})\}\{w_A(\mathbf{r}')\rho_\sigma^{S_1}(\mathbf{r}')\}\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&\quad -\sum_{\sigma=\alpha,\beta}\sum_{A\in S_2}\frac{1}{2N_{A,\sigma}}\iint \{w_A(\mathbf{r})\rho_\sigma^{S_2}(\mathbf{r})\}\{w_A(\mathbf{r}')\rho_\sigma^{S_2}(\mathbf{r}')\}\frac{\mathrm{erf}(\omega\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\
&= \sum_{\sigma=\alpha,\beta} E_{x,\sigma}^{\mathrm{LFA}}[\rho_\sigma^{S_1}]+\sum_{\sigma=\alpha,\beta} E_{x,\sigma}^{\mathrm{LFA}}[\rho_\sigma^{S_2}],
\end{aligned}
\tag{1}
$$

where $\sum_{A\in S_1}$ sums over all the atoms that belong to S_1, and $\sum_{A\in S_2}$ sums over all the atoms that belong to S_2.

The other term, E_{DC}, which is linear in the number of electrons N, can be easily shown

to be size-consistent:

$$\begin{aligned} E_{\mathrm{DC}} &= -\frac{\omega}{\sqrt{\pi}}N \\ &= -\frac{\omega}{\sqrt{\pi}}(N_1 + N_2) \\ &= -\frac{\omega}{\sqrt{\pi}}N_1 - \frac{\omega}{\sqrt{\pi}}N_2 \\ &= E_{\mathrm{DC}}^{S_1} + E_{\mathrm{DC}}^{S_2}, \end{aligned} \tag{2}$$

where N_1 is the number of electrons in S_1, and N_2 is the number of electrons in S_2. $E_{\mathrm{DC}}^{S_1}$ and $E_{\mathrm{DC}}^{S_2}$ are the DC energies for the isolated S_1 and S_2 subsystems, respectively.

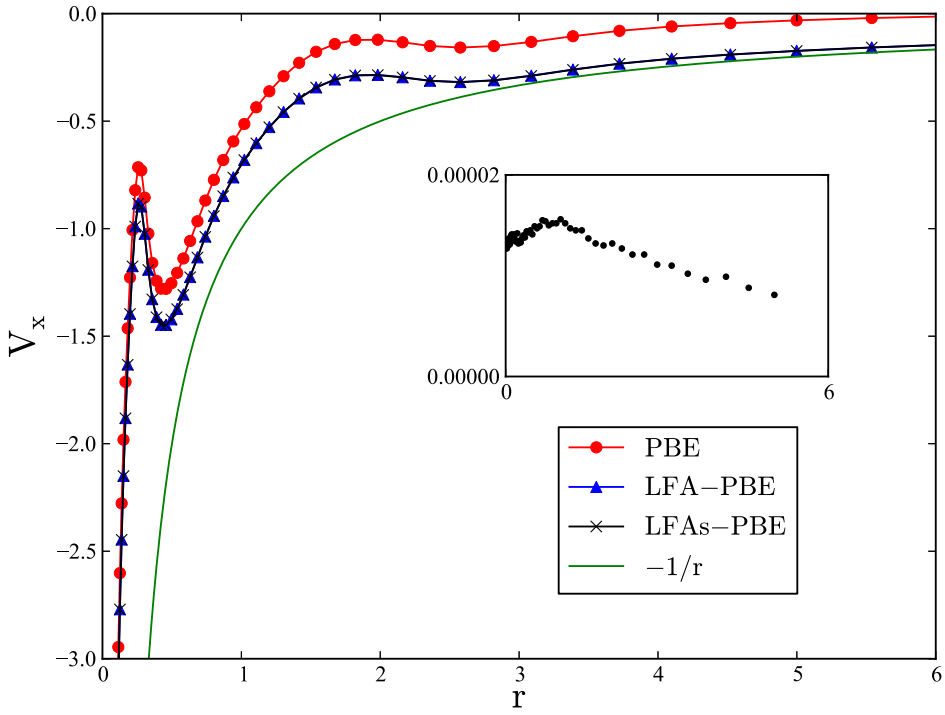

FIG. S1. Exchange potentials for the Ne atom (in atomic units). Inset shows the differences between the exchange potentials calculated by RILFA-PBE and LFA-PBE. $\omega = 0.15$ Bohr^{-1} is adopted for all the LFA-corrected PBE functionals.

