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短長程修正的混成密度泛函帶改善色散修正

Short- and Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections

王志維

Chih-Wei Wang

指導教授：蔡政達 博士

Advisor: Jeng-Da Chai, Ph.D.

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短長程修正的混成密度泛函帶改善色散修正
Short- and Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections

本論文係王志維君（R01222001）在國立臺灣大學物理學系、所完成之碩士學位論文，於民國 105 年 7 月 25 日承下列考試委員審查通過及口試及格，特此證明

口試委員：

蔡政達（簽名）

（指導教授）

趙聖德　　林祥泰

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摘要

爲了改善長程修正(LC)的混成密度泛函在核電子游離與核電子激發的表現，本研究藉由加一個餘補誤差函數至原本作爲分程函數的誤差函數上以調整Hartree-Fock交換能中的分程函數。此混成觀點被應用於LSDA、PBE、B97三種密度泛函近似之上，並加入改善的經驗原子-原子色散修正D3以減少非共價作用誤差。 我們透過ωB97訓練集最佳化泛函參數。所得之泛函：SLC-LDA-D3、SLC-PBE-D3、SLC-B97-D3，通稱短長程修正的(SLC)混成密度泛函，與PBE、LC-ωPBE、ωB97、ωB97X、ωB97X-D、ωB97X-D3在廣泛的測試集比較，包含核電子游離、核電子激發、S66集、AE113、IP131、EA131、FG131、雙同原子陽離子解離、價激發與Rydberg激發、長程電荷轉移激發。SLC泛函在核電子游離與核電子激發比起其他泛函準確很多，並在其他應用和LC泛函的表現相近。

關鍵詞：密度泛函理論、交換相關、分程的、色散修正、核電子游離、核電子激發

Abstract

In order to improve the performance of long-range corrected (LC) hybrid density functionals in core ionizations and core excitations, we adjust the range separation function for Hartree-Fock exchange by adding a complementary error function to the original error function. This hybrid scheme is applied to various density functional approximations including LSDA, PBE, and B97. The D3 empirical atom-atom dispersion corrections is also applied in order to correct non-covalent interactions. We optimize the functional parameters via the ωB97 training set. The resulting functionals, SLC-LDA-D3, SLC-PBE-D3, and SLC-B97-D3, are compared with PBE, LC-ωPBE, ωB97, ωB97X, ωB97X-D, and ωB97X-D3 on a wide range of test sets, including core ionizations, core excitations, S66 Set, AE113, IP131, EA131, and FG131 database, homonuclear diatomic cation dissociations, valence and Rydberg excitations, and long-range charge-transfer excitations. The SLC functionals are much more accurate in core ionizations and core excitations than other functionals, and perform similarly to the LC functionals in other applications.

Keywords: density functional theory, exchange-correlation, range-separated, dispersion correction, core ionization, core excitation

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Chapter 1

Introduction

As a way to calculate the electron ground-state energy of a system, Kohn-Sham density functional theory (KS-DFT)$^{1-3}$, or Generalized Kohn-Sham DFT^{4}, writes the electron energy as

$$E[\{\psi_{i\sigma}\}] = E_{ext}[\rho] + E_H[\rho] + T_s[\{\psi_{i\sigma}\}] + E_{xc}[\{\psi_{i\sigma}\}], \tag{1.1}$$

which are functionals of orthonormal orbitals $\{\psi_{i\sigma}(\mathbf{r})\}$. The σ-spin electron density is

$$\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \psi_{i\sigma}^*(\mathbf{r})\psi_{i\sigma}(\mathbf{r}), \tag{1.2}$$

and

$$\rho(\mathbf{r}) = \sum_\sigma \rho_\sigma(\mathbf{r}). \tag{1.3}$$

E_{ext} is the external potential energy of the external potential $v_{ext}(\mathbf{r})$,

$$E_{ext} = \int v_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{1.4}$$

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E_H is the Hartree interaction energy,

$$E_H = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{1.5}$$

$$r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|, \tag{1.6}$$

T_s is the non-interacting kinetic energy,

$$T_s = -\frac{1}{2}\sum_{\sigma}\sum_{i=1}^{N_\sigma}\int \psi_{i\sigma}^*(\mathbf{r})\nabla^2\psi_{i\sigma}(\mathbf{r})d\mathbf{r} \tag{1.7}$$

(atomic units are used throughout the article), and E_{xc} is the exchange-correlation energy, which will be discussed afterward. The ground-state energy and orbitals are acquired through minimization, that is, for all j and τ,

$$\frac{\delta}{\delta\psi_{j\tau}^*}\left[E - \sum_{\sigma}\sum_{i=1}^{N_\sigma}\epsilon_{i\sigma}\int \psi_{i\sigma}^*(\mathbf{r})\psi_{i\sigma}(\mathbf{r})d\mathbf{r}\right] = \frac{\delta E}{\delta\psi_{j\tau}^*} - \epsilon_{j\tau}\psi_{j\tau} = 0. \tag{1.8}$$

We then get the eigenequation

$$\frac{\delta E}{\delta\psi_{j\tau}^*} = \frac{\delta E}{\delta\rho}\psi_{j\tau} = \epsilon_{j\tau}\psi_{j\tau}, \tag{1.9}$$

where $\epsilon_{j\tau}$ is defined as the orbital energy of $\psi_{j\tau}$. For the excitation, there is a method called time-dependent density functional theory (TDDFT)[5,6] based on KS-DFT.

In KS-DFT, however, the exact exchange-correlation energy functional remains unknown and needs to be approximated. Among the approximations, long-range corrected (LC) hybrid functionals[7−21] whose exchange energy functional combines that of tradi-

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tional density functional approximations (DFA) with the form of Hartree-Fock (HF) exchange have been shown to be accurate for many applications,[22–24] such as thermochemistry, kinetics, frontier orbital energies, fundamental gaps, and long-range charge-transfer excitations. With dispersion corrections, calculations for non-covalent interactions can also be corrected. However, there are still some regions where LC hybrid functionals are not applicable, like strongly correlated systems, core excitations and core ionizations. For the former applications, considering fractional orbital occupations[25,26] may resolve the problem on strongly correlated systems, and core excitations together with core ionizations are the main targets of this research.

There are some functionals which focus on solving these problems, but for some other applications they do not have the advantages of LC hybrid functionals. For example, the short-range corrected functionals proposed by Besley et al.[27,28] and local hybrid functionals proposed by Maier et al.[29] can calculate core excitation energies accurately, but all of them do not have a correct $-1/R$ dependency in long-range charge-transfer excitations. We aim to improve core ionizations and core excitations and inherit the advantages from LC hybrid functionals at the same time.

From Besley et al.,[27] we know increasing the proportion of HF exchange at short-range may improve the performance in core region. This is expectable since HF exchange being exact when electrons are on top of each others, and short-range electron-electron interactions are dominating in core region. Following the philosophy of LC hybrids, which employ 100% HF exchange for long-range electron-electron interactions (to wit, the asymptotic regime) since HF exchange being exact as electrons at a distance approaching infinity from each others, we claim that full HF exchange at short-range

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is also necessary.

This kind of operators, which combine the long-range corrected hybrid with the short-range corrected hybrid, can be obtained as the sum of an error function and a complementary error function. To show the benefits of this hybrid scheme, we try it on various functionals: LSDA, PBE,[30] and B97.[31] The DFT-D3 scheme[32] is also applied in order to correct non-covalent interactions. The parameters of the functionals are optimized by ωB97 training set,[33] excluding the 18 atomic energies, and the results are tested on core excitations and core ionizations as well as noncovalent interactions, atomizations, frontier orbitals, fundamental gaps, symmetric radical cation dissociations, valence and Rydberg excitations and a charge-transfer excitation.

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Chapter 2

Methods

2.1 The short- and long-range corrected (SLC) hybrid scheme

In a standard LC hybrid scheme combining HF and DFA,

$$\begin{aligned} E_{xc}^{LC\text{-}DFA}(\omega) &= E_x^{LR\text{-}HF}(\omega) + [E_x^{DFA} - E_x^{LR\text{-}DFA}(\omega)] + E_c^{DFA} \\ &= E_x^{LR\text{-}HF}(\omega) + E_x^{SR\text{-}DFA}(\omega) + E_c^{DFA}, \qquad (2.1) \end{aligned}$$

where ω is the parameter of the range-separation function. Here, we adjust the above separation into

$$\begin{aligned} E_{xc}^{SLC\text{-}DFA}(\omega_S, \omega_L) &= E_x^{SLR\text{-}HF}(\omega_S, \omega_L) + [E_x^{DFA} - E_x^{LR\text{-}DFA}(\omega_L) - E_x^{SR\text{-}DFA}(\omega_S)] + E_c^{DFA} \\ &= E_x^{SLR\text{-}HF}(\omega_S, \omega_L) + [E_x^{SR\text{-}DFA}(\omega_L) - E_x^{SR\text{-}DFA}(\omega_S)] + E_c^{DFA}, \qquad (2.2) \end{aligned}$$

where

$$E_x^{SLR\text{-}HF} = -\frac{1}{2}\sum_{\sigma}\sum_{i,j}^{occ.}\int\int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_1)\frac{f(r_{12})}{r_{12}}\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.3}$$

is the HF type exchange energy functional computed by the occupied spin orbitals with the range separation function $f(r_{12})$,

$$f(r_{12}) = 1 - erf(\omega_S r_{12}) + erf(\omega_L r_{12}). \tag{2.4}$$

$E_x^{SR\text{-}DFA}$ varies with the DFA and will be stated afterward. E_c^{DFA} is the correlation functional.

It is obvious to see that $f(r_{12})$, the range separation function in HF exchange, satisfies

$$f(0) = 1, \tag{2.5}$$

since $\omega_S > \omega_L > 0$ in our case,

$$0 < f(r_{12}) < 1, r_{12} > 0, \tag{2.6}$$

and

$$\lim_{r_{12}\to\infty} f(r_{12}) = 1, \tag{2.7}$$

which means 100% HF exchange at $r_{12} = 0$ and $r_{12} = \infty$, the condition of short- and long-range corrected (SLC).

The parameter ω_S mainly controls the short-range behavior of $f(r_{12})$, and thus

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affects the short-range behavior of the exchange functional for the most part. ω_L on the other hand mainly controls the long-range behavior. As $\omega_S \to \infty$, $f(r_{12}) = erf(\omega_L r_{12})$, the SLC hybrid reduces to the pure LC hybrid, while the $\omega_L \to 0$ limit corresponds to pure SC. If $\omega_S \to \infty$ and $\omega_L \to 0$ at the same time, SLC scheme becomes the original DFA. In the limit $\omega_S = \omega_L$, we get full HF exchange with a DFA correlation.

In SLC-LDA,

$$E_x^{SR\text{-}LDA}(\omega_i) = \sum_\sigma \int e_{x\sigma}^{LSDA}(\rho_\sigma) F(a_{i,\sigma}) d\mathbf{r}, \tag{2.8}$$

where

$$e_{x\sigma}^{LSDA}(\rho_\sigma) = -\frac{3}{2}(\frac{3}{4\pi})^{1/3}\rho_\sigma^{4/3}, \tag{2.9}$$

$$a_{i,\sigma} \equiv \frac{\omega_i}{2(6\pi^2\rho_\sigma)^{1/3}}, \tag{2.10}$$

and

$$F(a) = 1 - \frac{8}{3}a[\sqrt{\pi} erf(\frac{1}{2a}) - 3a + 4a^3 + (2a - 4a^3)exp(\frac{-1}{4a^2})], \tag{2.11}$$

which is determined by the exact uniform electron gas (UEG) limit.[8,33–35] The correlation energy E_c^{LDA} is derived from Perdew-Wang.[36]

In SLC-PBE, $E_x^{SR\text{-}PBE}(\omega_i)$ is derived from Scuseria et al.,[37,38] starting from

$$E_x^{SR\text{-}PBE}(\omega_i) = 2\pi \int d\mathbf{r}\rho(\mathbf{r}) \int_0^\infty dr_{12} erfc(\omega_i r_{12}) r_{12} h_x^{PBE}(\mathbf{r}, r_{12}) \tag{2.12}$$

and modeling the spherically averaged exchange hole $h_x^{PBE}(\mathbf{r}, r_{12})$. The E_c^{PBE} for SLC-PBE is derived from Perdew-Burke-Ernzerhof.[30]

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2.2 The DFT-D3 scheme

For a static molecule, the total energy includes the electron energy and the nuclear-nuclear repulsion energy. In the DFT-D3 scheme,[32] an extra dispersion correction is also added. Here, we exclude the 3-body term and use the unscaled version given by

$$E_{disp}(D3) = -\sum_{n=6,8} \sum_{A<B}^{N} \frac{C_n^{AB}}{R_{AB}^n [1 + 6(s_{r,n} R_0^{AB} / R_{AB})^{n+8}]}. \tag{2.13}$$

R_{AB} is the interatomic distance of atom pair AB, R_0^{AB} is the cutoff radius, and C_n^{AB} is a function of fractional coordination numbers. R_0^{AB}, C_6^{AB}, C_8^{AB} for each pair of atoms from H to Pu are provided by Grimme et al.[32] $s_{r,6}$ and $s_{r,8}$ are the parameters to be determined.

2.3 Parameter optimization

The parameters is picked to minimize the root-mean-square error on ωB97 training set[33], including the atomization energies of the G3/99 set[39–41] (223 molecules), the ionization potentials of the G2-1 set[42] (40 molecules, excluding SH_2 and N_2 cations), the electron affinities of the G2-1 set (25 molecules), the proton affinities of the G2-1 set (8 molecules), the 76 barrier heights of the NHTBH38/04 and HTBH38/04 sets[43,44] and the 22 noncovalent interactions of the S22 set.[45–47] The D3 parameters $s_{r,6}, s_{r,8}$ are determined using this training set with the errors on the S22 set being multiplied by a scaling factor 10. ω_S is searched in {0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0} and ω_L is searched in {0.30, 0.35, 0.40, 0.45, 0.50}. $s_{r,6}$ and $s_{r,8}$ are scanned from 0.500 to 1.500

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with a 0.001 interval.

2.4 SLC-B97-D3

In order to improved the accuracy on thermochemistry, such as the atomization energies of the G3/99 set, we fix the range operator parameters (ω_S, ω_L) of SLC-PBE-D3 and change the SR-DFA exchange functional into[31]

$$E_x^{SR\text{-}B97}(\omega_i) = \sum_\sigma \int e_{x\sigma}^{B97}[\rho_\sigma] F(a_{i,\sigma}) d\mathbf{r}, \tag{2.14}$$

where

$$e_{x\sigma}^{B97}[\rho_\sigma] = e_{x\sigma}^{LSDA}(\rho_\sigma) \sum_{i=0}^{m} c_{x,i} \left(\frac{\gamma_x s_\sigma^2}{1+\gamma_x s_\sigma^2}\right)^i, \tag{2.15}$$

$$s_\sigma \equiv \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}}, \tag{2.16}$$

$\gamma_x = 0.004$, $c_{x,0} = 1$, and $c_{x,1} \sim c_{x,m}$ are parts of fitting parameters.

The correlation functional E_c^{B97} can be decomposed into same-spin $E_{c\sigma\sigma}^{B97}$ and opposite-spin $E_{c\alpha\beta}^{B97}$ components,[31]

$$E_c^{B97} = \sum_\sigma E_{c\sigma\sigma}^{B97} + E_{c\alpha\beta}^{B97}. \tag{2.17}$$

For the same-spin terms,

$$E_{c\sigma\sigma}^{B97} = \int e_{c\sigma\sigma}^{LSDA}(\rho_\sigma) \sum_{i=0}^{m} c_{ss,i} \left(\frac{\gamma_{ss} s_\sigma^2}{1+\gamma_{ss} s_\sigma^2}\right)^i d\mathbf{r}, \tag{2.18}$$

$\gamma_{ss} = 0.2$, and for the opposite-spin terms,

$$E_{c\alpha\beta}^{B97} = \int e_{c\alpha\beta}^{LSDA}(\rho_\alpha, \rho_\beta) \sum_{i=0}^{m} c_{os,i} (\frac{\gamma_{os} s^2}{1 + \gamma_{os} s^2})^i d\mathbf{r}, \tag{2.19}$$

$$s^2 = \frac{s_\alpha^2 + s_\beta^2}{2}, \tag{2.20}$$

$\gamma_{os} = 0.006$. $c_{ss,0} = c_{os,0} = 1$, and $c_{ss,1} \sim c_{ss,m}$, $c_{os,1} \sim c_{os,m}$ are parts of fitting parameters.

The correlation energy densities are derived from Perdew-Wang[36] parametrization of the LSDA correlation energy using the approach of Stoll et al.,[48]

$$e_{c\sigma\sigma}^{LSDA}(\rho_\sigma) = e_c^{LSDA}(\rho_\sigma, 0), \tag{2.21}$$

$$e_{c\alpha\beta}^{LSDA}(\rho_\alpha, \rho_\beta) = e_c^{LSDA}(\rho_\alpha, \rho_\beta) - e_c^{LSDA}(\rho_\alpha, 0) - e_c^{LSDA}(0, \rho_\beta). \tag{2.22}$$

The D3 parameters $s_{r,6}$, $s_{r,8}$ and the B97 expansion coefficients $c_{x,i}$, $c_{ss,i}$, $c_{os,i}$ of SLC-B97-D3 are determined using the ωB97 training set which includes 18 atomic energies from H to Ar[49]. The errors on the S22 set are multiplied by a scaling factor 10. These parameters are optimized self-consistently by the iterative procedure[33] using the SLC-PBE-D3 orbitals initially. Since there is no significant improvement on the statistical errors of the training set in the optimization for m>4, SLC-B97-D3 is truncated at m=4, as ref. 33, ref. 51, and ref. 23.

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Chapter 3

Results

All the calculations were performed with a development version of Q-Chem 4.3.[50] In the following, the functionals proposed above will be compared with PBE[30] and some LC hybrid functionals (LC-ωPBE,[37] ωB97,[33] ωB97X,[33] ωB97X-D,[51] ωB97X-D3[23]). The abbreviations for statistical errors are MSE (mean signed errors), MAE (mean absolute errors) and rms (root-mean-square errors). error = theoretical value − reference value. Most of the basis sets and grids are determined in accordance with the referential literatures.

3.1 Optimized parameters

The optimized parameters for various functionals are shown in Table 3.1. The optimal operators of the SLC hybrids and the compared LC hybrids are also plotted in Figure 3.1. These operators except for that of SLC-LDA-D3 intersect at around 0.8 Bohr in the middle-range region, as indicated in ref. 52 for LC hybrid functionals achieving good balanced performance for thermochemistry and barrier heights. It seem that, since LSDA having much larger error than the GGAs in the training set, larger proportion of HF exchange is needed to cancel the error, so the optimal operator of SLC-LDA-D3 is above those of the other hybrid functionals.

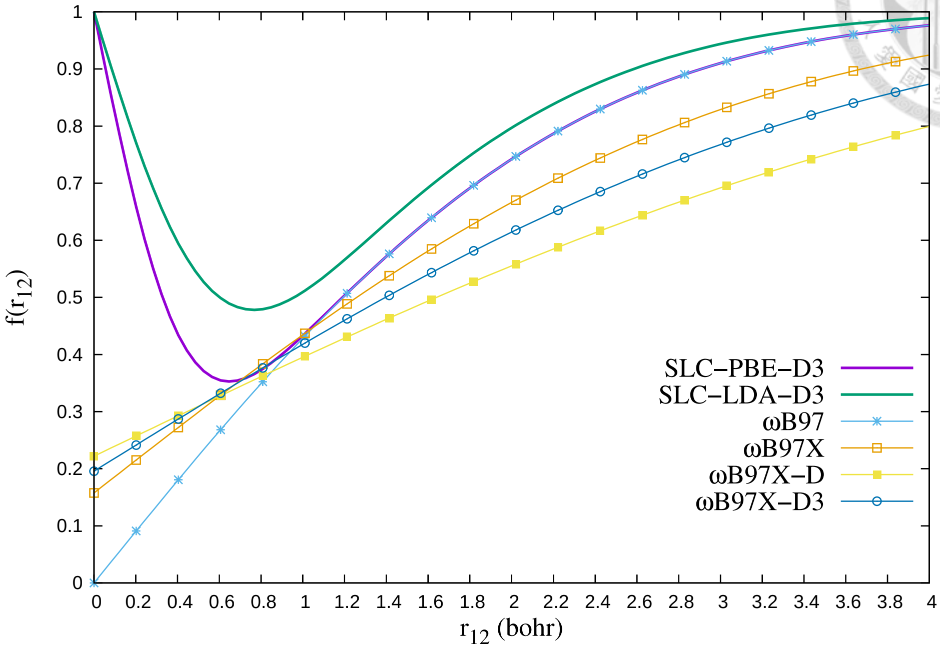
Table 3.1: Optimized parameters

	SLC-B97-D3	SLC-PBE-D3	SLC-LDA-D3
$\omega_S(bohr^{-1})$	2.0	2.0	1.5
$\omega_L(bohr^{-1})$	0.40	0.40	0.45
$s_{r,6}$	1.298	1.179	1.129
$s_{r,8}$	1.277	1.123	1.131
$c_{x,1}$	1.469313		
$c_{x,2}$	-6.185202		
$c_{x,3}$	23.053635		
$c_{x,4}$	-16.353923		
$c_{ss,1}$	-2.154721		
$c_{ss,2}$	10.271378		
$c_{ss,3}$	-23.966521		
$c_{ss,4}$	15.345722		
$c_{os,1}$	4.460711		
$c_{os,2}$	-25.043202		
$c_{os,3}$	22.506558		
$c_{os,4}$	-4.114590		

3.2 ωB97 training set

The results are computed using the 6-311++G(3df,3pd) basis set with EML(75, 302) grid.[53,54] The counterpoise correction is employed for the S22 set to reduce basis set superposition error.[55] The geometries and zero-point energies are obtained in ref. 33 and references therein. With the adjusted range separation function and the dispersion corrections as well, SLC-B97-D3 shows some improvements over ωB97 in ωB97 training set. The comparison between SLC-PBE-D3 and LC-ωPBE is also the same. Note that

Figure 3.1: The optimal operators of different functionals. The operators of SLC-B97-D3 and LC-ωPBE are the same as those of SLC-PBE-D3 and ωB97 respectively.



LC-ωPBE was not trained by this training set nevertheless. Overall, the functionals with B97 exchange-correlation perform the best since their very flexible functional forms parametrized by this set.

Table 3.2: Statistical errors (in kcal/mol) of the ωB97 training set

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
G3/99	MSE	20.90	3.12	-0.29	-0.20	-0.24	-0.14
(223)	MAE	21.51	5.86	2.63	2.13	1.93	2.06
	rms	26.30	7.43	3.58	2.88	2.77	2.81
IP	MSE	0.04	2.86	-0.50	-0.14	0.20	0.07
(40)	MAE	3.44	4.29	2.68	2.69	2.75	2.66

	rms	4.35	5.39	3.60	3.59	3.62	3.53
EA	MSE	1.72	0.18	1.52	-0.47	0.07	-0.37
(25)	MAE	2.42	3.00	2.72	2.04	1.91	1.93
	rms	3.06	3.50	3.11	2.57	2.38	2.41
PA	MSE	-0.83	0.86	0.67	0.56	1.42	1.10
(8)	MAE	1.60	1.41	1.48	1.21	1.50	1.29
	rms	1.91	2.04	2.18	1.70	2.05	1.92
NHTBH	MSE	-8.52	1.39	1.32	0.55	-0.45	0.04
(38)	MAE	8.62	2.47	2.32	1.75	1.51	1.53
	rms	10.61	3.07	2.82	2.08	2.00	1.89
HTBH	MSE	-9.67	-0.77	-0.66	-1.55	2.57	-2.08
(38)	MAE	9.67	1.39	2.11	2.27	2.70	2.40
	rms	10.37	1.90	2.47	2.60	3.10	2.75
S22	MSE	2.71	2.82	0.10	0.47	-0.14	-0.07
(22)	MAE	2.71	2.82	0.53	0.79	0.19	0.18
	rms	3.73	3.58	0.63	1.11	0.25	0.25
Total	MSE	10.32	2.30	-0.23	-0.21	-0.38	-0.28
(394)	MAE	14.63	4.50	2.42	2.06	1.94	1.97
	rms	20.40	6.09	3.27	2.76	2.73	2.69

System	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
G3/99	MSE	2.63	-0.57	-0.32
(223)	MAE	8.84	4.49	2.63

	rms	11.09	5.91	3.49
IP	MSE	11.60	1.85	-0.22
(40)	MAE	11.60	3.74	2.54
	rms	12.40	4.70	3.45
EA	MSE	8.96	-0.54	-1.66
(25)	MAE	8.96	3.05	2.66
	rms	9.62	3.52	3.06
PA	MSE	-1.91	0.84	0.80
(8)	MAE	2.31	1.36	1.44
	rms	2.54	2.01	2.19
NHTBH	MSE	1.99	1.29	1.38
(38)	MAE	3.32	2.38	2.13
	rms	3.77	2.86	2.55
HTBH	MSE	-0.27	-1.03	-0.96
(38)	MAE	1.99	1.41	2.04
	rms	2.59	1.77	2.33
S22	MSE	0.34	0.11	-0.20
(22)	MAE	0.45	0.30	0.23
	rms	0.61	0.39	0.33
Total	MSE	3.38	-0.12	-0.26
(394)	MAE	7.33	3.52	2.36
	rms	9.65	4.90	3.15

3.3 Test sets

3.3.1 Core ionization energies

Core ionization energies are computed by the opposite of core orbital energies as ref. 56, using the 6-311++G(3df,3pd) basis set with EML(75, 302) grid. We take 23 core ionization reference energies from ref. 57 with geometries obtained in ref. 33. The electrons are ionized from the 1s orbitals of C $\sim$ F. The atoms where the electrons are ionized or excited afterward are limited in the 1st and 2nd row elements in order to avoid strong relativistic effect. Table 3.3 below shows that LC hybrid does not improve the core ionizations much enough on PBE, and all the SLC functionals have significant improvements over PBE and LC hybrid functionals. Table B.3 in appendix provides detailed results of core ionizations. For each single ionization, the ionization energies calculated by different methods from lowest to highest are sorted as PBE, LC-ωPBE, ωB97, ωB97X, ωB97X-D3, ωB97X-D, SLC-PBE-D3, SLC-B97-D3, SLC-LDA-D3, where the results of LC-ωPBE and ωB97 are similar, ωB97X, ωB97X-D, and ωB97X-D3 are similar, SLC-PBE-D3 and SLC-B97-D3 are similar. Since the signed errors for PBE and LC hybrids are all negative, the absolute deviations from different methods for each ionization have the order PBE $>$ LC-ωPBE $>$ ωB97 $>$ ωB97X $>$ ωB97X-D3 $>$ ωB97X-D $>$ SLC hybrids, ωB97X-D has the smallest deviations among the LC hybrids. For PBE and LC hybrids, the signed errors of the 1s ionization energies are descending as the atomic number increases. The signed errors of 1s ionizations for SLC hybrids, on the other hand, are ascending with the atomic numbers. The errors are $-21.66 \sim -34.35$ eV for PBE, $-10.68 \sim -19.23$ eV for ωB97-D, $9.88 \sim -0.22$

eV for SLC-LDA-D3, 1.89 ∼ −6.08 eV for SLC-PBE-D3, and 2.89 ∼ −5.34 eV for SLC-B97-D3. These show that a large proportion of HF exchange in short-range is necessary to reduce errors on core ionizations.

Table 3.3: Statistical errors (in eV) of the 23 core ionization energies

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
Core	MSE	-26.25	-20.15	-19.39	-14.88	-13.74	-14.10
Ionization	MAE	26.25	20.15	19.39	14.88	13.74	14.10
(23)	rms	26.48	20.47	19.70	15.10	13.91	14.29
System	Error		SLC-LDA-D3		SLC-PBE-D3		SLC-B97-D3
Core	MSE		4.25		-2.36		-1.53
Ionization	MAE		4.27		2.77		2.53
(23)	rms		5.27		3.36		2.91

3.3.2 Core excitation energies

We take 38 core excitation reference energies collected in ref [27] with geometries obtained in ref. 33. The electrons are excited from the 1s orbitals of C ∼ Cl, limited in 1st and 2nd row elements to avoid strong relativistic effect. In order to reduce the rise in computational cost for calculations of the core excitations, since normally a large number of single excited state roots are needed to find core excited states, we perform TDDFT calculations with the Tamm-Dancoff approximation (TDA)[58] and reduced single excitation spaces,[59] which limit the occupied orbitals to the core orbitals which we are interested at. 6-311(2+,2+)G** basis set and EML(100, 302) grid are used. Table 3.4 below shows that LC hybrid does not improve the core excitations much enough on PBE, and all the SLC functionals have significant improvements over PBE and LC hybrid functionals for both core→valence excitations and core→Rydberg excitations. Table B.4 in appendix provides detailed results of core excitations. We can see that all the properties of the results of core ionizations are the same as core excitations. For 1st row elements, the errors are $-16.63 \sim -28.33$ eV for PBE, $-9.94 \sim -16.72$ eV for ωB97-D, $8.60 \sim -1.02$ eV for SLC-LDA-D3, $2.19 \sim -5.91$ eV for SLC-PBE-D3, and $3.28 \sim -5.12$ eV for SLC-B97-D3. For 2nd row elements, the errors are $-63.23 \sim -87.31$ eV for PBE, $-42.98 \sim -61.95$ eV for ωB97-D, $9.71 \sim 7.55$ eV for SLC-LDA-D3, $1.44 \sim -1.03$ eV for SLC-PBE-D3, and $3.04 \sim 0.51$ eV for SLC-B97-D3. These show the benefit of having a large proportion of HF exchange in short-range on core excitations.

Table 3.4: Statistical errors (in eV) of the 38 core excitation energies

State	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
core→	MSE	-42.32	-41.30	-40.31	-31.95	-28.74	-30.05
valence	MAE	42.32	41.30	40.31	31.95	28.74	30.05
(15)	rms	50.91	49.93	48.96	39.29	35.56	37.08
core→	MSE	-32.26	-29.35	-28.38	-22.26	-20.35	-21.12
Rydberg	MAE	32.26	29.35	28.38	22.26	20.35	21.12
(23)	rms	39.91	37.64	36.78	29.43	26.90	27.93

State	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
core→	MSE	4.81	-1.46	-0.38
valence	MAE	5.12	2.22	2.53
(15)	rms	6.25	2.91	2.84
core→	MSE	3.36	-2.93	-1.93
Rydberg	MAE	3.50	3.22	2.94
(23)	rms	4.94	3.81	3.26

Relativistic corrections

Since relativistic effects are some of the reasons which cause the errors in the calculations of the core excitation and ionization energies using DFT, some methods apply relativistic corrections heightening the calculated energies. Here, we take a shot at applying the shifts depending on the atoms where the 1s electrons are excited or ionized. They are 0.12 eV, 0.24 eV, 0.45 eV, 0.75 eV for C, N, O, F,[29] and 3.4 eV, 4.6 eV, 5.9 eV, 7.9 eV for Si, P, S, Cl,[27] respectively. Comparing Table 3.5 below with Table 3.3, Table 3.4 above, applying relativistic corrections increases the errors of the SLC hybrids, especially for 2nd row elements, though still much better than LC hybrids and PBE. It seems that these SLC hybrids capture some of those shifts, at least in 1st and 2nd row nuclei. Thus we do not suggest using relativistic corrections here in SLC hybrid scheme.

Table 3.5: Statistical errors (in eV) of the core excitation and ionization energies with relativistic corrections

State	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
core→	MSE	-39.78	-38.76	-37.77	-29.41	-26.20	-27.51
valence	MAE	39.78	38.76	37.77	29.41	26.20	27.51
(15)	rms	47.20	46.21	45.23	35.54	31.80	33.33
core→	MSE	-30.89	-27.98	-27.01	-20.89	-18.97	-19.75
Rydberg	MAE	30.89	27.98	27.01	20.89	18.97	19.75
(23)	rms	37.32	34.99	34.11	26.74	24.21	25.24
Core	MSE	-25.95	-19.86	-19.10	-14.59	-13.45	-13.81
Ionization	MAE	25.95	19.86	19.10	14.59	13.45	13.81
(23)	rms	26.16	20.15	19.38	14.78	13.60	13.97

State	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
core→	MSE	7.35	1.08	2.16
valence	MAE	7.61	4.42	4.96
(15)	rms	9.73	4.80	5.50
core→	MSE	4.73	-1.56	-0.56
Rydberg	MAE	4.83	4.23	4.12
(23)	rms	7.43	4.67	4.69
Core	MSE	4.54	-2.07	-1.24
Ionization	MAE	4.55	2.78	2.60
(23)	rms	5.62	3.30	2.93

3.3.3 The S66 set

The S66 set,[60] a database of noncovalent interaction energies, was presented by the laboratory which developed the popular S22 set. It is designed to cover the common types of noncovalent interactions in biomolecules, while keeping a balanced representa-

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tion of dispersion and electrostatic contributions. The performance of the functionals is evaluated using the 6-311++G(3df,3pd) basis set with EML(99, 590) grid and summarized in Table 3.6. The counterpoise correction is employed for the S66 set to reduce basis set superposition error. The geometries and reference energies are obtained in ref. 60. SLC-LDA-D3 has the best performance in the S66 set. The performance of SLC-PBE-D3 is similar to that of ωB97X-D3, and SLC-B97-D3 is similar to ωB97X-D and ωB97. Although without long-range dynamical correlation, ωB97 shows the accuracy comparable to the functionals with dispersion corrections in S66 noncovalent interaction.

Table 3.6: Statistical errors (in kcal/mol) of the S66 set

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
S66	MSE	2.22	2.46	-0.15	0.16	-0.30	-0.23
(66)	MAE	2.23	2.46	0.37	0.49	0.35	0.26
	rms	2.75	2.80	0.47	0.65	0.51	0.35
System	Error		SLC-LDA-D3		SLC-PBE-D3		SLC-B97-D3
S66	MSE		0.04		-0.06		-0.35
(66)	MAE		0.21		0.27		0.37
	rms		0.30		0.35		0.46

3.3.4 Atomization energies

The AE113 database[22] consists of the atomization energies of 113 molecules in IP131 (AE131 and FG131 as well) with experimental geometries.[61] The performance is examined using the 6-311++G(3df,3pd) basis set with EML(75, 302) grid. As shown in Table 3.7, the functionals with B97 exchange-correlation have the best performance.

Table 3.7: Statistical errors (in eV) of the atomization energies for the AE113 database

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
AE113	MSE	0.83	0.10	0.05	0.05	0.04	0.05
(113)	MAE	0.88	0.27	0.11	0.10	0.10	0.10
	rms	1.06	0.41	0.15	0.13	0.14	0.13
System	Error		SLC-LDA-D3		SLC-PBE-D3		SLC-B97-D3
AE113	MSE		0.04		-0.03		0.04
(113)	MAE		0.28		0.17		0.11
	rms		0.34		0.23		0.14

3.3.5 Frontier orbital energies

For the exact KS-DFT, vertical IP is identical to the opposite HOMO energy of the N-electron system,[62–67] and vertical EA is identical to the opposite HOMO energy of the system with one more electron. Recent studies[68–72] shows that vertical EA is also close to the opposite LUMO energy for LC hybrid functionals since[63,67,73–82]

$$HOMO(N+1) - LUMO(N) = \lim_{\mu \to 0^+} \left\{ \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}\bigg|_{N+\mu} - \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}\bigg|_{N-\mu} \right\} \tag{3.1}$$

is close to zero for LC hybrid functionals. Below, the performance on IP131 and EA131 databases[22,61] is evaluated using the 6-311++G(3df,3pd) basis set with EML(75, 302) grid. For the IP131 database, vertical IPs and opposite HOMO energies are both calculated. Similarly, for the EA131 set, vertical EAs, -HOMO(N+1), and -LUMO(N) are all computed. As shown in Table 3.8 and Table 3.9, all the tested functionals are accurate reasonably in direct vertical IP and EA calculations. In contrast, PBE severely underestimates the energies for the calculations using HOMO energies, and overestimates them by using LUMO energies. The LC and SLC hybrid functionals yield accurate energies from orbital energy calculations.