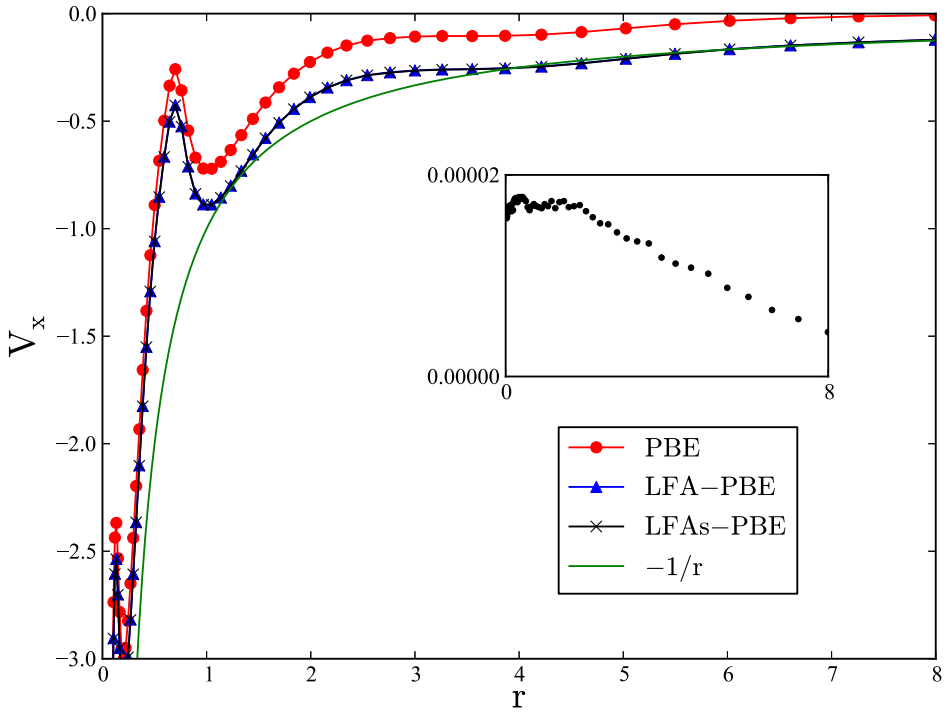

FIG. S2. Same as Fig. S1, but for the Ar atom.

TABLE S1. Absolute percentage errors of the LFA-PBE, RILFA-PBE, and LFAs-PBE energies with respect to the PBE energy (in hartree). $\omega = 0.15$ Bohr^{-1} is adopted for all the LFA-corrected PBE functionals.

	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE
System	Energy	error %	error %	error %
C	-37.793956	1.30	1.30	1.32
N	-54.528970	1.06	1.06	1.07
O	-75.004532	0.88	0.88	0.89
F	-99.661035	0.75	0.75	0.76
Ne	-128.845640	0.65	0.65	0.65
HCl	-460.629551	0.32	0.32	0.33
NaCl	-622.267085	0.37	0.37	0.38
CO_2	-188.469386	0.97	0.97	0.98
HOOH	-151.456785	0.98	0.98	0.99
CH_3OH	-115.627227	1.28	1.28	1.30
C_6H_6	-232.010609	1.49	1.49	1.51

TABLE S2: Vertical ionization potentials (in eV) for the IP131 database [1]. $\omega = 0.15$ Bohr^{-1} is adopted for all the LFA-corrected LDA and PBE functionals. The notation used for characterizing statistical errors is as follows: mean signed errors (MSEs), mean absolute errors (MAEs), and root-mean-square (RMS) errors.