Table 3.8: Statistical errors (in eV) of the frontier orbital energies for the IP131 database

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
IP							
IP131	MSE	-0.26	0.10	0.00	0.00	-0.03	-0.02
(131)	MAE	0.36	0.28	0.19	0.18	0.19	0.18
	rms	0.52	0.46	0.26	0.26	0.27	0.26
-HOMO(N)							
IP131	MSE	-4.40	-0.15	-0.24	-0.48	-1.01	-0.71
(131)	MAE	4.40	0.42	0.40	0.51	1.01	0.72
	rms	4.50	0.68	0.63	0.75	1.18	0.93

System	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
IP				
IP131	MSE	0.57	0.09	0.02
(131)	MAE	0.58	0.20	0.18
	rms	0.64	0.28	0.26
-HOMO(N)				
IP131	MSE	0.61	-0.09	-0.18
(131)	MAE	0.70	0.36	0.37
	rms	0.77	0.56	0.59

Table 3.9: Statistical errors (in eV) of the frontier orbital energies for the EA131 database

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
EA							
EA131	MSE	0.10	-0.11	-0.24	-0.19	-0.14	-0.16
(131)	MAE	0.21	0.36	0.34	0.31	0.26	0.29
	rms	0.34	0.54	0.44	0.41	0.36	0.39
-HOMO(N+1)							
EA131	MSE	-2.03	0.00	-0.13	-0.17	-0.32	-0.23
(131)	MAE	2.03	0.34	0.34	0.32	0.39	0.33
	rms	2.30	0.43	0.43	0.41	0.51	0.44
-LUMO(N)							
EA131	MSE	2.43	-0.19	-0.38	-0.31	0.01	-0.15
(131)	MAE	2.45	0.42	0.49	0.52	0.54	0.49
	rms	2.72	0.51	0.59	0.62	0.63	0.57

System	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
EA				
EA131	MSE	0.23	-0.08	-0.22
(131)	MAE	0.33	0.27	0.32
	rms	0.45	0.35	0.42
-HOMO(N+1)				

EA131	MSE	0.40	0.08	-0.10
(131)	MAE	0.47	0.30	0.33
	rms	0.62	0.38	0.41
-LUMO(N)				
EA131	MSE	0.10	-0.25	-0.34
(131)	MAE	0.30	0.39	0.44
	rms	0.40	0.47	0.53

3.3.6 Fundamental gaps

The fundamental gap is the difference between the vertical IP and EA. Just like the different ways to compute frontier orbital energies, 3 different ways to compute the FGs of FG131 database[22,61] as shown in Table 3.10 are used, with the 6-311++G(3df,3pd) basis set and EML(75, 302) grid. As predicted by the results of frontier orbital energies, the KS gap calculations yield severely underestimated results for PBE. HOMO(N+1) - HOMO(N) calculations for PBE perform not well either. On the other hand, the LC and SLC functionals perform better in the fundamental gaps computed by the orbital energies.

Table 3.10: Statistical errors (in eV) of the fundamental gaps for the FG131 database

System	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
IP - EA							

FG131	MSE	-0.46	0.10	0.13	0.08	-0.01	0.03
(131)	MAE	0.57	0.44	0.32	0.29	0.27	0.28
	rms	0.76	0.74	0.42	0.40	0.38	0.39
HOMO(N+1) - HOMO(N)							
FG131	MSE	-2.48	-0.26	-0.22	-0.42	-0.80	-0.59
(131)	MAE	2.48	0.50	0.44	0.50	0.81	0.62
	rms	2.69	0.70	0.59	0.65	0.93	0.77
HOMO-LUMO gaps							
FG131	MSE	-6.94	-0.07	0.04	-0.27	-1.12	-0.67
(131)	MAE	6.94	0.53	0.49	0.57	1.15	0.77
	rms	7.15	0.80	0.65	0.77	1.40	1.02

System	Error	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
IP - EA				
FG131	MSE	0.23	0.05	0.13
(131)	MAE	0.39	0.30	0.32
	rms	0.47	0.39	0.41
HOMO(N+1) - HOMO(N)				
FG131	MSE	0.09	-0.27	-0.18
(131)	MAE	0.47	0.43	0.43
	rms	0.57	0.57	0.57
HOMO-LUMO gaps				
FG131	MSE	0.40	0.05	0.05

(131)	MAE	0.54	0.45	0.45
	rms	0.63	0.59	0.60

3.3.7 Dissociation of symmetric radical cations

Due to the severe SIEs of semilocal functionals, spurious fractional charge dissociation can occur,[83–90] especially for symmetric charges radicals such as H_2^+, He_2^+, Ne_2^+, and Ar_2^+. The dissociation curves for these cations are calculated using the 6-311++G(3df,3pd) basis set with EML(75, 302) grid to examine the performance of the methods upon the SIE problems. The results are compared with HF theory for H_2^+ and CCSD(T) theory for other cations. Figure 3.2 ∼ 3.5 show that, just like the LC hybrids, the SLC hybrids remove the unphysical barriers of the dissociation curves. However, the cations still do not dissociate successfully in the SLC hybrids, as one of the problems of the LC hybrids.

Figure 3.2: Dissociation curve of H_2^+. Zero level is set to E(H) + E(H^+) for each method.

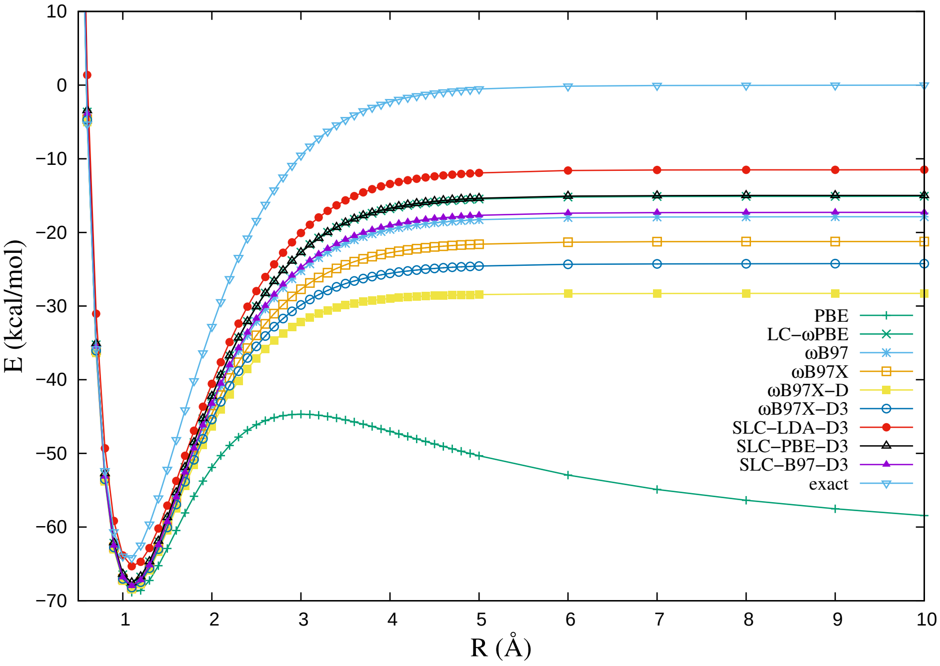


Figure 3.3: Dissociation curve of He_2^+. Zero level is set to E(He) + E(He^+) for each method.

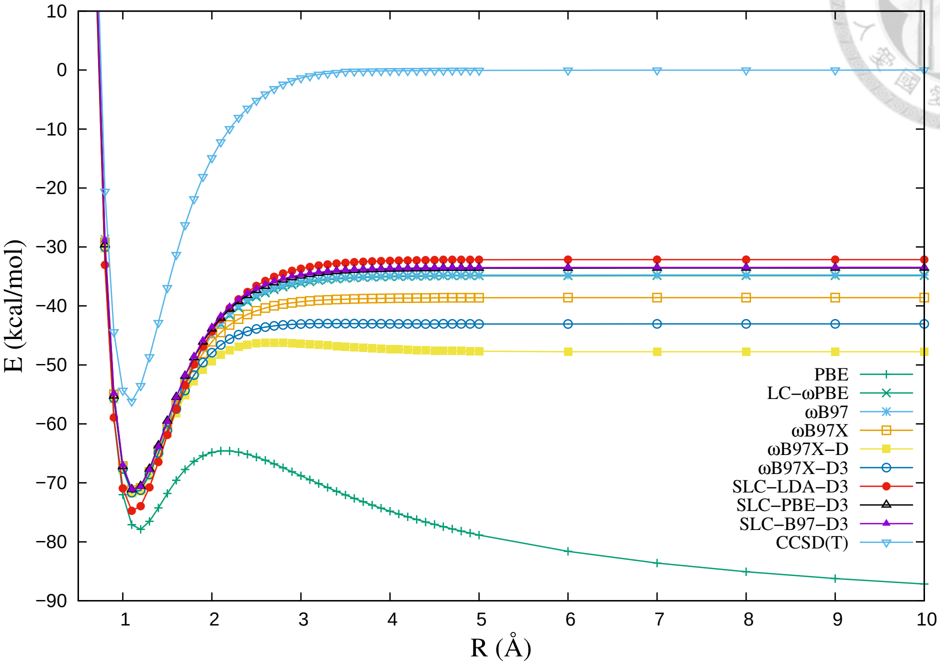


Figure 3.4: Dissociation curve of Ne_2^+. Zero level is set to E(Ne) + E(Ne^+) for each method.

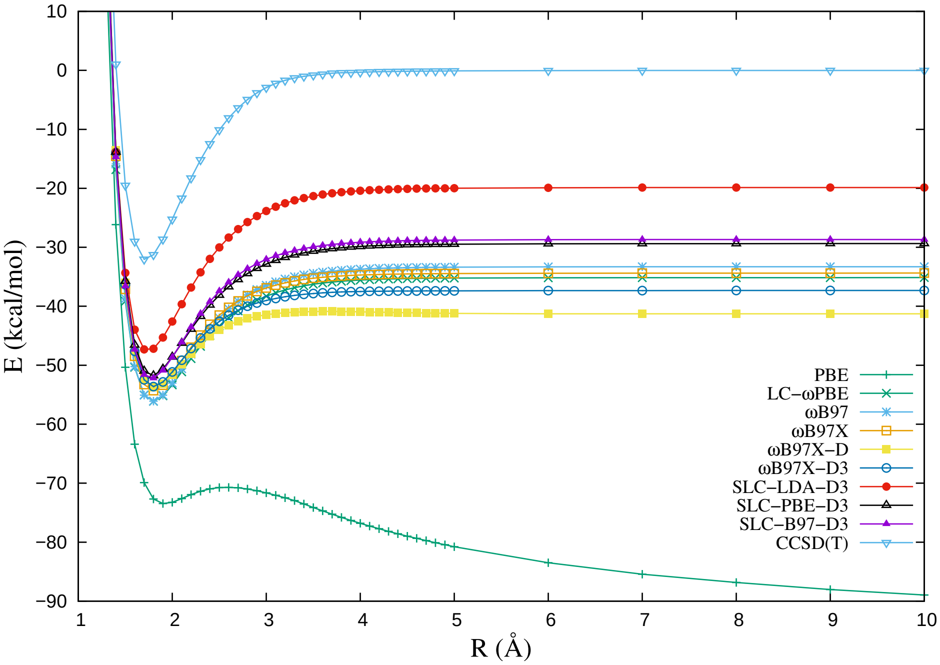
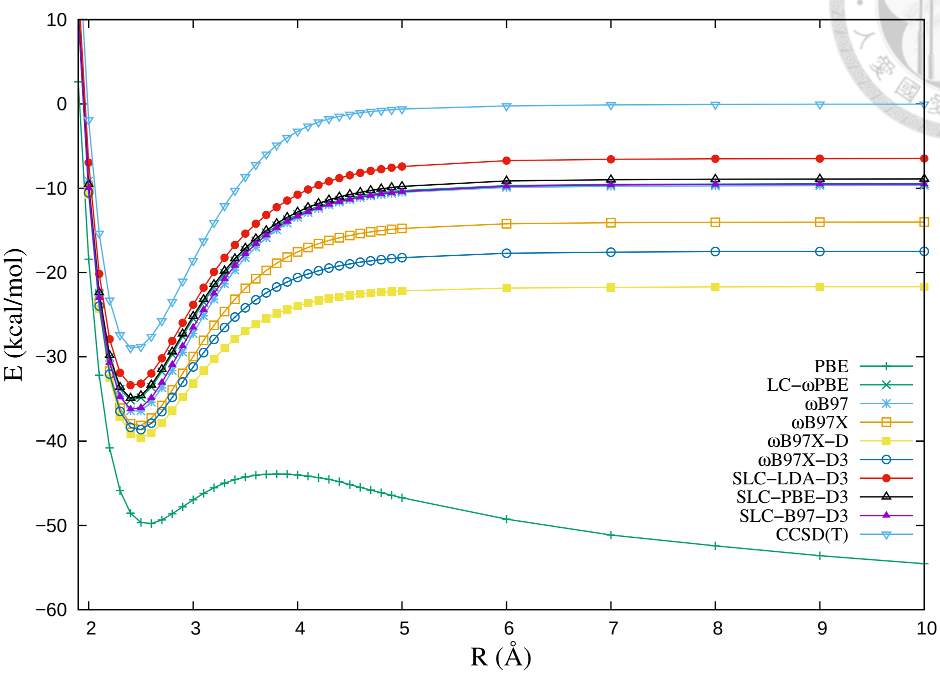


Figure 3.5: Dissociation curve of Ar_2^+. Zero level is set to E(Ar) + E(Ar^+) for each method.



3.3.8 Valence and Rydberg excitation energies

We perform TDDFT calculations on nitrogen gas, carbon monoxide, water, ethylene and formaldehyde using the 6-311(2+,2+)G** basis set with EML(99, 590) grid. The experimental values of the excitation energies are taken from ref. 91 with geometries obtained in ref. 33. All the tested functionals perform reasonably well for the valence excitations. PBE severely underestimates the Rydberg excitations, and SLC-LDA-D3 slightly overestimates them. Other LC and SLC hybrid functionals perform well for the Rydberg excitations as for the valence excitations.

Table 3.11: Statistical errors (in eV) of the 19 valence and 23 Rydberg excitation energies

State	Error	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3
valence	MSE	-0.30	-0.36	-0.23	-0.28	-0.29	-0.28
(19)	MAE	0.31	0.39	0.27	0.30	0.30	0.29
	rms	0.38	0.47	0.34	0.37	0.37	0.37
Rydberg	MSE	-1.29	0.19	0.24	0.12	-0.30	-0.12
(23)	MAE	1.29	0.29	0.28	0.21	0.35	0.22
	rms	1.35	0.38	0.37	0.30	0.40	0.30
State	Error		SLC-LDA-D3		SLC-PBE-D3		SLC-B97-D3
valence	MSE		-0.32		-0.37		-0.23
(19)	MAE		0.37		0.40		0.27
	rms		0.46		0.48		0.35
Rydberg	MSE		0.51		0.20		0.22
(23)	MAE		0.51		0.28		0.27
	rms		0.58		0.37		0.36

3.3.9 Long-range charge-transfer excitations

Correct long-range charge-transfer (CT) excitations between a donor and an acceptor should have the asymptote[92]

$$\omega_{CT}(R \to \infty) \approx IP_D - EA_A - 1/R, \tag{3.2}$$

where IP_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor and R is the intermolecular distance.

We perform TDDFT calculations for the lowest CT excitations on ethylene tetrafluoroethylene dimers separated by different distances. The results are computed using the 6-31G* basis set with EML(99, 590) grid. Geometries of C_2H_4 and C_2F_4 are obtained in ref. 33. The results by the symmetry-adapted-cluster configuration-interaction (SAC-CI) method from Tawada et al.[93] are taken for comparison.

Figure 3.6 and Figure 3.7 show that all the SLC and LC hybrids, which have full HF exchange in long-range, have a correct $-1/R$ dependency.

Figure 3.6: The lowest CT excitation energies of $C_2H_4 \cdots C_2F_4$ dimers.

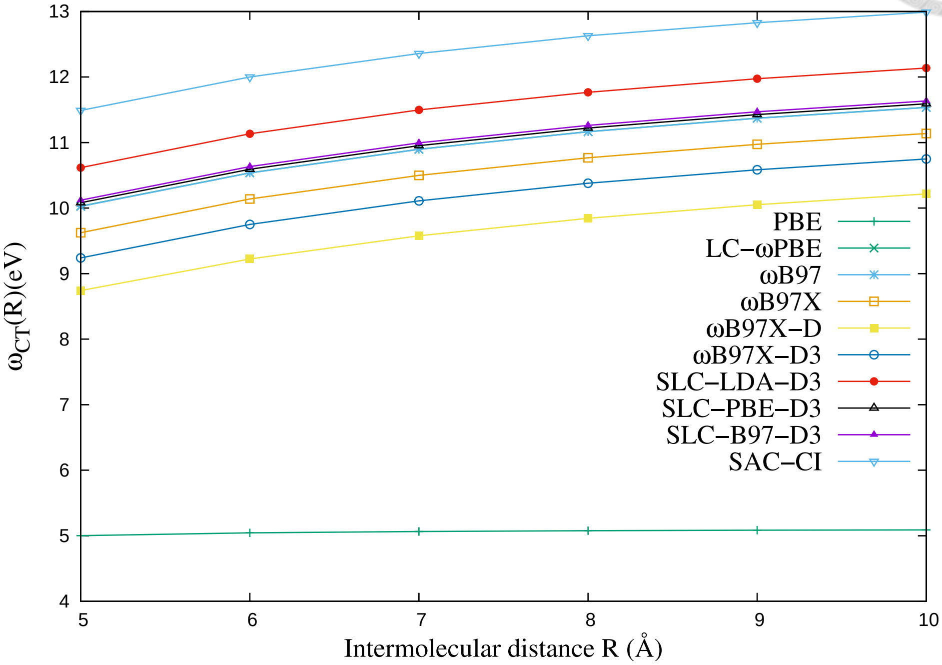
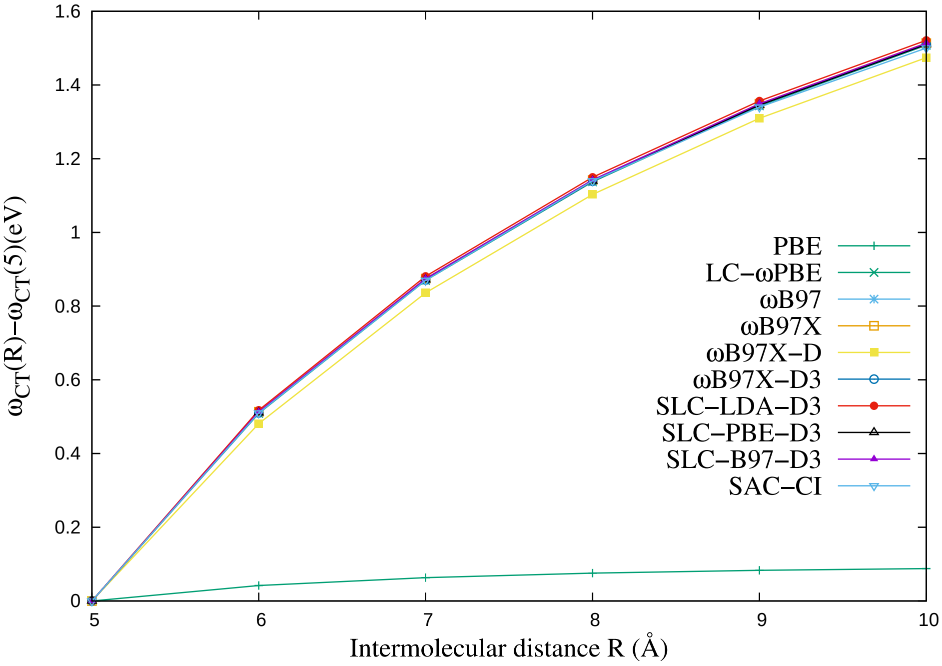


Figure 3.7: Relative excitation energies for the lowest CT excitation of $C_2H_4 \cdots C_2F_4$ dimers.



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Chapter 4

Conclusion

Following the SLC hybrid scheme, which employs 100% HF exchange for both short-range and long-range, we have developed three functionals: SLC-LDA-D3, SLC-PBE-D3, and SLC-B97-D3, by using the ωB97 training set. We test them with other functionals, including PBE and some LC hybrid functionals. As predicted from the philosophy of SLC hybrid, these functionals show significant improvements in core ionizations and core excitations over LC hybrid functionals, even though the SLC hybrids are not specially optimized on core results. In other test sets, including noncovalent interactions, atomization energies, frontier orbital energies, fundamental gaps, homonuclear diatomic cation dissociations, valence and Rydberg excitations, and a charge-transfer excitation, proposed functionals are accurate reasonably as the LC hybrid functionals. The performance of proposed functionals supports that the SLC hybrid scheme is feasible for improving the LC hybrids.

Adding a complementary error function to an error function is not the only way to satisfy the philosophy of the SLC hybrid scheme. Including more parameters to optimize or finding another function type as a better range separation function is a possible attempt to improve the accuracy. Trying more DFA exchange-correlations is also thinkable.

Appendix A

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Appendix B

Supporting Information

Table B.1: SLC-LDA-D3 rms errors (in kcal/mol) of the training set with various ω_S, ω_L (in $bohr^{-1}$).

$\omega_L \backslash \omega_S$	0.8	1.0	1.5	2.0	2.5	3.0	3.5	4.0
0.30	19.13	16.86	28.33	34.73	38.49	41.04	42.91	44.33
0.35	19.24	10.66	19.42	25.56	29.24	31.75	33.59	34.99
0.40	21.34	10.84	12.82	18.19	21.67	24.08	25.87	27.23
0.45	23.76	13.48	9.65	12.98	15.91	18.09	19.74	21.03
0.50	24.80	16.31	10.64	10.63	12.33	13.97	15.33	16.44

Table B.2: SLC-PBE-D3 rms errors (in kcal/mol) of the training set with various ω_S, ω_L (in $bohr^{-1}$).

$\omega_L \backslash \omega_S$	0.8	1.0	1.5	2.0	2.5	3.0	3.5	4.0
0.30	11.90	8.60	6.00	8.06	9.24	9.81	10.17	10.44
0.35	13.26	9.70	5.36	5.87	6.78	7.27	7.60	7.85
0.40	14.80	11.11	5.94	4.90	5.20	5.51	5.75	5.96
0.45	16.32	12.66	7.12	5.34	5.02	5.03	5.11	5.21
0.50	17.83	14.20	8.54	6.44	5.85	5.72	5.70	5.71

Table B.3: The 23 core ionization energies (in eV) calculated by various methods. Bold type denotes the atom where the 1s electron is ionized. The experimental energies are collected in ref. 57 with geometries obtained in ref. 33.

Molecule	Exp.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3

$\mathbf{C}_2H_2$	290.82	269.16	275.23	275.90	279.36	280.14	279.93	292.73	287.04	287.76
$\mathbf{C}H_4$	290.91	268.37	274.41	275.13	278.54	279.29	279.09	291.82	286.15	286.91
$\mathbf{C}H_3OH$	292.42	269.96	276.09	276.81	280.22	280.96	280.76	293.53	287.83	288.59
$CH_3\mathbf{C}N$	292.45	270.03	276.22	276.85	280.32	281.09	280.88	293.79	288.04	288.74
$\mathbf{C}H_3CN$	292.98	270.39	276.50	277.19	280.61	281,37	281.16	293.93	288.24	288.99
$H\mathbf{C}N$	293.40	270.38	276.51	277.15	280.63	281.42	281.19	294.09	288.32	289.04
$H_2\mathbf{C}O$	294.47	271.57	277.78	278.47	281.91	282.67	282.46	295.34	289.55	290.31
$\mathbf{C}O$	296.21	272.02	278.23	278.88	282.39	283.17	282.95	295.99	290.13	290.87
$\mathbf{C}O_2$	297.69	273.66	280.33	280.95	284.44	285.21	284.99	298.14	292.14	292.87
$\mathbf{N}H_3$	405.56	379.92	385.83	386.69	391.09	392.19	391.86	409.67	403.09	403.97
$CH_3C\mathbf{N}$	405.64	380.34	386.40	387.17	391.64	392.76	392.42	410.37	403.74	404.57
$HC\mathbf{N}$	406.78	381.10	387.12	387.89	392.37	393.50	393.15	411.13	404.47	405.31
$\mathbf{N}NO$	408.71	382.89	389.27	390.02	394.50	395.63	395.28	413.43	406.61	407.45
$\mathbf{N}_2$	409.98	383.12	389.27	390.02	394.52	395.67	395.31	413.38	406.63	407.46
$N\mathbf{N}O$	412.59	386.30	393.02	393.76	398.20	399.26	398.94	417.13	410.30	411.12
$CH_3\mathbf{O}H$	539.11	510.22	516.05	516.94	522.38	523.87	523.37	546.62	539.34	540.28
$H_2C\mathbf{O}$	539.48	510.77	516.56	517.41	522.89	524.39	523.89	547.21	539.90	540.80
$H_2\mathbf{O}$	539.90	510.28	516.15	517.07	522.50	523.97	523.48	546.76	539.43	540.40
$C\mathbf{O}_2$	541.28	512.36	518.34	519.16	524.64	526.13	525.64	549.05	541.66	542.55
$NN\mathbf{O}$	541.42	512.97	518.72	519.56	525.06	526.61	526.08	549.40	542.04	542.95
$C\mathbf{O}$	542.55	513.06	518.98	519.76	525.26	526.76	526.26	549.66	542.33	543.17
$H\mathbf{F}$	694.23	659.88	665.77	666.71	673.16	675.00	674.35	703.26	695.36	696.38
$\mathbf{F}_2$	696.69	662.88	668.98	669.87	676.34	678.19	677.54	706.57	698.58	699.58
MSE		-26.25	-20.15	-19.39	-14.88	-13.74	-14.10	4.25	-2.36	-1.53
MAE		26.25	20.15	19.39	14.88	13.74	14.10	4.27	2.77	2.53
rms		26.48	20.47	19.70	15.10	13.91	14.29	5.27	3.36	2.91

Table B.4: The 38 core excitation energies (in eV) calculated by various methods. The experimental energies are collected in ref. 27 with geometries obtained in ref. 33.

Excitation	Exp.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
core → valence										
C_2H_4 C(1s) → π*	284.7	268.07	269.02	269.74	273.37	274.76	274.20	284.98	280.51	281.23
C_2H_2 C(1s) → π*	285.8	268.92	269.99	270.69	274.34	275.74	275.18	286.02	281.52	282.22
H_2CO C(1s) → π*	286.0	269.25	269.79	270.48	274.08	275.51	274.93	285.48	281.18	281.85
CO C(1s) → π*	287.4	270.40	270.79	271.37	274.93	276.35	275.78	286.38	282.18	282.78
CO_2 C(1s) → π*	290.8	273.74	274.49	275.08	278.62	280.01	279.44	289.97	285.73	286.33
N_2 N(1s) → π*	401.0	381.56	382.07	382.83	387.32	389.03	388.34	403.64	398.66	399.42
H_2CO O(1s) → π*	530.8	508.53	509.21	510.13	515.48	517.45	516.66	537.09	531.52	532.43
CO O(1s) → π*	534.2	511.37	512.23	513.14	518.59	520.59	519.79	540.48	534.72	535.64
HF F(1s) → σ*	687.4	659.07	660.67	661.81	668.40	670.68	669.71	696.00	689.59	690.68
SiH_4 Si(1s) → σ*	1842.5	1779.27	1781.21	1782.55	1794.84	1799.52	1797.60	1852.21	1843.94	1845.54

PH_3 P(1s) → σ*	2145.8	2075.69	2077.03	2078.32	2091.78	2096.99	2094.85	2154.80	2146.59	2148.12
H_2S S(1s) → σ*	2473.1	2395.39	2396.48	2397.78	2412.37	2418.02	2415.71	2481.33	2473.07	2474.61
SO_2 S(1s) → π*	2473.8	2396.11	2396.92	2398.22	2412.79	2418.47	2416.14	2481.35	2473.12	2474.67
HCl Cl(1s) → σ*	2823.9	2739.15	2740.77	2742.07	2757.51	2763.51	2761.06	2831.99	2823.59	2825.08
Cl_2 Cl(1s) → σ_u*	2821.3	2737.15	2738.27	2739.59	2754.88	2760.83	2758.40	2828.90	2820.64	2822.15
core → Rydberg										
C_2H_4 C(1s) → 3s	287.1	268.59	271.54	272.41	275.96	276.93	276.54	288.25	283.25	284.08
C_2H_2 C(1s) → 3s	287.7	268.88	271.81	272.66	276.25	277.21	276.82	288.57	283.54	284.36
C_2H_2 C(1s) → $3p_\pi$	288.7	269.60	272.84	273.66	277.24	278.08	277.76	289.96	284.64	285.45
C_2H_2 C(1s) → $3p_\sigma$	288.8	269.21	272.32	273.12	276.75	277.76	277.38	289.16	284.08	284.88
H_2CO C(1s) → $3sa_1$	290.2	271.21	273.98	274.86	278.42	279.44	279.01	290.59	285.62	286.45
H_2CO C(1s) → $3pb_2$	291.3	271.87	274.91	275.77	279.46	280.46	280.07	291.96	286.72	287.58
H_2CO C(1s) → $3pb_1$	291.7	271.77	274.97	275.84	279.39	280.29	279.92	291.64	286.66	287.49
CO C(1s) → 3s	292.4	272.05	274.96	275.79	279.49	280.44	280.04	292.14	286.81	287.65
CO C(1s) → $3p_\pi$	293.3	272.58	275.78	276.58	280.24	281.08	280.75	293.14	287.65	288.48
CO C(1s) → $3p_\sigma$	293.5	272.53	275.74	276.55	280.24	281.12	280.79	293.14	287.66	288.49
CO_2 C(1s) → 3s	292.7	272.78	274.99	275.72	279.60	281.03	280.43	291.85	286.79	287.58
CO_2 C(1s) → 3p	295.0	274.12	277.74	278.55	282.22	283.08	282.73	295.19	289.56	290.39
N_2 N(1s) → 3s	406.2	383.23	385.80	386.75	391.46	392.81	392.24	409.28	403.09	404.02
N_2 N(1s) → $3p_\pi$	407.1	383.82	386.66	387.59	392.28	393.54	393.03	410.37	404.00	404.93
N_2 N(1s) → $3p_\sigma$	407.3	383.77	386.88	387.80	392.50	393.71	393.23	410.70	404.26	405.18
H_2CO O(1s) → $3sa_1$	535.4	510.30	513.14	514.20	519.85	521.54	520.86	543.15	536.40	537.43
H_2CO O(1s) → $3pa_1$	536.3	510.95	514.00	515.06	520.70	522.26	521.65	544.32	537.36	538.38
CO O(1s) → 3s	538.9	513.06	515.39	516.39	522.13	523.86	523.14	545.37	538.63	539.60
CO O(1s) → $3p_\pi$	539.9	513.58	516.37	517.35	523.07	524.66	524.02	546.71	539.72	540.68
H_2S S(1s) → 4p	2476.3	2396.11	2399.32	2400.71	2415.18	2420.27	2418.20	2485.48	2476.55	2478.13
SO_2 S(1s) → 4p	2478.4	2400.56	2402.69	2404.00	2418.65	2424.29	2421.98	2487.91	2479.43	2480.98
HCl Cl(1s) → $4p_\pi$	2827.8	2740.76	2743.73	2745.09	2760.58	2766.13	2763.87	2836.44	2827.28	2828.81
Cl_2 Cl(1s) → 4p	2828.5	2741.19	2743.97	2745.32	2760.78	2766.55	2764.20	2836.39	2827.47	2829.01
core → valence	MSE	-42.32	-41.30	-40.31	-31.95	-28.74	-30.05	4.81	-1.46	-0.38
	MAE	42.32	41.30	40.31	31.95	28.74	30.05	5.12	2.22	2.53
	rms	50.91	49.93	48.96	39.29	35.56	37.08	6.25	2.91	2.84
core → Rydberg	MSE	-32.26	-29.35	-28.38	-22.26	-20.35	-21.12	3.36	-2.93	-1.93
	MAE	32.26	29.35	28.38	22.26	20.35	21.12	3.50	3.22	2.94
	rms	39.91	37.64	36.78	29.43	26.90	27.93	4.94	3.81	3.26

Table B.5: The 23 core ionization energies (in eV) calculated by various methods. Bold type denotes the atom where the 1s electron is ionized. The relativistic corrections[29] are subtracted from the experimental energies.[57]

Molecule	Exp.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3

$\mathbf{C}_2H_2$	290.70	269.16	275.23	275.90	279.36	280.14	279.93	292.73	287.04	287.76
$\mathbf{C}H_4$	290.79	268.37	274.41	275.13	278.54	279.29	279.09	291.82	286.15	286.91
$\mathbf{C}H_3OH$	292.30	269.96	276.09	276.81	280.22	280.96	280.76	293.53	287.83	288.59
$CH_3\mathbf{C}N$	292.33	270.03	276.22	276.85	280.32	281.09	280.88	293.79	288.04	288.74
$\mathbf{C}H_3CN$	292.86	270.39	276.50	277.19	280.61	281,37	281.16	293.93	288.24	288.99
$H\mathbf{C}N$	293.28	270.38	276.51	277.15	280.63	281.42	281.19	294.09	288.32	289.04
$H_2\mathbf{C}O$	294.35	271.57	277.78	278.47	281.91	282.67	282.46	295.34	289.55	290.31
$\mathbf{C}O$	296.09	272.02	278.23	278.88	282.39	283.17	282.95	295.99	290.13	290.87
$\mathbf{C}O_2$	297.57	273.66	280.33	280.95	284.44	285.21	284.99	298.14	292.14	292.87
$\mathbf{N}H_3$	405.32	379.92	385.83	386.69	391.09	392.19	391.86	409.67	403.09	403.97
$CH_3C\mathbf{N}$	405.40	380.34	386.40	387.17	391.64	392.76	392.42	410.37	403.74	404.57
$HC\mathbf{N}$	406.54	381.10	387.12	387.89	392.37	393.50	393.15	411.13	404.47	405.31
$\mathbf{N}NO$	408.47	382.89	389.27	390.02	394.50	395.63	395.28	413.43	406.61	407.45
$\mathbf{N}_2$	409.74	383.12	389.27	390.02	394.52	395.67	395.31	413.38	406.63	407.46
$N\mathbf{N}O$	412.35	386.30	393.02	393.76	398.20	399.26	398.94	417.13	410.30	411.12
$CH_3\mathbf{O}H$	538.66	510.22	516.05	516.94	522.38	523.87	523.37	546.62	539.34	540.28
$H_2C\mathbf{O}$	539.03	510.77	516.56	517.41	522.89	524.39	523.89	547.21	539.90	540.80
$H_2\mathbf{O}$	539.45	510.28	516.15	517.07	522.50	523.97	523.48	546.76	539.43	540.40
$C\mathbf{O}_2$	540.83	512.36	518.34	519.16	524.64	526.13	525.64	549.05	541.66	542.55
$NN\mathbf{O}$	540.97	512.97	518.72	519.56	525.06	526.61	526.08	549.40	542.04	542.95
$C\mathbf{O}$	542.10	513.06	518.98	519.76	525.26	526.76	526.26	549.66	542.33	543.17
$H\mathbf{F}$	693.48	659.88	665.77	666.71	673.16	675.00	674.35	703.26	695.36	696.38
$\mathbf{F}_2$	695.94	662.88	668.98	669.87	676.34	678.19	677.54	706.57	698.58	699.58
MSE		-25.95	-19.86	-19.10	-14.59	-13.45	-13.81	4.54	-2.07	-1.24
MAE		25.95	19.86	19.10	14.59	13.45	13.81	4.55	2.78	2.60
rms		26.16	20.15	19.38	14.78	13.60	13.97	5.62	3.30	2.93

Table B.6: The 38 core excitation energies (in eV) calculated by various methods. The relativistic corrections[27,29] are subtracted from the experimental energies.[27]

Excitation	Exp.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
core → valence										
C_2H_4 C(1s) → π^*	284.58	268.07	269.02	269.74	273.37	274.76	274.20	284.98	280.51	281.23
C_2H_2 C(1s) → π^*	285.68	268.92	269.99	270.69	274.34	275.74	275.18	286.02	281.52	282.22
H_2CO C(1s) → π^*	285.88	269.25	269.79	270.48	274.08	275.51	274.93	285.48	281.18	281.85
CO C(1s) → π^*	287.28	270.40	270.79	271.37	274.93	276.35	275.78	286.38	282.18	282.78
CO_2 C(1s) → π^*	290.68	273.74	274.49	275.08	278.62	280.01	279.44	289.97	285.73	286.33
N_2 N(1s) → π^*	400.76	381.56	382.07	382.83	387.32	389.03	388.34	403.64	398.66	399.42
H_2CO O(1s) → π^*	530.35	508.53	509.21	510.13	515.48	517.45	516.66	537.09	531.52	532.43
CO O(1s) → π^*	533.75	511.37	512.23	513.14	518.59	520.59	519.79	540.48	534.72	535.64
HF F(1s) → σ^*	686.65	659.07	660.67	661.81	668.40	670.68	669.71	696.00	689.59	690.68
SiH_4 Si(1s) → σ^*	1839.1	1779.27	1781.21	1782.55	1794.84	1799.52	1797.60	1852.21	1843.94	1845.54