Molecule	Reference	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE	LDA	LFA-LDA	RILFA-LDA	LFAs-LDA
H	13.60	7.59	11.94	11.94	12.03	7.32	11.64	11.64	11.75
He	24.59	15.63	20.24	20.13	20.28	15.52	19.88	19.88	20.04
Li	5.39	3.22	7.05	7.04	7.22	3.16	6.99	6.99	7.15
Be	9.32	5.61	9.71	9.71	9.82	5.60	9.71	9.71	9.81
B	8.30	4.17	8.32	8.32	8.43	4.11	8.27	8.27	8.36
C	11.26	6.10	10.36	10.36	10.45	6.13	10.39	10.39	10.48

N	14.53	8.31	12.65	12.65	12.72	8.42	12.76	12.76	12.83
O	13.62	7.60	12.00	12.00	12.03	7.47	11.86	11.86	11.89
F	17.42	10.32	14.74	14.74	14.78	10.40	14.82	14.82	14.86
Ne	21.57	13.38	17.82	17.82	17.86	13.60	18.06	18.06	18.09
Na	5.14	3.03	6.91	6.91	6.98	3.08	6.96	6.96	7.04
Mg	7.65	4.70	8.73	8.73	8.79	4.77	8.81	8.81	8.87
Al	5.99	3.09	7.05	7.04	7.12	3.00	6.94	6.96	7.02
Si	8.15	4.61	8.68	8.68	8.76	4.56	8.62	8.65	8.71
P	10.49	6.30	10.47	10.47	10.55	6.30	10.47	10.47	10.53
S	10.36	6.15	10.39	10.39	10.43	6.16	10.39	10.39	10.43
Cl	12.97	8.14	12.43	12.43	12.48	8.22	12.51	12.51	12.56
Ar	15.76	10.30	14.63	14.63	14.67	10.41	14.74	14.74	14.78
CH_3	9.84	5.42	9.74	9.74	9.80	5.39	9.68	9.68	9.76
CH_4	13.60	9.45	13.82	13.82	13.89	9.48	13.84	13.84	13.91
NH	13.49	7.92	12.27	12.27	12.33	7.98	12.32	12.32	12.39
NH_2	12.00	7.22	11.56	11.56	11.63	7.21	11.56	11.56	11.62
NH_3	10.82	6.18	10.53	10.53	10.58	6.28	10.61	10.61	10.68
OH	13.02	7.38	11.75	11.75	11.81	7.43	11.80	11.80	11.85
H_2O	12.62	7.24	11.61	11.61	11.67	7.40	11.75	11.75	11.82
HF	16.12	9.65	14.04	14.04	14.10	9.83	14.23	14.23	14.28
SiH_3	8.74	5.37	9.57	9.57	9.65	5.31	9.52	9.52	9.57
SiH_4	12.30	8.52	12.81	12.81	12.89	8.53	12.81	12.81	12.89
PH_3	10.59	6.72	10.99	10.99	11.05	6.77	11.02	11.02	11.09
SH_2	10.50	6.31	10.55	10.55	10.62	6.40	10.64	10.66	10.71
HCl	12.77	8.05	12.35	12.35	12.40	8.16	12.46	12.46	12.50
HCCH	11.49	7.20	11.51	11.51	11.56	7.38	11.67	11.67	11.74
CH_2CH_2	10.68	6.74	11.04	11.04	11.12	6.93	11.23	11.23	11.31
CH_3CH_3	11.99	8.17	12.54	12.54	12.62	8.16	12.54	12.54	12.60
HCN	13.61	9.02	13.36	13.36	13.41	9.20	13.55	13.55	13.60
CO	14.01	9.04	13.38	13.38	13.44	9.13	13.46	13.46	13.52