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PH_3 P(1s) → σ*	2141.2	2075.69	2077.03	2078.32	2091.78	2096.99	2094.85	2154.80	2146.59	2148.12
H_2S S(1s) → σ*	2467.2	2395.39	2396.48	2397.78	2412.37	2418.02	2415.71	2481.33	2473.07	2474.61
SO_2 S(1s) → π*	2467.9	2396.11	2396.92	2398.22	2412.79	2418.47	2416.14	2481.35	2473.12	2474.67
HCl Cl(1s) → σ*	2816.0	2739.15	2740.77	2742.07	2757.51	2763.51	2761.06	2831.99	2823.59	2825.08
Cl_2 Cl(1s) → σ_u*	2813.4	2737.15	2738.27	2739.59	2754.88	2760.83	2758.40	2828.90	2820.64	2822.15
core → Rydberg										
C_2H_4 C(1s) → 3s	286.98	268.59	271.54	272.41	275.96	276.93	276.54	288.25	283.25	284.08
C_2H_2 C(1s) → 3s	287.58	268.88	271.81	272.66	276.25	277.21	276.82	288.57	283.54	284.36
C_2H_2 C(1s) → $3p_\pi$	288.58	269.60	272.84	273.66	277.24	278.08	277.76	289.96	284.64	285.45
C_2H_2 C(1s) → $3p_\sigma$	288.68	269.21	272.32	273.12	276.75	277.76	277.38	289.16	284.08	284.88
H_2CO C(1s) → $3sa_1$	290.08	271.21	273.98	274.86	278.42	279.44	279.01	290.59	285.62	286.45
H_2CO C(1s) → $3pb_2$	291.18	271.87	274.91	275.77	279.46	280.46	280.07	291.96	286.72	287.58
H_2CO C(1s) → $3pb_1$	291.58	271.77	274.97	275.84	279.39	280.29	279.92	291.64	286.66	287.49
CO C(1s) → 3s	292.28	272.05	274.96	275.79	279.49	280.44	280.04	292.14	286.81	287.65
CO C(1s) → $3p_\pi$	293.18	272.58	275.78	276.58	280.24	281.08	280.75	293.14	287.65	288.48
CO C(1s) → $3p_\sigma$	293.38	272.53	275.74	276.55	280.24	281.12	280.79	293.14	287.66	288.49
CO_2 C(1s) → 3s	292.58	272.78	274.99	275.72	279.60	281.03	280.43	291.85	286.79	287.58
CO_2 C(1s) → 3p	294.88	274.12	277.74	278.55	282.22	283.08	282.73	295.19	289.56	290.39
N_2 N(1s) → 3s	405.96	383.23	385.80	386.75	391.46	392.81	392.24	409.28	403.09	404.02
N_2 N(1s) → $3p_\pi$	406.86	383.82	386.66	387.59	392.28	393.54	393.03	410.37	404.00	404.93
N_2 N(1s) → $3p_\sigma$	407.06	383.77	386.88	387.80	392.50	393.71	393.23	410.70	404.26	405.18
H_2CO O(1s) → $3sa_1$	534.95	510.30	513.14	514.20	519.85	521.54	520.86	543.15	536.40	537.43
H_2CO O(1s) → $3pa_1$	535.85	510.95	514.00	515.06	520.70	522.26	521.65	544.32	537.36	538.38
CO O(1s) → 3s	538.45	513.06	515.39	516.39	522.13	523.86	523.14	545.37	538.63	539.60
CO O(1s) → $3p_\pi$	539.45	513.58	516.37	517.35	523.07	524.66	524.02	546.71	539.72	540.68
H_2S S(1s) → 4p	2470.4	2396.11	2399.32	2400.71	2415.18	2420.27	2418.20	2485.48	2476.55	2478.13
SO_2 S(1s) → 4p	2472.5	2400.56	2402.69	2404.00	2418.65	2424.29	2421.98	2487.91	2479.43	2480.98
HCl Cl(1s) → $4p_\pi$	2819.9	2740.76	2743.73	2745.09	2760.58	2766.13	2763.87	2836.44	2827.28	2828.81
Cl_2 Cl(1s) → 4p	2820.6	2741.19	2743.97	2745.32	2760.78	2766.55	2764.20	2836.39	2827.47	2829.01
core → valence	MSE	-39.78	-38.76	-37.77	-29.41	-26.20	-27.51	7.35	1.08	2.16
	MAE	39.78	38.76	37.77	29.41	26.20	27.51	7.61	4.42	4.96
	rms	47.20	46.21	45.23	35.54	31.80	33.33	9.73	4.80	5.50
core → Rydberg	MSE	-30.89	-27.98	-27.01	-20.89	-18.97	-19.75	4.73	-1.56	-0.56
	MAE	30.89	27.98	27.01	20.89	18.97	19.75	4.83	4.23	4.12
	rms	37.32	34.99	34.11	26.74	24.21	25.24	7.43	4.67	4.69

Table B.7: The nonhydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set. The geometries and reference energies are obtained in ref. 44.

Reaction	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
Heavy-atom transfer reactions										

$H + N_2O \rightarrow OH + N_2$										
V^f	18.14	9.97	17.86	20.68	19.23	17.47	18.16	15.31	17.59	20.18
V^r	83.22	52.46	77.26	81.91	80.58	77.75	78.82	85.59	79.02	81.91
$H + FH \rightarrow HF + H$										
V^f	42.18	27.07	40.39	44.78	43.10	40.56	41.46	37.83	40.09	43.74
V^r	42.18	27.07	40.39	44.78	43.10	40.56	41.46	37.83	40.09	43.74
$H + ClH \rightarrow HCl + H$										
V^f	18.00	9.64	18.30	23.17	20.71	18.19	19.33	17.30	17.99	22.25
V^r	18.00	9.64	18.30	23.17	20.71	18.19	19.33	17.30	17.99	22.25
$H + FCH_3 \rightarrow HF + CH_3$										
V^f	30.38	18.51	32.56	33.44	32.11	30.02	30.98	30.25	32.09	33.45
V^r	57.02	41.00	56.65	55.78	55.35	54.47	54.75	57.90	56.16	55.38
$H + F_2 \rightarrow HF + F$										
V^f	2.27	-9.86	0.32	1.99	0.89	-0.60	0.10	-1.56	0.30	2.26
V^r	106.18	80.86	102.53	103.62	104.26	103.96	104.08	108.23	103.81	104.40
$CH_3 + FCl \rightarrow CH_3F + Cl$										
V^f	7.43	-6.48	9.39	4.61	3.88	2.76	3.61	9.22	8.61	5.54
V^r	60.17	41.63	63.40	59.96	58.48	56.55	57.85	65.59	62.69	60.96
Nucleophilic substitution reactions										
$F^- + CH_3F \rightarrow FCH_3 + F^-$										
V^f	-0.34	-8.31	0.96	-2.61	-2.27	-1.37	-1.55	3.03	1.16	-1.34
V^r	-0.34	-8.31	0.96	-2.61	-2.27	-1.37	-1.55	3.03	1.16	-1.34
$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$										
V^f	13.38	7.06	14.37	13.29	13.25	12.85	13.06	16.66	14.86	13.54
V^r	13.38	7.06	14.37	13.29	13.25	12.85	13.06	16.66	14.86	13.54
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$										
V^f	3.10	-3.80	8.42	6.22	4.72	3.70	4.38	8.56	7.82	6.48
V^r	3.10	-3.80	8.42	6.22	4.72	3.70	4.38	8.56	7.82	6.48
$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$										
V^f	13.61	7.15	17.80	17.69	16.04	14.30	15.20	18.38	17.81	17.24
V^r	13.61	7.15	17.80	17.69	16.04	14.30	15.20	18.38	17.81	17.24
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$										
V^f	-12.54	-19.52	-9.42	-11.70	-13.14	-13.58	-13.14	-9.57	-9.94	-11.43
V^r	20.11	12.31	23.54	20.15	20.79	21.26	21.33	26.89	23.87	21.89
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$										
V^f	2.89	-0.67	5.42	5.41	4.20	3.07	3.60	5.59	5.36	4.96
V^r	29.62	21.45	32.11	30.89	31.08	30.50	30.91	35.79	32.90	31.72
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$										
V^f	-2.78	-10.59	-1.19	-4.00	-3.67	-3.31	-3.19	1.35	-1.01	-2.84
V^r	17.33	9.14	21.34	17.87	17.58	17.90	17.89	22.68	21.01	18.47
$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$										
V^f	10.96	3.88	11.88	11.62	11.54	10.57	11.06	14.69	12.39	11.75
V^r	47.20	43.21	52.43	49.19	49.36	49.20	49.43	54.19	52.50	50.19
Unimolecular and association reactions										

$H + N_2 \rightarrow HN_2$										
V^f	14.69	5.19	12.14	15.46	13.99	12.32	12.96	11.36	12.33	15.20
V^r	10.72	9.08	13.10	15.08	14.32	13.40	13.74	13.10	12.72	14.42
$H + CO \rightarrow HCO$										
V^f	3.17	-1.69	2.32	5.64	4.55	3.37	3.71	1.27	2.29	5.33
V^r	22.68	24.66	26.04	27.07	26.74	26.20	26.24	24.79	25.37	26.13
$H + C_2H_4 \rightarrow CH_3CH_2$										
V^f	1.72	-0.14	2.05	4.95	4.09	3.03	3.42	0.44	1.80	4.54
V^r	41.75	40.19	47.53	48.46	47.01	45.37	46.01	46.97	47.22	47.82
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$										
V^f	6.85	1.50	6.98	4.80	5.03	4.57	4.93	8.35	6.06	4.90
V^r	32.97	29.76	39.34	36.71	35.37	33.85	34.64	37.18	39.06	37.03
$HCN \rightarrow HNC$										
V^f	48.16	45.60	46.67	45.86	46.28	46.42	46.19	46.35	46.24	45.26
V^r	33.11	30.50	33.20	32.79	33.13	33.27	33.07	33.59	32.57	32.36
MSE		-8.52	1.39	1.32	0.55	-0.45	0.04	1.99	1.29	1.38
MAE		8.62	2.47	2.32	1.75	1.51	1.53	3.32	2.38	2.13
rms		10.61	3.07	2.82	2.08	2.00	1.89	3.77	2.86	2.55

Table B.8: The hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set. The geometries and reference energies are obtained in ref. 44.

Reaction	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
$H + HCl \rightarrow H_2 + Cl$										
V^f	5.70	0.56	5.85	6.55	5.24	4.08	4.71	2.61	5.54	6.44
V^r	8.70	-1.95	5.78	6.58	5.30	4.58	4.98	8.27	5.98	6.34
$OH + H_2 \rightarrow H + H_2O$										
V^f	5.10	-6.36	2.74	3.24	2.54	2.22	2.48	4.45	3.27	3.11
V^r	21.20	13.69	21.14	20.38	19.50	18.77	19.13	17.23	20.34	20.44
$CH_3 + H_2 \rightarrow H + CH_4$										
V^f	12.10	3.82	9.98	10.25	9.58	9.06	9.36	11.35	9.69	9.80
V^r	15.30	9.32	14.87	16.29	15.05	13.54	14.22	11.74	14.56	16.10
$OH + CH_4 \rightarrow CH_3 + H_2O$										
V^f	6.70	-5.65	4.88	4.46	3.89	3.04	3.43	6.24	5.09	4.27
V^r	19.60	8.91	18.39	15.56	15.37	15.11	15.22	18.62	17.30	15.30
$H + H_2 \rightarrow H_2 + H$										
V^f	9.60	3.64	7.89	12.37	10.73	9.21	9.77	5.84	7.84	11.67
V^r	9.60	3.64	7.89	12.37	10.73	9.21	9.77	5.84	7.84	11.67
$OH + NH_3 \rightarrow H_2O + NH_2$										
V^f	3.20	-11.94	2.93	2.80	1.60	-0.02	0.85	4.90	3.32	2.71
V^r	12.70	-0.71	13.00	12.06	10.96	9.69	10.38	14.55	12.67	11.89
$HCl + CH_3 \rightarrow Cl + CH_4$										

V^f	1.70	-5.94	1.28	-0.58	-1.19	-1.86	-1.45	1.80	0.60	-0.77
V^r	7.90	-2.95	6.10	5.49	4.34	3.11	3.69	7.85	5.91	5.43
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$										
V^f	3.40	-9.03	2.42	1.76	1.16	0.17	0.56	3.47	2.40	1.49
V^r	19.90	10.76	20.06	17.27	17.18	16.57	16.82	19.97	18.64	16.90
$F + H_2 \rightarrow HF + H$										
V^f	1.80	-12.97	-2.87	-3.79	-3.89	-3.70	-3.55	-1.06	-1.71	-2.85
V^r	33.40	25.12	32.70	29.79	29.17	29.01	29.20	27.67	30.93	29.99
$O + CH_4 \rightarrow OH + CH_3$										
V^f	13.70	-0.79	9.83	10.40	9.84	9.20	9.55	12.28	10.44	10.48
V^r	8.10	-0.57	7.98	4.78	4.83	4.67	4.71	7.74	7.36	4.60
$H + PH_3 \rightarrow PH_2 + H_2$										
V^f	3.10	-1.79	2.90	5.86	4.63	3.28	3.79	0.73	2.63	5.36
V^r	23.20	17.91	23.04	25.29	24.15	23.46	23.78	25.51	23.02	24.72
$H + HO \rightarrow H_2 + O$										
V^f	10.70	3.75	10.52	10.68	9.82	8.84	9.17	6.66	10.16	10.48
V^r	13.10	-1.98	7.48	10.25	9.35	8.89	9.15	10.81	8.37	10.06
$H + H_2S \rightarrow H_2 + HS$										
V^f	3.50	-1.22	3.77	6.89	5.52	4.05	4.62	1.63	3.53	6.38
V^r	17.30	9.10	15.69	18.48	17.19	16.31	16.64	18.96	15.81	17.85
$O + HCl \rightarrow OH + Cl$										
V^f	9.80	-10.54	7.88	8.39	6.94	5.47	6.42	10.89	8.52	8.38
V^r	10.40	-7.33	10.84	8.84	7.46	5.92	6.71	12.39	10.74	8.71
$NH_2 + CH_3 \rightarrow CH_4 + NH$										
V^f	8.00	0.71	9.29	6.92	6.49	5.65	6.13	9.44	8.73	6.60
V^r	22.40	10.56	20.18	20.01	19.34	18.41	18.99	22.02	19.97	19.89
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$										
V^f	7.50	2.89	10.88	8.76	8.41	7.26	7.83	10.81	9.98	8.26
V^r	18.30	7.51	17.63	17.44	16.72	15.69	16.23	19.27	17.19	17.18
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$										
V^f	10.40	1.44	11.31	10.92	10.03	8.60	9.26	12.33	10.74	10.33
V^r	17.40	9.99	18.90	17.17	16.70	15.29	16.00	19.17	17.63	16.56
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$										
V^f	14.50	4.39	13.70	13.43	12.56	11.28	11.95	14.98	13.37	12.96
V^r	17.80	7.71	17.15	15.26	14.69	13.65	14.21	17.71	16.23	14.80
s-trans cis-$C_5H_8 \rightarrow$ s-trans cis-C_5H_8										
V^f	38.40	31.19	40.09	42.88	41.46	39.07	39.92	44.37	39.90	41.80
V^r	38.40	31.19	40.09	42.88	41.46	39.07	39.92	44.37	39.90	41.80
MSE		-9.67	-0.77	-0.66	-1.55	2.57	-2.08	-0.27	-1.03	-0.96
MAE		9.67	1.39	2.11	2.27	2.70	2.40	1.99	1.41	2.04
rms		10.37	1.90	2.47	2.60	3.10	2.75	2.59	1.77	2.33

Table B.9: The interaction energies (in kcal/mol) of the S22 set. The reference energies are obtained in ref. 47 with geometries in ref. 45.

Complex	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
Hydrogen bonded complexes										
NH_3 dimer (C2H)	-3.133	-2.83	-2.35	-3.66	-3.59	-3.08	-3.09	-2.82	-2.85	-3.27
H_2O dimer (Cs)	-4.989	-4.91	-4.37	-5.65	-5.59	-4.97	-5.04	-4.95	-4.69	-5.21
Formic acid dimer (C2h)	-18.753	-18.08	-17.79	-20.11	-19.95	-19.28	-19.51	-19.20	-18.88	-19.83
Formamide dimer (C2h)	-16.062	-14.69	-14.00	-16.77	-16.65	-16.17	-16.26	-15.73	-15.40	-16.40
Uracil dimer (C2h)	-20.641	-18.45	-17.54	-20.31	-20.29	-20.43	-20.51	-20.19	-19.61	-20.56
2-pyridone$\cdots$2-aminopyridine (C1)	-16.934	-15.27	-13.80	-16.39	-16.37	-17.06	-16.98	-16.28	-16.36	-16.93
Adenine$\cdots$thymine WC (C1)	-16.66	-14.29	-13.04	-16.04	-15.90	-16.46	-16.43	-15.94	-15.91	-16.47
Dispersion complexes										
CH_4 dimer (D3d)	-0.527	-0.08	0.13	-0.43	-0.57	-0.57	-0.61	-0.74	-0.69	-0.56
C_2H_4 dimer (D2d)	-1.472	-0.31	-0.15	-1.90	-1.77	-1.79	-1.54	-1.52	-1.53	-1.46
Benzene$\cdots CH_4$	-1.448	-0.01	0.01	-1.58	-1.43	-1.70	-1.64	-1.38	-1.57	-1.68
Benzene dimer (C2h)	-2.654	1.90	1.64	-2.27	-1.52	-3.16	-3.00	-1.99	-2.89	-3.18
Pyrazine dimer (Cs)	-4.255	0.73	0.36	-3.73	-2.91	-4.27	-4.15	-3.40	-4.13	-4.27
Uracil dimer (C2)	-9.805	-2.69	-3.24	-8.92	-7.85	-9.79	-9.83	-9.49	-9.83	-9.96
Indole$\cdots$Benzene (C1)	-4.524	2.24	1.73	-3.68	-2.46	-5.10	-4.61	-3.13	-4.49	-4.90
Adenine$\cdots$thymine (C1)	-11.73	-1.33	-2.57	-10.38	-8.49	-11.86	-11.26	-10.08	-11.32	-11.76
Mixed complexes										
Ethene$\cdots$Ethine (C2v)	-1.496	-1.16	-0.87	-1.62	-1.66	-1.63	-1.65	-1.59	-1.61	-1.63
Benzene$\cdots H_2O$ (Cs)	-3.275	-2.03	-2.13	-3.56	-3.39	-3.50	-3.58	-3.52	-3.73	-3.71
Benzene$\cdots NH_3$ (Cs)	-2.312	-0.91	-0.95	-2.44	-2.30	-2.53	-2.56	-2.42	-2.60	-2.63
Benzene$\cdots$HCN (Cs)	-4.541	-2.81	-3.30	-4.90	-4.61	-4.79	-4.65	-4.41	-4.80	-4.88
Benzene dimer (C2v)	-2.717	-0.10	-0.21	-2.37	-2.11	-2.89	-2.82	-2.37	-2.75	-2.94
Indole$\cdots$Benzene (Cs)	-5.627	-2.02	-2.27	-4.87	-4.46	-5.64	-5.52	-5.14	-5.77	-5.75
Phenol dimer (C1)	-7.097	-3.86	-3.84	-6.93	-6.48	-6.99	-7.00	-6.83	-6.73	-7.14
MSE		2.71	2.82	0.10	0.47	-0.14	-0.07	0.34	0.11	-0.20
MAE		2.71	2.82	0.53	0.79	0.19	0.18	0.45	0.30	0.23
rms		3.73	3.58	0.63	1.11	0.25	0.25	0.61	0.39	0.33

Table B.10: The interaction energies (in kcal/mol) of the S66 set. The geometries and reference energies are obtained in ref. 60.

Complex	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
Hydrogen bonded complexes										
Water$\cdots$Water	-4.918	-4.87	-4.37	-5.62	-5.56	-4.93	-5.01	-4.96	-4.69	-5.17

Water· · ·MeOH	-5.592	-5.16	-4.70	-6.18	-6.10	-5.56	-5.64	-5.68	-5.33	-5.81
Water· · ·MeNH$_2$	-6.908	-7.15	-6.34	-7.58	-7.57	-7.33	-7.34	-7.08	-7.03	-7.43
Water· · ·Peptide	-8.103	-7.28	-6.98	-9.03	-8.82	-8.13	-8.27	-8.23	-7.90	-8.50
MeOH· · ·MeOH	-5.757	-5.08	-4.54	-6.04	-6.00	-5.69	-5.75	-5.78	-5.45	-5.88
MeOH· · ·MeNH$_2$	-7.554	-7.19	-6.29	-7.93	-7.93	-7.99	-7.92	-7.68	-7.68	-7.95
MeOH· · ·Peptide	-8.230	-7.18	-6.64	-8.81	-8.64	-8.39	-8.47	-8.33	-8.07	-8.64
MeOH· · ·Water	-5.009	-4.78	-4.22	-5.50	-5.46	-4.94	-5.03	-4.97	-4.70	-5.16
MeNH$_2$ · · ·MeOH	-3.059	-2.22	-1.68	-3.16	-3.16	-3.05	-3.11	-3.19	-3.00	-3.13
MeNH$_2$ · · ·MeNH$_2$	-4.160	-3.08	-2.51	-4.61	-4.43	-4.36	-4.16	-3.88	-3.92	-4.28
MeNH$_2$ · · ·Peptide	-5.419	-3.39	-3.08	-5.86	-5.54	-5.54	-5.51	-5.21	-5.19	-5.68
MeNH$_2$ · · ·Water	-7.266	-7.14	-6.45	-7.96	-7.89	-7.52	-7.52	-7.32	-7.25	-7.66
Peptide· · ·MeOH	-6.187	-4.53	-4.24	-6.36	-6.22	-6.14	-6.22	-6.25	-6.00	-6.35
Peptide· · ·MeNH$_2$	-7.454	-6.12	-5.42	-7.53	-7.46	-7.91	-7.73	-7.41	-7.49	-7.77
Peptide· · ·Peptide	-8.630	-6.36	-6.04	-8.72	-8.50	-8.94	-8.95	-8.83	-8.69	-9.03
Peptide· · ·Water	-5.124	-4.32	-3.96	-5.41	-5.36	-4.88	-5.07	-5.09	-4.85	-5.20
Uracil· · ·Uracil (BP)	-17.182	-15.49	-14.38	-17.19	-17.16	-17.26	-17.36	-16.98	-16.49	-17.39
Water· · ·Pyridine	-6.857	-6.82	-6.01	-7.34	-7.31	-7.06	-7.16	-7.02	-6.83	-7.21
MeOH· · ·Pyridine	-7.410	-6.92	-6.01	-7.50	-7.50	-7.57	-7.65	-7.46	-7.32	-7.65
AcOH· · ·AcOH	-19.093	-18.59	-18.12	-20.50	-20.34	-19.84	-20.06	-19.76	-19.39	-20.37
AcNH$_2$ · · ·AcNH$_2$	-16.265	-15.02	-14.14	-16.94	-16.83	-16.50	-16.58	-16.04	-15.69	-16.72
AcOH· · ·Uracil	-19.491	-18.31	-17.58	-20.20	-20.10	-19.87	-20.03	-19.70	-19.22	-20.22
AcNH$_2$ · · ·Uracil	-19.189	-17.67	-16.83	-19.56	-19.51	-19.44	-19.52	-19.12	-18.65	-19.60
MSE		0.88	1.49	-0.46	-0.37	-0.17	-0.23	-0.05	0.18	-0.34
MAE		0.90	1.49	0.46	0.38	0.21	0.23	0.15	0.23	0.34
rms		1.10	1.63	0.56	0.48	0.28	0.31	0.20	0.29	0.43
Dispersion complexes										
Benzene· · ·Benzene (pi-pi)	-2.822	1.22	1.11	-2.38	-1.84	-3.26	-3.25	-2.47	-3.10	-3.35
Pyridine· · ·Pyridine (pi-pi)	-3.895	0.48	0.22	-3.43	-2.81	-4.32	-4.24	-3.51	-4.17	-4.34
Uracil· · ·Uracil (pi-pi)	-9.829	-2.51	-3.13	-8.91	-7.79	-9.74	-9.77	-9.36	-9.78	-9.92
Benzene· · ·Pyridine (pi-pi)	-3.439	0.81	0.61	-2.99	-2.40	-3.86	-3.81	-3.05	-3.71	-3.91
Benzene· · ·Uracil (pi-pi)	-5.713	0.36	-0.25	-5.08	-4.06	-5.79	-5.80	-5.11	-5.87	-6.07
Pyridine· · ·Uracil (pi-pi)	-6.819	-0.74	-1.33	-6.22	-5.23	-6.80	-6.82	-6.29	-6.86	-7.06
Benzene· · ·Ethene	-1.432	0.76	0.89	-1.58	-1.26	-1.71	-1.80	-1.15	-1.59	-1.91
Uracil· · ·Ethene	-3.380	-0.34	-0.44	-3.48	-3.00	-3.54	-3.59	-3.19	-3.48	-3.74
Uracil· · ·Ethyne	-3.738	-1.03	-1.16	-4.02	-3.59	-3.72	-3.82	-3.41	-3.63	-3.94
Pyridine· · ·Ethene	-1.872	0.45	0.59	-2.02	-1.67	-2.10	-2.16	-1.56	-1.95	-2.25
Pentane· · ·Pentane	-3.776	0.42	0.68	-4.17	-3.48	-5.32	-4.34	-4.05	-4.34	-4.54
Pentane· · ·Neopentane	-2.613	0.18	0.59	-2.47	-2.13	-3.38	-2.88	-2.61	-2.81	-3.08
Neopentane· · ·Neopentane	-1.777	0.14	0.52	-2.70	-2.35	-3.58	-3.08	-2.75	-2.98	-3.31
Neopentane· · ·Cyclopentane	-2.404	0.11	0.62	-3.02	-2.56	-4.10	-3.31	-3.05	-3.21	-3.52
Cyclopentane· · ·Cyclopentane	-2.997	0.05	0.54	-1.69	-1.59	-2.38	-2.22	-1.98	-2.11	-2.38
Benzene· · ·Cyclopentane	-3.575	0.30	0.24	-3.41	-2.82	-4.38	-4.00	-3.49	-3.96	-4.10
Benzene· · ·Neopentane	-2.895	0.09	0.12	-2.77	-2.41	-3.50	-3.42	-2.97	-3.35	-3.54
Uracil· · ·Pentane	-4.848	0.52	0.34	-4.65	-3.77	-5.63	-5.21	-4.91	-5.30	-5.37
Uracil· · ·Cyclopentane	-4.138	0.58	0.59	-3.72	-3.01	-4.68	-4.30	-4.07	-4.34	-4.45

Uracil···Neopentane	-3.712	0.08	0.08	-3.41	-2.91	-4.22	-4.03	-3.85	-4.04	-4.14
Ethene···Pentane	-2.005	0.01	0.29	-2.32	-2.04	-2.59	-2.22	-2.08	-2.19	-2.24
Ethyne···Pentane	-1.748	-0.09	0.17	-1.94	-1.81	-2.05	-2.03	-1.87	-1.99	-2.00
Peptide···Pentane	-4.264	0.07	0.14	-4.55	-3.79	-5.13	-4.55	-4.26	-4.52	-4.73
MSE		3.72	3.73	0.12	0.67	-0.53	-0.30	0.12	-0.24	-0.44
MAE		3.72	3.73	0.42	0.74	0.59	0.38	0.32	0.33	0.50
rms		4.00	3.92	0.51	0.92	0.77	0.47	0.42	0.44	0.58
Mixed complexes										
Benzene···Benzene (TS)	-2.876	-0.19	-0.30	-2.61	-2.31	-3.12	-3.02	-2.67	-3.00	-3.07
Pyridine···Pyridine (TS)	-3.535	-0.75	-0.87	-3.42	-3.05	-3.72	-3.60	-3.28	-3.52	-3.62
Benzene···Pyridine (TS)	-3.331	-0.61	-0.82	-3.13	-2.80	-3.62	-3.50	-3.15	-3.51	-3.57
Benzene···Ethyne (CH-pi)	-2.867	-1.23	-1.41	-3.03	-2.82	-3.02	-2.91	-2.70	-2.96	-3.00
Ethyne···Ethyne (TS)	-1.524	-1.20	-0.89	-1.71	-1.73	-1.56	-1.56	-1.48	-1.48	-1.57
Benzene···AcOH (OH-pi)	-4.707	-2.32	-2.62	-4.57	-4.22	-4.64	-4.75	-4.60	-5.05	-4.97
Benzene···AcNH$_2$ (NH-pi)	-4.361	-2.34	-2.29	-4.45	-4.18	-4.51	-4.56	-4.43	-4.60	-4.62
Benzene···Water (OH-pi)	-3.277	-1.98	-2.10	-3.61	-3.40	-3.50	-3.57	-3.48	-3.73	-3.72
Benzene···MeOH (OH-pi)	-4.188	-1.86	-1.95	-4.26	-3.89	-4.41	-4.35	-4.14	-4.54	-4.51
Benzene···MeNH$_2$ (NH-pi)	-3.231	-0.77	-0.83	-3.28	-2.93	-3.58	-3.49	-3.18	-3.54	-3.61
Benzene···Peptide (NH-pi)	-5.282	-1.68	-2.02	-5.05	-4.56	-5.79	-5.62	-5.23	-5.80	-5.81
Pyridine···Pyridine (CH-N)	-4.146	-2.49	-2.18	-4.21	-4.01	-3.89	-3.85	-3.54	-3.54	-4.05
Ethyne···Water (CH-O)	-2.850	-2.63	-2.30	-3.23	-3.24	-2.73	-2.86	-2.91	-2.73	-2.94
Ethyne···AcOH (OH-pi)	-4.868	-4.10	-3.78	-5.65	-5.41	-4.98	-5.10	-4.79	-4.91	-5.28
Pentane···AcOH	-2.912	0.07	0.30	-2.99	-2.59	-3.37	-3.21	-3.21	-3.29	-3.30
Pentane···AcNH$_2$	-3.534	-0.26	-0.01	-3.81	-3.28	-4.14	-3.87	-3.68	-3.85	-3.99
Benzene···AcOH	-3.801	-0.53	-0.84	-3.82	-3.32	-4.12	-4.05	-3.64	-4.07	-4.26
Peptide···Ethene	-2.999	-0.95	-0.74	-3.27	-3.00	-3.14	-3.14	-3.05	-3.06	-3.17
Pyridine···Ethyne	-3.991	-3.64	-3.04	-4.20	-4.24	-4.15	-4.20	-4.04	-3.94	-4.19
MeNH$_2$···Pyridine	-3.968	-1.73	-1.44	-4.11	-3.78	-4.08	-3.99	-3.65	-3.78	-4.09
MSE		2.05	2.11	-0.11	0.17	-0.19	-0.15	0.07	-0.13	-0.25
MAE		2.05	2.11	0.20	0.33	0.24	0.18	0.16	0.23	0.26
rms		2.28	2.27	0.26	0.38	0.28	0.21	0.21	0.29	0.30
MSE		2.22	2.46	-0.15	0.16	-0.30	-0.23	0.04	-0.06	-0.35
MAE		2.23	2.46	0.37	0.49	0.35	0.26	0.21	0.27	0.37
rms		2.75	2.80	0.47	0.65	0.51	0.35	0.30	0.35	0.46

Table B.11: The atomization energies (in eV) of the AE113 database. The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
CH$_3$	13.32	13.44	13.38	13.27	13.30	13.31	13.30	13.65	13.33	13.24
CH$_4$	18.19	18.21	18.11	18.11	18.14	18.16	18.15	18.58	18.06	18.10

NH	3.60	3.84	3.70	3.66	3.65	3.65	3.65	3.73	3.69	3.65
NH_2	7.91	8.18	5.95	7.94	7.94	7.95	7.94	8.11	7.93	7.93
NH_3	12.91	13.10	12.83	12.86	12.88	12.90	12.89	13.16	12.78	12.87
OH	4.65	4.78	4.65	4.60	4.63	4.65	4.64	4.73	4.60	4.60
H_2O	10.11	10.18	9.97	9.92	9.97	10.02	10.00	10.20	9.85	9.94
HF	6.16	6.18	6.06	6.04	6.04	6.07	6.06	6.16	5.93	6.01
SiH_3	9.88	9.62	9.77	9.86	9.89	9.88	9.88	10.24	9.71	9.84
SiH_4	14.07	13.58	13.78	14.07	14.07	14.04	14.05	14.53	13.72	14.04
PH_3	10.46	10.40	10.25	10.48	10.57	10.62	10.61	10.84	10.22	10.50
SH_2	7.93	7.90	7.72	7.86	7.92	7.96	7.96	8.05	7.69	7.88
HCl	4.65	4.64	4.52	4.58	4.60	4.63	4.63	4.67	4.50	4.59
HCCH	17.49	18.00	17.45	17.35	17.39	17.40	17.39	17.47	17.38	17.31
CH_2CH_2	24.38	24.80	24.35	24.28	24.33	24.35	24.34	24.63	24.28	24.26
CH_3CH_3	30.84	31.09	30.88	30.82	30.84	30.85	30.85	31.40	30.80	30.81
HCN	13.51	14.17	13.51	13.47	13.46	13.45	13.45	13.42	13.46	13.47
CO	11.22	11.70	11.26	11.19	11.17	11.17	11.17	11.13	11.15	11.22
HCO	12.01	12.78	12.20	12.05	12.06	12.09	12.07	12.06	12.07	12.05
CH_2O	16.20	16.78	16.26	16.17	16.19	16.22	16.21	16.31	16.12	16.17
CH_3OH	22.22	22.57	22.23	22.13	22.17	22.21	22.19	22.55	22.08	22.15
N_2	9.85	10.56	9.91	9.95	9.86	9.79	9.82	9.71	9.88	9.98
NH_2NH_2	18.82	19.49	18.90	18.91	18.90	18.90	18.90	19.15	18.81	18.95
NO	6.57	7.23	6.74	6.52	6.48	6.45	6.46	6.89	6.59	6.53
O_2	5.20	6.24	5.60	5.51	5.44	5.42	5.43	5.31	5.46	5.53
HOOH	11.62	12.19	11.51	11.42	11.46	11.52	11.50	11.56	11.32	11.46
F_2	1.67	2.25	1.60	1.61	1.54	1.52	1.53	1.36	1.42	1.56
CO_2	16.85	18.13	17.20	16.95	16.97	17.03	17.00	16.76	16.96	16.98
P_2	4.99	5.30	4.39	4.71	4.93	5.07	5.01	4.47	4.36	4.74
S_2	4.41	4.97	4.26	4.38	4.48	4.57	4.54	4.08	4.23	4.42
Cl_2	2.53	2.82	2.36	2.41	2.47	2.54	2.51	2.22	2.34	2.45
NaCl	4.32	4.13	4.18	4.46	4.46	4.35	4.36	4.25	4.14	4.39
SiO	8.25	8.48	8.02	8.12	8.14	8.13	8.13	8.03	7.89	8.13
CS	7.37	7.79	7.01	7.17	7.22	7.28	7.26	6.89	6.99	7.18
ClO	2.74	3.53	2.85	2.81	2.85	2.90	2.88	2.63	2.77	2.84
ClF	2.68	3.12	2.67	2.67	2.67	2.68	2.68	2.52	2.55	2.66
SiH_3SiH_3	23.19	22.49	22.82	23.30	23.27	23.19	23.23	23.76	22.72	23.25
CH_3Cl	17.08	17.35	17.05	17.07	17.09	17.10	17.10	17.23	16.98	17.06
CH_3SH	20.50	20.72	20.39	20.47	20.52	20.54	20.54	20.73	20.32	20.48
SO_2	10.97	12.09	11.03	10.92	10.99	11.07	11.04	10.68	10.81	11.00
BF_3	20.40	20.93	20.65	20.37	20.35	20.30	20.31	20.39	20.22	20.29
BCl_3	14.02	14.67	14.17	14.18	14.19	14.18	14.18	13.67	14.07	14.16
$AlCl_3$	13.57	13.35	13.35	13.52	13.49	13.42	13.46	13.06	13.23	13.51
CF_4	20.80	21.94	21.35	21.00	20.91	20.82	20.88	20.83	20.83	20.97
CCl_4	13.59	14.57	13.59	13.70	13.67	13.62	13.65	12.83	13.49	13.70
OCS	14.45	15.64	14.53	14.47	14.53	14.63	14.59	14.14	14.37	14.50
CS_2	12.00	13.09	11.70	11.83	11.96	12.12	12.05	11.35	11.62	11.85
CF_2O	18.21	19.53	18.71	18.42	18.38	18.36	18.38	18.21	18.33	18.41