HCO	9.31	5.16	9.49	9.49	9.55	5.12	9.47	9.47	9.52
CH_2O	10.89	6.26	10.61	10.61	10.68	6.35	10.72	10.72	10.77
CH_3OH	10.96	6.26	10.61	10.61	10.68	6.36	10.72	10.72	10.79
N_2	15.58	10.28	14.63	14.63	14.69	10.43	14.80	14.80	14.85
NH_2NH_2	8.98	5.30	9.66	9.66	9.71	5.36	9.71	9.71	9.77
NO	9.26	4.52	8.89	8.89	8.94	4.57	8.92	8.92	8.99
O_2	12.30	6.84	11.23	11.23	11.29	6.97	11.37	11.37	11.42
HOOH	11.70	6.46	10.83	10.83	10.89	6.61	10.99	10.99	11.04
F_2	15.70	9.48	13.93	13.93	13.96	9.69	14.12	14.12	14.16
CO_2	13.78	9.09	13.46	13.46	13.51	9.33	13.71	13.71	13.75
P_2	10.62	7.15	11.34	11.34	11.39	7.26	11.45	11.45	11.50
S_2	9.55	5.83	10.06	10.06	10.13	5.83	10.06	10.06	10.13
Cl_2	11.49	7.33	11.61	11.61	11.67	7.44	11.72	11.75	11.79
NaCl	9.80	5.30	9.47	9.47	9.51	5.44	9.60	9.60	9.65
SiO	11.61	7.48	11.72	11.72	11.77	7.61	11.83	11.83	11.89
CS	11.34	7.40	11.67	11.67	11.73	7.45	11.72	11.72	11.78
ClO	11.01	6.30	10.61	10.64	10.67	6.37	10.69	10.69	10.74
ClF	12.77	7.86	12.19	12.19	12.24	8.00	12.32	12.32	12.38
SiH_3SiH_3	10.53	7.19	11.45	11.45	11.53	7.26	11.51	11.53	11.59
CH_3Cl	11.29	7.12	11.42	11.42	11.48	7.20	11.51	11.51	11.57
CH_3SH	9.44	5.57	9.85	9.85	9.90	5.65	9.93	9.93	9.98
SO_2	12.50	8.08	12.40	12.40	12.44	8.28	12.59	12.59	12.64
BF_3	15.96	10.07	14.44	14.44	14.50	10.32	14.69	14.69	14.75
BCl_3	11.64	7.72	12.02	12.02	12.06	7.85	12.13	12.13	12.19
$AlCl_3$	12.01	8.02	12.27	12.27	12.33	8.16	12.40	12.43	12.47
CF_4	16.20	10.42	14.82	14.82	14.87	10.68	15.07	15.10	15.13
CCl_4	11.69	7.69	12.00	12.00	12.04	7.82	12.10	12.10	12.16
OCS	11.19	7.50	11.78	11.78	11.84	7.66	11.94	11.94	12.00
CS_2	10.09	6.82	11.07	11.07	11.13	6.94	11.18	11.18	11.24
CF_2O	13.60	8.52	12.89	12.89	12.95	8.77	13.14	13.14	13.20

SiF_4	16.40	10.69	15.04	15.04	15.10	10.96	15.31	15.31	15.36
N_2O	12.89	8.40	12.78	12.78	12.83	8.65	13.03	13.03	13.07
NF_3	13.60	8.45	12.87	12.87	12.90	8.63	13.03	13.03	13.08
PF_3	12.20	7.36	11.64	11.64	11.70	7.51	11.80	11.80	11.85
O_3	12.73	8.02	12.40	12.40	12.46	8.25	12.62	12.62	12.68
F_2O	13.26	7.72	12.13	12.13	12.18	7.91	12.32	12.32	12.38
ClF_3	13.05	8.00	12.38	12.38	12.41	8.18	12.57	12.57	12.60
CF_2CF_2	10.69	6.31	10.69	10.69	10.74	6.56	10.93	10.93	10.99
CF_3CN	14.30	9.57	13.93	13.93	13.98	9.77	14.12	14.12	14.18
CH_3CCH	10.37	6.49	10.80	10.80	10.87	6.64	10.96	10.96	11.02
CH_2CCH_2	10.20	6.56	10.88	10.88	10.95	6.72	11.02	11.02	11.10
$cylC_3H_4$	9.86	6.11	10.45	10.44	10.51	6.23	10.55	10.55	10.63
$cylC_3H_6$	10.54	7.07	11.42	11.42	11.48	7.23	11.56	11.56	11.64
$CH_3CH_2CH_3$	11.51	7.75	12.10	12.13	12.19	7.73	12.10	12.10	12.17
CH_3CCCH_3	9.79	5.93	10.25	10.25	10.32	6.06	10.39	10.39	10.45
$cylC_4H_6$	9.43	6.04	10.36	10.36	10.43	6.19	10.50	10.50	10.58
isobutane	11.13	7.58	11.94	11.94	12.01	7.59	11.94	11.94	12.02
benzene	9.25	6.33	10.64	10.64	10.71	6.54	10.85	10.85	10.92
CH_2F_2	13.27	8.15	12.54	12.54	12.60	8.25	12.65	12.65	12.70
CF_3H	15.50	9.35	13.74	13.74	13.80	9.51	13.90	13.90	13.96
CH_2Cl_2	11.40	7.38	11.70	11.70	11.74	7.48	11.78	11.78	11.83
CCl_3H	11.50	7.42	11.72	11.72	11.77	7.55	11.83	11.83	11.89
CH_3NO_2	11.29	6.92	11.29	11.29	11.34	7.11	11.48	11.48	11.54
CH_3SiH_3	11.60	7.92	12.21	12.24	12.30	8.01	12.32	12.32	12.38
HCOOH	11.50	6.73	11.07	11.07	11.13	6.92	11.26	11.26	11.32
CH_3CONH_2	10.00	5.79	10.12	10.15	10.19	5.95	10.28	10.28	10.35
$cylNHC_2H_4$	9.85	5.78	10.12	10.12	10.18	5.88	10.23	10.23	10.28
NCCN	13.51	9.39	13.74	13.74	13.79	9.64	13.98	13.98	14.03
CH_3NHCH_3	8.95	5.06	9.41	9.41	9.47	5.13	9.47	9.47	9.54
CH_2CO	9.64	5.91	10.23	10.23	10.29	6.09	10.42	10.42	10.48