SiF_4	24.92	24.58	24.54	24.59	24.44	24.24	24.33	24.35	23.94	24.45
N_2O	11.66	13.51	11.97	11.89	11.82	11.82	11.83	11.38	11.80	11.90
NF_3	8.94	10.67	9.47	9.40	9.22	9.11	9.17	8.90	9.10	9.35
PF_3	15.64	15.99	15.62	15.59	15.59	15.52	15.56	15.52	15.21	15.58
O_3	6.26	8.04	6.10	6.00	5.95	6.01	5.98	5.40	5.82	5.99
F_2O	4.04	5.35	4.15	4.11	4.02	3.98	4.00	3.71	3.87	4.07
ClF_3	5.43	7.12	5.70	5.60	5.54	5.54	5.54	5.09	5.32	5.54
CF_2CF_2	25.54	27.50	26.37	25.91	25.84	25.78	25.81	25.56	25.80	25.83
CF_3CN	27.77	29.67	28.40	28.06	27.94	27.83	27.89	27.61	27.96	28.02
CH_3CCH	30.43	31.26	30.57	30.39	30.43	30.42	30.42	30.65	30.46	30.36
CH_2CCH_2	30.40	31.42	30.56	30.39	30.45	30.48	30.46	30.63	30.46	30.36
cylC_3H_4	29.45	30.45	29.83	29.65	29.59	29.52	29.57	29.72	29.71	29.60
cylC_3H_6	36.91	37.68	37.33	37.15	37.09	37.02	37.06	37.50	37.22	37.12
$CH_3CH_2CH_3$	43.58	44.02	43.72	43.61	43.62	43.63	43.62	44.31	43.63	43.60
CH_3CCCH_3	43.32	44.48	43.60	43.37	43.39	43.37	43.37	43.73	43.47	43.33
cylC_4H_6	43.28	44.43	43.73	43.43	43.40	43.39	43.40	43.67	43.61	43.42
isobutane	56.37	56.98	56.57	56.44	56.42	56.42	56.41	57.25	56.49	56.42
benzene	59.14	61.17	59.69	59.19	59.26	59.29	59.28	59.26	59.53	59.19
CH_2F_2	18.99	19.62	19.22	19.08	19.04	19.01	19.03	19.18	18.93	19.03
CF_3H	19.92	20.84	20.31	20.07	20.01	19.94	19.98	20.02	19.90	20.03
CH_2Cl_2	16.05	16.55	16.05	16.09	16.11	16.11	16.11	15.93	15.97	16.09
CCl_3H	14.87	15.61	14.87	14.95	14.94	14.91	14.94	14.44	14.78	14.95
CH_3NO_2	26.01	27.91	26.45	26.29	26.24	26.22	26.24	26.14	26.19	26.31
CH_3SiH_3	27.22	26.95	27.05	27.26	27.26	27.22	27.24	27.82	26.97	27.23
HCOOH	21.49	22.50	21.71	21.49	21.54	21.58	21.56	21.61	21.47	21.53
CH_3CONH_2	37.48	38.87	37.89	37.70	37.69	37.69	37.70	37.96	37.69	37.72
cylNHC_2H_4	31.11	32.10	31.53	31.39	31.32	31.26	31.30	31.57	31.41	31.39
NCCN	21.59	23.39	21.85	21.68	21.64	21.62	21.62	21.23	21.73	21.67
CH_3NHCH_3	37.66	38.33	37.83	37.75	37.75	37.76	37.75	38.31	37.72	37.76
CH_2CO	23.03	24.26	23.35	23.13	23.17	23.22	23.20	23.17	23.18	23.14
cylOC_2H_4	28.18	29.11	28.55	28.33	28.30	28.28	28.30	28.53	28.37	28.35
OCHCHO	27.39	28.84	27.69	27.47	27.48	27.49	27.49	27.40	27.44	27.48
CH_3CH_2OH	35.06	35.62	35.17	35.02	35.05	35.07	35.06	35.57	35.00	35.04
CH_3OCH_3	34.55	35.15	34.67	34.54	34.58	34.59	34.59	35.11	34.50	34.56
cylSC_2H_4	27.06	27.78	27.20	27.18	27.16	27.14	27.17	27.15	27.10	27.18
CH_3SOCH_3	36.89	37.82	36.98	36.92	36.96	36.99	36.99	37.19	36.81	36.95
CH_2CHF	24.81	25.62	25.00	24.84	24.85	24.85	24.85	25.01	24.80	24.80
CH_3CH_2Cl	29.96	30.42	30.03	30.00	30.02	30.01	30.02	30.28	29.96	30.00
CH_2CHCl	23.51	24.22	23.55	23.49	23.53	23.54	23.54	23.53	23.46	23.48
CH_3CClO	28.90	30.11	29.13	29.00	29.02	29.04	29.04	28.96	28.96	29.01
prplCl	42.65	43.35	42.81	42.75	42.74	42.73	42.74	43.14	42.72	42.74
NC_3H_9	50.20	51.08	50.45	50.35	50.33	50.32	50.32	51.03	50.34	50.36
cylOC_4H_4	42.99	44.80	43.60	43.07	43.12	43.14	43.15	43.15	43.37	43.11
cylNHC_4H_4	46.34	48.23	47.02	46.54	46.56	46.58	46.58	46.62	46.85	46.56
NO_2	9.80	11.75	7.41	10.14	10.07	10.08	10.09	9.66	10.07	10.15
SF_6	20.77	21.99	21.20	20.79	20.66	20.46	20.59	20.33	20.42	20.76

$CFCl_3$	15.22	16.35	15.41	15.42	15.37	15.30	15.34	14.71	15.20	15.40
$CClF_3$	18.85	20.06	19.32	19.10	19.01	18.92	18.98	18.74	18.90	19.07
$CBrF_3$	18.34	19.60	18.81	18.55	18.46	18.37	18.43	18.16	18.36	18.51
HCCF	17.19	18.19	17.45	17.23	17.24	17.24	17.24	17.17	17.24	17.18
HCCCN	25.93	27.58	26.11	25.88	25.90	25.90	25.89	25.61	25.98	25.84
NCCCCN	34.15	36.94	34.64	34.26	34.27	34.27	34.24	33.66	34.46	34.22
C_2N_2	21.59	23.39	21.85	21.68	21.64	21.62	21.62	21.23	21.73	21.67
C_3O_2	28.58	31.24	29.25	28.77	28.88	29.03	28.94	28.40	28.93	28.78
FCN	13.19	14.37	13.45	13.31	13.27	13.25	13.26	13.04	13.26	13.29
HCCCCH	30.05	31.55	30.19	29.89	29.97	30.00	29.96	29.81	30.04	29.83
H_2CS	14.07	14.45	13.85	13.92	14.00	14.06	14.04	13.92	13.78	13.92
$HCONH_2$	24.56	25.70	24.86	24.70	24.73	24.75	24.74	24.84	24.67	24.72
CH_2CHCHO	35.76	37.06	35.97	35.76	35.81	35.83	35.82	35.91	35.79	35.75
CH_2CCl_2	22.48	23.46	22.60	22.55	22.57	22.55	22.57	22.26	22.49	22.54
$CHFCF_2$	25.31	26.91	25.91	25.57	25.52	25.48	25.50	25.38	25.47	25.50
CH_2CF_2	25.38	26.57	25.80	25.54	25.52	25.50	25.52	25.55	25.48	25.49
CH_3F	18.31	18.64	18.39	18.32	18.32	18.32	18.32	18.60	18.22	18.29
CF_2Cl_2	16.97	18.17	17.33	17.23	17.15	17.06	17.11	16.67	17.01	17.20
SiF_2	12.93	12.95	12.70	12.86	12.79	12.67	12.72	12.68	12.40	12.78
MSE		0.83	0.10	0.05	0.05	0.04	0.05	0.04	-0.03	0.04
MAE		0.88	0.27	0.11	0.10	0.10	0.10	0.28	0.17	0.11
rms		1.06	0.41	0.15	0.13	0.14	0.13	0.34	0.23	0.14

Table B.12: The frontier orbital energies (in eV) of the IP131 database calculated from vertical IP. The reference energies are taken from ref. 61 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	13.60	13.60	13.77	13.64	13.65	13.68	13.67	13.90	13.76	13.66
He	24.59	24.47	24.63	24.67	24.65	24.71	24.69	25.19	24.55	24.62
Li	5.39	5.57	3.74	5.31	5.29	5.36	5.36	5.82	5.58	5.39
Be	9.32	9.00	9.03	8.91	8.86	8.83	8.85	9.55	9.05	8.96
B	8.30	8.67	8.76	8.39	8.51	8.55	8.52	9.04	8.74	8.39
C	11.26	11.54	11.68	11.30	11.40	11.44	11.41	11.99	11.64	11.32
N	14.53	14.74	14.89	14.53	14.59	14.63	14.60	15.21	14.82	14.53
O	13.62	14.07	14.12	13.83	13.83	13.82	13.81	14.31	14.03	13.79
F	17.42	17.68	17.78	17.51	17.52	17.54	17.52	18.02	17.58	17.44
Ne	21.57	21.70	21.82	21.61	21.58	21.62	21.58	22.05	21.52	21.45
Na	5.14	5.35	5.20	4.87	4.87	4.95	4.94	5.58	5.22	4.95
Mg	7.65	7.62	7.47	7.65	7.60	7.48	7.48	8.03	7.50	7.56
Al	5.99	6.07	6.20	5.89	5.95	6.00	5.98	6.37	6.17	5.91
Si	8.15	8.20	8.32	8.03	8.07	8.11	8.10	8.51	8.29	8.05
P	10.49	10.49	10.62	10.39	10.39	10.41	10.42	10.83	10.59	10.41

S	10.36	10.43	10.52	10.41	10.46	10.49	10.48	10.96	10.49	10.44
Cl	12.97	12.98	13.07	12.96	13.01	13.03	13.02	13.53	13.03	13.00
Ar	15.76	15.72	15.83	15.75	15.76	15.79	15.78	16.29	15.78	15.78
CH_3	9.84	10.02	10.11	9.72	9.76	9.77	9.76	10.33	10.08	9.73
CH_4	13.60	13.96	14.23	14.19	14.19	14.16	14.18	14.70	14.23	14.21
NH	13.49	13.80	13.92	13.56	13.60	13.63	13.61	14.20	13.86	13.57
NH_2	12.00	12.18	10.17	12.14	12.10	12.08	12.10	12.64	12.16	12.18
NH_3	10.82	10.97	10.97	10.95	10.93	10.93	10.93	11.45	10.95	10.98
OH	13.02	13.30	13.34	13.17	13.18	13.17	13.16	13.70	13.26	13.16
H_2O	12.62	12.81	12.83	12.75	12.73	12.73	12.73	13.25	12.75	12.75
HF	16.12	16.34	16.40	16.27	16.23	16.24	16.23	16.74	16.23	16.21
SiH_3	8.74	8.95	9.11	8.77	8.84	8.88	8.86	9.35	9.09	8.79
SiH_4	12.30	12.14	12.82	12.74	12.68	12.58	12.63	13.27	12.77	12.76
PH_3	10.59	10.48	10.52	10.48	10.53	10.56	10.55	10.98	10.53	10.53
SH_2	10.50	10.41	10.46	10.39	10.43	10.46	10.45	10.87	10.43	10.42
HCl	12.77	12.73	12.79	12.72	12.75	12.77	12.77	13.23	12.76	12.75
HCCH	11.49	11.41	11.36	11.21	11.25	11.28	11.27	11.74	11.33	11.24
CH_2CH_2	10.68	10.62	10.50	10.39	10.42	10.44	10.43	10.88	10.48	10.41
CH_3CH_3	11.99	11.91	12.60	12.56	12.49	12.38	12.43	13.10	12.59	12.57
HCN	13.61	13.75	13.70	13.53	13.56	13.59	13.58	14.09	13.66	13.55
CO	14.01	13.86	14.17	14.19	14.16	14.12	14.15	14.84	14.18	14.26
HCO	9.31	9.77	10.14	9.92	9.96	9.97	9.96	10.56	10.12	9.94
CH_2O	10.89	10.75	10.94	10.85	10.86	10.85	10.85	11.36	10.89	10.86
CH_3OH	10.96	10.69	11.04	10.96	10.93	10.90	10.91	11.48	10.99	10.96
N_2	15.58	15.40	16.06	15.92	15.94	15.90	15.91	16.71	16.06	15.98
NH_2NH_2	8.98	9.40	9.80	9.74	9.71	9.67	9.69	10.31	9.79	9.77
NO	9.26	9.91	10.29	10.04	10.12	10.15	10.13	10.76	10.25	10.06
O_2	12.30	12.58	13.07	12.89	12.97	13.00	12.98	13.66	13.03	12.92
HOOH	11.70	11.30	11.83	11.73	11.73	11.71	11.72	12.39	11.79	11.76
F_2	15.70	15.39	16.03	15.90	15.97	15.99	15.97	16.71	15.97	15.93
CO_2	13.78	13.67	14.00	13.87	13.85	13.83	13.84	14.44	13.93	13.88
P_2	10.62	10.52	10.43	10.30	10.38	10.45	10.42	10.70	10.39	10.32
S_2	9.55	9.47	9.97	9.81	9.75	9.69	9.73	10.29	9.94	9.83
Cl_2	11.49	11.21	11.76	11.67	11.62	11.54	11.58	12.22	11.72	11.69
NaCl	9.80	9.35	9.28	9.23	9.27	9.29	9.28	9.72	9.25	9.24
SiO	11.61	11.31	11.67	11.54	11.57	11.54	11.56	12.14	11.64	11.58
CS	11.34	11.29	12.96	11.54	11.50	11.49	11.51	12.07	11.52	11.59
ClO	11.01	10.77	11.23	11.08	11.09	11.06	11.07	11.69	11.18	11.09
ClF	12.77	12.43	12.85	12.74	12.76	12.76	12.76	13.37	12.81	12.78
SiH_3SiH_3	10.53	10.29	10.59	10.48	10.49	10.48	10.50	10.97	10.57	10.51
CH_3Cl	11.29	11.10	11.43	11.34	11.34	11.32	11.33	11.86	11.39	11.37
CH_3SH	9.44	9.26	9.43	9.35	9.37	9.38	9.38	9.84	9.40	9.38
SO_2	12.50	12.14	13.61	12.58	12.59	12.55	12.56	13.26	12.68	12.63
BF_3	15.96	14.47	15.77	15.63	15.59	15.46	15.52	16.57	15.75	15.70
BCl_3	11.64	10.81	12.04	11.95	11.79	11.55	11.68	12.54	12.01	11.97
$AlCl_3$	12.01	10.89	12.29	12.20	12.03	11.76	11.90	12.79	12.27	12.22

CF_4	16.20	14.56	16.05	15.88	15.86	15.73	15.79	16.93	16.02	15.97
CCl_4	11.69	10.55	11.95	11.87	11.68	11.40	11.54	12.48	11.92	11.88
OCS	11.19	11.25	11.34	11.23	11.27	11.32	11.30	11.74	11.30	11.27
CS_2	10.09	10.04	10.10	10.00	10.03	10.08	10.07	10.46	10.06	10.03
CF_2O	13.60	13.17	13.63	13.49	13.50	13.48	13.49	14.11	13.55	13.50
SiF_4	16.40	14.47	16.16	15.99	15.91	15.71	15.81	17.01	16.13	16.08
N_2O	12.89	12.91	12.95	12.81	12.84	12.87	12.85	13.35	12.88	12.82
NF_3	13.60	12.95	13.58	13.49	13.51	13.49	13.49	14.21	13.53	13.51
PF_3	12.20	11.29	11.63	11.59	11.64	11.64	11.64	12.28	11.64	11.66
O_3	12.73	12.64	13.38	13.29	13.29	13.23	13.25	13.59	13.35	13.32
F_2O	13.26	12.73	13.52	13.40	13.45	13.44	13.44	14.19	13.48	13.43
ClF_3	13.05	12.00	13.02	12.92	12.92	12.84	12.87	13.72	13.00	12.97
CF_2CF_2	10.69	10.10	10.55	10.41	10.48	10.48	10.47	11.13	10.52	10.44
CF_3CN	14.30	13.49	14.09	13.92	13.94	13.92	13.93	14.55	14.05	13.94
CH_3CCH	10.37	10.21	10.36	10.23	10.25	10.24	10.25	10.75	10.34	10.25
CH_2CCH_2	10.20	10.08	10.15	10.04	10.06	10.07	10.07	10.55	10.13	10.07
cylC_3H_4	9.86	9.71	9.86	9.73	9.73	9.72	9.73	10.23	9.84	9.74
cylC_3H_6	10.54	10.74	10.96	10.84	10.83	10.81	10.82	11.36	10.94	10.86
$CH_3CH_2CH_3$	11.51	11.10	11.94	11.91	11.83	11.68	11.75	12.46	11.94	11.93
CH_3CCCH_3	9.79	9.30	9.56	9.44	9.45	9.42	9.43	9.95	9.54	9.46
cylC_4H_6	9.43	9.41	9.50	9.37	9.38	9.39	9.39	9.86	9.48	9.39
isobutane	11.13	10.74	11.52	11.51	11.44	11.30	11.36	11.99	11.48	11.51
benzene	9.25	9.27	9.39	9.26	9.27	9.26	9.27	9.74	9.37	9.28
CH_2F_2	13.27	12.43	13.23	13.16	13.16	13.10	13.12	13.90	13.22	13.20
CF_3H	15.50	13.54	14.48	14.41	14.40	14.32	14.35	15.20	14.46	14.45
CH_2Cl_2	11.40	10.70	11.74	11.63	11.52	11.33	11.43	12.21	11.68	11.65
CCl_3H	11.50	10.53	11.70	11.61	11.46	11.23	11.35	12.20	11.66	11.62
CH_3NO_2	11.29	11.01	11.58	11.73	11.68	11.58	11.63	12.40	11.79	11.76
CH_3SiH_3	11.60	11.26	11.77	11.65	11.65	11.62	11.64	12.18	11.75	11.68
HCOOH	11.50	11.11	11.34	11.24	11.23	11.21	11.22	11.77	11.27	11.24
CH_3CONH_2	10.00	9.66	10.54	9.87	9.85	9.81	9.82	10.37	9.89	9.87
cylNHC_2H_4	9.85	9.62	9.84	9.76	9.75	9.72	9.73	10.27	9.82	9.79
NCCN	13.51	13.14	13.58	13.40	13.38	13.32	13.35	14.00	13.54	13.43
CH_3NHCH_3	8.95	8.77	9.02	8.97	8.95	8.91	8.93	9.46	9.00	8.99
CH_2CO	9.64	9.71	9.80	9.70	9.74	9.75	9.74	10.25	9.78	9.73
cylOC_2H_4	10.57	10.47	10.74	10.64	10.63	10.60	10.61	11.14	10.69	10.65
OCHCHO	10.60	9.99	10.84	10.76	10.73	10.60	10.66	11.43	10.82	10.79
CH_3CH_2OH	10.64	10.19	10.72	10.65	10.62	10.56	10.58	11.18	10.67	10.65
CH_3OCH_3	10.10	9.73	10.10	10.02	10.00	9.96	9.97	10.52	10.05	10.03
cylSC_2H_4	9.05	8.93	9.07	8.98	9.00	9.01	9.02	9.46	9.04	9.01
CH_3SOCH_3	9.10	8.81	9.06	8.98	8.97	8.94	8.95	9.49	9.03	9.00
CH_2CHF	10.63	10.37	10.46	10.33	10.37	10.39	10.38	10.89	10.43	10.36
CH_3CH_2Cl	11.06	10.66	11.15	11.08	11.07	11.02	11.05	11.59	11.12	11.09
CH_2CHCl	10.20	9.83	10.12	10.00	9.98	9.94	9.97	10.52	10.09	10.02
CH_3CClO	11.03	10.75	11.98	11.09	11.06	11.01	11.03	11.59	11.12	11.09
prplCl	10.88	10.36	11.02	10.95	10.92	10.84	10.88	11.46	10.99	10.96