cylOC_2H_4	10.57	6.27	10.64	10.64	10.69	6.39	10.74	10.74	10.81
OCHCHO	10.60	6.39	10.74	10.74	10.80	6.53	10.88	10.88	10.94
CH_3CH_2OH	10.64	6.15	10.50	10.50	10.58	6.27	10.64	10.64	10.69
CH_3OCH_3	10.10	5.83	10.17	10.17	10.25	5.93	10.28	10.28	10.34
cylSC_2H_4	9.05	5.37	9.63	9.63	9.70	5.46	9.74	9.74	9.79
CH_3SOCH_3	9.10	5.38	9.68	9.68	9.74	5.52	9.82	9.82	9.88
CH_2CHF	10.63	6.52	10.85	10.85	10.92	6.72	11.04	11.04	11.11
CH_3CH_2Cl	11.06	6.97	11.29	11.29	11.34	7.07	11.37	11.37	11.43
CH_2CHCl	10.20	6.42	10.72	10.72	10.79	6.59	10.88	10.88	10.95
CH_3CClO	11.03	7.13	11.45	11.45	11.52	7.29	11.61	11.61	11.68
prplCl	10.88	6.94	11.26	11.26	11.31	7.04	11.34	11.34	11.40
NC_3H_9	8.54	4.85	9.17	9.17	9.25	4.92	9.25	9.25	9.32
cylOC_4H_4	8.90	5.67	9.98	9.98	10.05	5.88	10.20	10.20	10.27
cylNHC_4H_4	8.23	5.13	9.44	9.44	9.51	5.33	9.63	9.63	9.71
NO_2	11.23	6.50	10.88	10.88	10.92	6.60	10.96	10.96	11.02
SF_6	15.70	10.14	14.53	14.52	14.57	10.40	14.80	14.80	14.84
$CFCl_3$	11.76	7.75	12.05	12.05	12.10	7.88	12.19	12.19	12.23
$CClF_3$	13.08	8.56	12.89	12.89	12.93	8.73	13.06	13.06	13.10
$CBrF_3$	12.08	7.80	12.10	12.10	12.15	8.00	12.29	12.29	12.33
HCCF	11.50	7.01	11.34	11.34	11.40	7.22	11.53	11.53	11.60
HCCCN	11.75	7.87	12.19	12.19	12.24	8.08	12.40	12.40	12.46
NCCCCN	11.84	8.44	12.76	12.76	12.82	8.68	13.00	13.00	13.07
C_2N_2	13.51	9.39	13.74	13.74	13.79	9.64	13.98	13.98	14.03
C_3O_2	10.80	7.27	11.61	11.61	11.66	7.50	11.83	11.83	11.90
FCN	13.65	8.73	13.08	13.08	13.13	8.97	13.30	13.30	13.37
HCCCCH	10.30	6.64	10.93	10.93	11.01	6.83	11.12	11.12	11.20
H_2CS	9.38	5.53	9.79	9.79	9.86	5.61	9.87	9.87	9.93
$HCONH_2$	10.40	6.02	10.36	10.36	10.42	6.17	10.50	10.50	10.56
CH_2CHCHO	10.10	6.00	10.34	10.34	10.41	6.15	10.50	10.50	10.55
CH_2CCl_2	10.00	6.44	10.74	10.74	10.80	6.61	10.91	10.91	10.97

$CHFCF_2$	10.62	6.22	10.58	10.58	10.64	6.45	10.80	10.80	10.87
CH_2CF_2	10.70	6.57	10.91	10.91	10.97	6.78	11.12	11.12	11.18
CH_3F	13.04	8.09	12.49	12.48	12.53	8.19	12.57	12.57	12.63
CF_2Cl_2	12.24	8.08	12.40	12.40	12.44	8.23	12.54	12.54	12.59
SiF_2	11.08	7.14	11.40	11.40	11.44	7.27	11.51	11.51	11.57
MSE		−4.42	−0.10	−0.10	−0.03	−4.30	0.01	0.01	0.09
MAE		4.42	0.66	0.66	0.67	4.30	0.68	0.68	0.69
RMS		4.52	0.93	0.93	0.93	4.41	0.93	0.93	0.94

TABLE S3. Comparison of errors (in kcal/mol) of the reaction energies of 30 chemical reactions [2], calculated by the PBE and LFA-corrected PBE functionals ($\omega = 0.15$ Bohr^{-1}). (1 kcal/mol = 0.0434 eV = 0.00159 hartree.)

Reactions	ΔE_{ref}	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE
$H + N_2O \rightarrow OH + N_2$	−65.08	22.59	22.53	22.52	22.57
$H + FCH_3 \rightarrow HF + CH_3$	−26.64	4.16	4.22	4.23	4.24
$H + F_2 \rightarrow HF + F$	−103.91	13.19	12.95	12.95	13.09
$CH_3 + FCl \rightarrow CH_3F + Cl$	−52.74	4.64	4.24	4.24	4.42
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	−32.65	0.83	3.67	3.69	2.41
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	−26.73	4.61	6.14	6.15	5.45
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	−20.11	0.38	−0.70	−0.70	−0.27
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	−36.24	−3.09	−4.11	−4.11	−3.68
$H + N_2 \rightarrow HN_2$	3.97	−7.86	−8.26	−8.25	−8.06
$H + CO \rightarrow HCO$	−19.51	−6.84	−7.48	−7.47	−7.15
$H + C_2H_4 \rightarrow CH_3CH_2$	−40.03	−0.31	−1.12	−1.13	−0.73
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	−26.12	−2.14	−2.74	−2.74	−2.48
$HCN \rightarrow HNC$	15.05	0.06	0.47	0.47	0.29
$H + HCl \rightarrow H_2 + Cl$	−3.0	5.51	4.78	4.76	5.11
$OH + H_2 \rightarrow H + H_2O$	−16.1	−3.95	−3.47	−3.45	−3.68
$CH_3 + H_2 \rightarrow H + CH_4$	−3.2	−2.30	−2.10	−2.09	−2.20
$OH + CH_4 \rightarrow CH_3 + H_2O$	−12.9	−1.66	−1.38	−1.37	−1.47
$OH + NH_3 \rightarrow H_2O + NH_2$	−9.5	−1.73	−1.78	−1.78	−1.75
$HCl + CH_3 \rightarrow Cl + CH_4$	−6.2	3.21	2.69	2.67	2.90
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	−16.5	−3.28	−3.01	−3.00	−3.11
$F + H_2 \rightarrow HF + H$	−31.6	−6.49	−6.03	−6.01	−6.20
$O + CH_4 \rightarrow OH + CH_3$	5.6	−5.83	−5.55	−5.54	−5.63
$H + PH_3 \rightarrow PH_2 + H_2$	−20.1	0.40	0.00	−0.01	0.19
$H + HO \rightarrow H_2 + O$	−2.4	8.13	7.65	7.62	7.84
$H + H_2S \rightarrow H_2 + HS$	−13.8	3.48	2.79	2.80	3.11
$O + HCl \rightarrow OH + Cl$	−0.6	−2.61	−2.87	−2.87	−2.73
$NH_2 + CH_3 \rightarrow CH_4 + NH$	−14.4	4.55	4.24	4.23	4.36
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	−10.8	6.17	5.88	5.86	5.99
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	−7.0	−1.54	−1.23	−1.22	−1.36
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	−3.3	−0.02	0.30	0.31	0.18
MSE		1.08	1.02	1.03	1.05
MAE		4.38	4.48	4.47	4.42
RMS		6.24	6.24	6.24	6.23

TABLE S4. The 19 valence and 23 Rydberg excitation energies (in eV) of N_2, CO, water, ethylene, and formaldehyde, calculated by the PBE and LFA-corrected PBE functionals ($\omega = 0.15$ Bohr^{-1}). The molecular geometries and experimental reference values are taken from Ref. [3].

		Expt.	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE
N_2	$V^1\Pi_g$	9.31	9.12	9.15	9.15	9.15
	$V^1\Sigma_u^-$	9.97	9.70	9.72	9.72	9.72
	$V^1\Delta_u$	10.27	10.12	10.14	10.14	10.14
	$V^3\Sigma_u^+$	7.75	7.56	7.56	7.56	7.56
	$V^3\Pi_g$	8.04	7.42	7.43	7.43	7.43
	$V^3\Delta_u$	8.88	8.37	8.38	8.38	8.38
	$V^3\Sigma_u^-$	9.67	9.70	9.72	9.72	9.72
	$V^3\Pi_u$	11.19	10.40	10.42	10.42	10.42
CO	$V^1\Pi$	8.51	8.25	8.33	8.33	8.33
	$V^1\Sigma^-$	9.88	9.86	9.91	9.91	9.91
	$V^3\Pi$	6.32	5.74	5.75	5.75	5.75
	$V^3\Sigma^+$	8.51	8.11	8.14	8.14	8.14
	$V^3\Delta$	9.36	8.77	8.80	8.80	8.80
	$V^3\Sigma^-$	9.88	9.86	9.91	9.91	9.91
H_2O	R^1B_1	7.4	6.33	6.77	6.77	6.72
	R^1A_2	9.1	7.44	8.42	8.42	8.27
	R^1A_1	9.7	8.18	8.91	8.91	9.21
	R^1B_1	10.0	7.84	9.52	9.52	9.25
	R^1A_1	10.17	8.48	9.52	9.52	8.85
	R^3B_1	7.2	6.00	6.35	6.35	6.31
C_2H_4	R^1B_{3u}	7.11	6.40	7.07	7.07	7.00
	V^1B_{1u}	7.60	7.29	7.60	7.60	7.60
	R^1B_{1g}	7.80	6.87	7.68	7.68	7.59
	R^1B_{2g}	8.01	6.83	7.69	7.69	7.58
	R^1A_g	8.29	7.18	8.71	8.71	8.40
	R^1B_{3u}	8.62	7.42	8.91	8.91	8.76
	V^3B_{1u}	4.36	4.26	4.26	4.26	4.26
	R^3B_{3u}	6.98	6.31	6.91	6.91	6.86
	R^3B_{1g}	7.79	6.83	7.17	7.17	7.53
	R^3B_{2g}	7.79	6.78	7.54	7.54	7.45
	R^3A_g	8.15	7.06	8.37	8.37	8.51
CH_2O	V^1A_2	4.07	3.74	3.77	3.77	3.77
	R^1B_2	7.11	5.77	6.40	6.40	6.37
	R^1B_2	7.97	6.54	7.62	7.62	7.52
	R^1A_1	8.14	7.11	9.16	9.16	8.94
	R^1A_2	8.37	6.69	8.24	8.24	7.96
	R^1B_2	8.88	6.81	8.99	9.00	8.63
	V^3A_2	3.50	3.00	3.03	3.03	3.03
	V^3A_1	5.86	5.57	5.58	5.58	5.58
	R^3B_2	6.83	5.63	6.16	6.16	6.13
	R^3B_2	7.79	6.47	7.44	7.44	7.36
	R^3A_1	7.96	6.35	7.22	7.23	7.17
MAE	Valence (19)		0.32	0.29	0.29	0.29
	Rydberg (23)		1.30	0.46	0.46	0.49