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NC_3H_9	8.54	8.25	8.46	8.43	8.40	8.36	8.38	8.89	8.44	8.43
cylOC_4H_4	8.90	8.90	9.00	8.86	8.87	8.87	8.87	9.37	8.97	8.87
cylNHC_4H_4	8.23	8.27	8.31	8.19	8.21	8.21	8.21	8.68	8.29	8.21
NO_2	11.23	11.18	9.01	11.70	11.74	11.71	11.71	12.51	11.88	11.74
SF_6	15.70	13.73	15.52	15.44	15.40	15.22	15.31	16.48	15.57	15.53
$CFCl_3$	11.76	10.84	12.07	11.98	11.83	11.59	11.71	12.59	12.04	12.00
$CClF_3$	13.08	12.56	13.11	13.02	13.04	13.02	13.03	13.61	13.07	13.05
$CBrF_3$	12.08	11.70	12.06	11.90	11.95	11.95	11.97	12.57	12.04	11.99
HCCF	11.50	11.17	11.30	11.16	11.20	11.22	11.21	11.75	11.28	11.19
HCCCN	11.75	11.37	11.68	11.52	11.51	11.48	11.50	12.08	11.65	11.55
NCCCCN	11.84	11.51	12.07	11.91	11.87	11.80	11.83	12.50	12.04	11.93
C_2N_2	13.51	13.14	13.58	13.40	13.38	13.32	13.35	14.00	13.54	13.43
C_3O_2	10.80	10.76	10.85	10.72	10.77	10.81	10.79	11.30	10.81	10.75
FCN	13.65	13.31	13.49	13.33	13.37	13.39	13.38	13.96	13.46	13.36
HCCCCH	10.30	9.93	10.19	10.04	10.04	10.01	10.02	10.59	10.17	10.07
H_2CS	9.38	9.26	9.36	9.26	9.30	9.32	9.32	9.75	9.32	9.29
$HCONH_2$	10.40	10.23	10.91	10.30	10.29	10.27	10.28	10.80	10.31	10.30
CH_2CHCHO	10.10	9.81	10.13	10.04	10.02	9.98	10.00	10.54	10.08	10.04
CH_2CCl_2	10.00	9.56	10.00	9.88	9.85	9.78	9.82	10.41	9.97	9.90
$CHFCF_2$	10.62	10.01	10.33	10.20	10.26	10.27	10.26	10.85	10.30	10.23
CH_2CF_2	10.70	10.38	10.58	10.45	10.50	10.51	10.51	11.06	10.55	10.48
CH_3F	13.04	12.72	13.25	13.17	13.16	13.12	13.14	13.78	13.21	13.18
CF_2Cl_2	12.24	11.51	12.46	12.38	12.28	12.13	12.21	12.96	12.42	12.39
SiF_2	11.08	10.83	11.00	11.10	11.10	11.07	11.09	11.64	11.03	11.14
MSE		-0.26	0.10	0.00	0.00	-0.03	-0.02	0.57	0.09	0.02
MAE		0.36	0.28	0.19	0.18	0.19	0.18	0.58	0.20	0.18
rms		0.52	0.46	0.26	0.26	0.27	0.26	0.64	0.28	0.26

Table B.13: The frontier orbital energies (in eV) of the IP131 database calculated from -HOMO(N). The reference energies are taken from ref. 61 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	13.60	7.59	12.21	11.91	11.62	11.05	11.38	12.68	12.21	11.98
He	24.59	15.76	21.19	21.13	20.90	20.26	20.62	22.41	21.30	21.28
Li	5.39	3.22	3.78	5.32	5.31	5.21	5.30	5.83	5.61	5.38
Be	9.32	5.61	8.92	8.76	8.63	8.29	8.49	9.33	8.94	8.81
B	8.30	4.17	8.21	7.91	7.73	7.24	7.51	8.66	8.20	7.92
C	11.26	6.10	10.69	10.36	10.14	9.57	9.88	11.30	10.68	10.41
N	14.53	8.31	13.27	12.94	12.72	12.14	12.46	14.12	13.30	13.03
O	13.62	7.60	12.60	12.38	12.12	11.49	11.83	13.39	12.63	12.43
F	17.42	10.32	15.58	15.43	15.23	14.63	14.96	16.76	15.67	15.57
Ne	21.57	13.38	18.83	18.73	18.63	18.08	18.39	20.47	19.06	19.02

Na	5.14	3.03	5.24	4.82	4.91	4.87	4.92	5.58	5.26	4.87
Mg	7.65	4.70	7.50	7.35	7.31	7.08	7.22	7.92	7.52	7.37
Al	5.99	3.09	6.20	5.88	5.77	5.47	5.66	6.39	6.18	5.90
Si	8.15	4.61	8.23	7.93	7.72	7.30	7.55	8.49	8.20	7.95
P	10.49	6.30	10.33	10.08	9.78	9.26	9.57	10.69	10.31	10.10
S	10.36	6.15	10.31	10.08	9.83	9.31	9.60	10.83	10.29	10.11
Cl	12.97	8.14	12.60	12.45	12.15	11.56	11.88	13.24	12.59	12.48
Ar	15.76	10.30	15.00	14.89	14.56	13.92	14.28	15.77	15.01	14.95
CH_3	9.84	5.42	9.80	9.41	9.15	8.59	8.90	10.27	9.79	9.44
CH_4	13.60	9.45	14.00	13.91	13.60	12.99	13.32	14.69	14.01	13.95
NH	13.49	7.92	12.81	12.49	12.24	11.65	11.97	13.59	12.82	12.56
NH_2	12.00	7.22	9.88	11.65	11.36	10.75	11.09	12.52	11.81	11.72
NH_3	10.82	6.18	10.72	10.64	10.33	9.73	10.06	11.48	10.74	10.70
OH	13.02	7.38	12.30	12.16	11.89	11.27	11.61	13.21	12.34	12.24
H_2O	12.62	7.24	12.11	12.02	11.73	11.11	11.45	13.06	12.15	12.11
HF	16.12	9.65	14.82	14.73	14.50	13.89	14.23	16.06	14.92	14.90
SiH_3	8.74	5.37	9.13	8.78	8.59	8.16	8.41	9.46	9.12	8.81
SiH_4	12.30	8.52	12.76	12.66	12.37	11.82	12.13	13.34	12.76	12.69
PH_3	10.59	6.72	10.61	10.49	10.26	9.77	10.04	11.14	10.62	10.54
SH_2	10.50	6.31	10.42	10.30	10.01	9.46	9.77	10.95	10.40	10.33
HCl	12.77	8.05	12.46	12.37	12.05	11.44	11.78	13.10	12.45	12.40
HCCH	11.49	7.20	11.35	11.21	10.92	10.36	10.67	11.88	11.34	11.23
CH_2CH_2	10.68	6.74	10.70	10.55	10.28	9.75	10.05	11.18	10.68	10.57
CH_3CH_3	11.99	8.17	12.51	12.43	12.15	11.59	11.90	13.17	12.52	12.46
HCN	13.61	9.02	13.41	13.25	12.94	12.35	12.68	14.02	13.40	13.28
CO	14.01	9.04	13.84	13.75	13.44	12.81	13.16	14.69	13.87	13.83
HCO	9.31	5.16	9.61	9.40	9.17	8.63	8.93	10.32	9.64	9.46
CH_2O	10.89	6.26	10.68	10.58	10.36	9.82	10.13	11.51	10.71	10.66
CH_3OH	10.96	6.26	10.84	10.75	10.49	9.92	10.24	11.68	10.87	10.83
N_2	15.58	10.28	15.30	15.17	14.91	14.29	14.63	16.29	15.34	15.27
NH_2NH_2	8.98	5.30	9.74	9.66	9.38	8.80	9.12	10.49	9.76	9.72
NO	9.26	4.52	9.38	9.15	8.93	8.35	8.67	10.26	9.40	9.23
O_2	12.30	6.84	11.94	11.79	11.59	11.01	11.33	13.08	12.02	11.92
HOOH	11.70	6.46	11.34	11.24	10.98	10.38	10.71	12.32	11.38	11.34
F_2	15.70	9.48	14.74	14.64	14.47	13.90	14.22	16.09	14.87	14.83
CO_2	13.78	9.09	13.54	13.41	13.18	12.65	12.95	14.38	13.56	13.49
P_2	10.62	7.15	10.64	10.49	10.30	9.90	10.14	10.96	10.61	10.49
S_2	9.55	5.83	9.88	9.70	9.41	8.88	9.19	10.33	9.85	9.72
Cl_2	11.49	7.33	11.60	11.50	11.20	10.63	10.95	12.21	11.58	11.52
NaCl	9.80	5.30	9.34	9.25	8.96	8.41	8.71	9.94	9.34	9.27
SiO	11.61	7.48	11.59	11.44	11.25	10.77	11.05	12.25	11.60	11.51
CS	11.34	7.40	11.88	11.78	11.50	10.92	11.25	12.58	11.88	11.84
ClO	11.01	6.30	10.87	10.73	10.48	9.91	10.23	11.64	10.88	10.79
ClF	12.77	7.86	12.43	12.33	12.04	11.45	11.78	13.20	12.44	12.38
SiH_3SiH_3	10.53	7.19	10.94	10.82	10.59	10.13	10.39	11.41	10.93	10.84
CH_3Cl	11.29	7.12	11.39	11.31	11.00	10.43	10.75	12.01	11.39	11.33

CH_3SH	9.44	5.57	9.60	9.49	9.21	8.68	8.98	10.13	9.59	9.51
SO_2	12.50	8.08	12.48	12.35	12.13	11.61	11.90	13.29	12.50	12.43
BF_3	15.96	10.07	15.15	15.01	14.84	14.28	14.59	16.38	15.25	15.19
BCl_3	11.64	7.72	12.00	11.90	11.59	11.02	11.34	12.61	11.98	11.92
$AlCl_3$	12.01	8.02	12.27	12.17	11.86	11.30	11.61	12.87	12.26	12.19
CF_4	16.20	10.42	15.55	15.43	15.26	14.69	15.01	16.81	15.65	15.61
CCl_4	11.69	7.69	11.99	11.90	11.59	11.01	11.33	12.61	11.97	11.92
OCS	11.19	7.50	11.35	11.22	10.99	10.53	10.80	11.89	11.33	11.26
CS_2	10.09	6.82	10.31	10.18	9.97	9.57	9.80	10.75	10.28	10.21
CF_2O	13.60	8.52	13.33	13.20	12.97	12.39	12.71	14.31	13.36	13.30
SiF_4	16.40	10.69	15.73	15.61	15.42	14.85	15.17	16.92	15.82	15.77
N_2O	12.89	8.40	12.58	12.44	12.23	11.74	12.02	13.33	12.58	12.50
NF_3	13.60	8.45	13.21	13.13	12.90	12.33	12.64	14.20	13.23	13.21
PF_3	12.20	7.36	11.54	11.44	11.21	10.69	10.98	12.29	11.57	11.52
O_3	12.73	8.02	12.88	12.78	12.55	11.97	12.29	13.75	12.93	12.88
F_2O	13.26	7.72	12.91	12.81	12.62	12.03	12.35	14.12	12.99	12.95
ClF_3	13.05	8.00	12.78	12.68	12.44	11.87	12.19	13.74	12.81	12.77
CF_2CF_2	10.69	6.31	10.57	10.42	10.22	9.71	9.99	11.31	10.55	10.47
CF_3CN	14.30	9.57	14.06	13.90	13.60	13.00	13.33	14.72	14.04	13.93
CH_3CCH	10.37	6.49	10.55	10.42	10.14	9.60	9.90	11.07	10.53	10.44
CH_2CCH_2	10.20	6.56	10.51	10.38	10.12	9.60	9.89	11.03	10.50	10.40
$cylC_3H_4$	9.86	6.11	10.01	9.88	9.62	9.11	9.40	10.51	10.00	9.90
$cylC_3H_6$	10.54	7.07	11.24	11.11	10.83	10.28	10.59	11.82	11.23	11.14
$CH_3CH_2CH_3$	11.51	7.75	12.00	11.93	11.66	11.11	11.41	12.64	12.00	11.96
CH_3CCCH_3	9.79	5.93	9.89	9.78	9.51	8.99	9.28	10.41	9.88	9.79
$cylC_4H_6$	9.43	6.04	9.87	9.74	9.49	8.99	9.27	10.35	9.86	9.76
isobutane	11.13	7.58	11.74	11.68	11.42	10.87	11.17	12.38	11.74	11.70
benzene	9.25	6.33	9.83	9.69	9.49	9.06	9.30	10.25	9.81	9.71
CH_2F_2	13.27	8.15	12.85	12.76	12.54	11.98	12.29	13.79	12.89	12.85
CF_3H	15.50	9.35	14.09	14.01	13.79	13.22	13.53	15.08	14.13	14.10
CH_2Cl_2	11.40	7.38	11.67	11.58	11.29	10.72	11.03	12.29	11.65	11.60
CCl_3H	11.50	7.42	11.69	11.60	11.29	10.71	11.03	12.30	11.67	11.61
CH_3NO_2	11.29	6.92	11.64	11.53	11.30	10.73	11.05	12.59	11.68	11.63
CH_3SiH_3	11.60	7.92	12.06	11.94	11.66	11.13	11.43	12.63	12.05	11.97
HCOOH	11.50	6.73	11.26	11.16	10.92	10.35	10.67	12.14	11.29	11.24
CH_3CONH_2	10.00	5.79	10.23	10.15	9.91	9.35	9.66	11.08	10.27	10.23
$cylNHC_2H_4$	9.85	5.78	10.04	9.94	9.67	9.12	9.43	10.71	10.05	9.99
NCCN	13.51	9.39	13.51	13.34	13.07	12.54	12.83	14.11	13.49	13.37
CH_3NHCH_3	8.95	5.06	9.27	9.19	8.93	8.39	8.69	9.96	9.28	9.24
CH_2CO	9.64	5.91	9.86	9.72	9.50	9.01	9.29	10.45	9.85	9.76
$cylOC_2H_4$	10.57	6.27	10.79	10.70	10.46	9.90	10.22	11.65	10.84	10.78
OCHCHO	10.60	6.39	10.70	10.62	10.41	9.88	10.18	11.53	10.73	10.68
CH_3CH_2OH	10.64	6.15	10.70	10.62	10.37	9.79	10.11	11.53	10.73	10.69
CH_3OCH_3	10.10	5.83	10.21	10.14	9.90	9.36	9.66	11.02	10.24	10.21
$cylSC_2H_4$	9.05	5.37	9.38	9.26	8.98	8.46	8.75	9.90	9.36	9.28
CH_3SOCH_3	9.10	5.38	9.38	9.29	9.07	8.58	8.85	10.07	9.40	9.35

CH_2CHF	10.63	6.52	10.57	10.43	10.18	9.66	9.95	11.14	10.56	10.46
CH_3CH_2Cl	11.06	6.97	11.24	11.16	10.86	10.28	10.60	11.86	11.23	11.18
CH_2CHCl	10.20	6.42	10.30	10.18	9.92	9.41	9.70	10.82	10.28	10.19
CH_3CClO	11.03	7.13	11.36	11.27	11.04	10.52	10.81	12.12	11.38	11.32
prplCl	10.88	6.94	11.20	11.12	10.82	10.25	10.57	11.82	11.19	11.14
NC_3H_9	8.54	4.85	8.89	8.83	8.59	8.07	8.35	9.56	8.90	8.87
$cylOC_4H_4$	8.90	5.67	9.34	9.20	8.97	8.51	8.77	9.80	9.32	9.21
$cylNHC_4H_4$	8.23	5.13	8.71	8.58	8.36	7.92	8.17	9.15	8.69	8.59
NO_2	11.23	6.50	8.49	11.16	10.94	10.37	10.69	12.31	11.39	11.26
SF_6	15.70	10.14	15.24	15.12	14.96	14.41	14.72	16.50	15.34	15.29
$CFCl_3$	11.76	7.75	12.07	11.97	11.66	11.08	11.40	12.69	12.04	11.99
$CClF_3$	13.08	8.56	13.08	12.97	12.66	12.06	12.40	13.78	13.07	13.01
$CBrF_3$	12.08	7.82	12.08	11.88	11.64	11.12	11.42	12.73	12.08	11.95
HCCF	11.50	7.01	11.23	11.09	10.82	10.28	10.58	11.84	11.22	11.12
HCCCN	11.75	7.87	11.77	11.62	11.36	10.87	11.14	12.32	11.76	11.64
NCCCCN	11.84	8.44	12.24	12.08	11.83	11.36	11.62	12.79	12.22	12.10
C_2N_2	13.51	9.39	13.51	13.34	13.07	12.54	12.83	14.11	13.49	13.37
C_3O_2	10.80	7.27	10.95	10.81	10.63	10.22	10.46	11.56	10.94	10.86
FCN	13.65	8.73	13.17	13.02	12.74	12.17	12.49	13.88	13.17	13.06
HCCCCH	10.30	6.64	10.39	10.24	10.00	9.52	9.79	10.89	10.37	10.26
H_2CS	9.38	5.53	9.52	9.40	9.14	8.62	8.91	10.05	9.51	9.43
$HCONH_2$	10.40	6.02	10.47	10.39	10.15	9.59	9.90	11.34	10.51	10.47
CH_2CHCHO	10.10	6.00	10.46	10.37	10.14	9.59	9.90	11.30	10.50	10.45
CH_2CCl_2	10.00	6.44	10.30	10.17	9.92	9.42	9.70	10.81	10.27	10.18
$CHFCF_2$	10.62	6.22	10.38	10.24	10.02	9.52	9.80	11.06	10.37	10.28
CH_2CF_2	10.70	6.57	10.68	10.54	10.30	9.78	10.07	11.30	10.67	10.58
CH_3F	13.04	8.09	12.79	12.70	12.48	11.91	12.23	13.73	12.85	12.81
CF_2Cl_2	12.24	8.08	12.44	12.35	12.04	11.45	11.78	13.09	12.42	12.37
SiF_2	11.08	7.14	11.00	10.88	10.70	10.24	10.50	11.65	11.03	10.96
MSE		-4.40	-0.15	-0.24	-0.48	-1.01	-0.71	0.61	-0.09	-0.18
MAE		4.40	0.42	0.40	0.51	1.01	0.72	0.70	0.36	0.37
rms		4.50	0.68	0.63	0.75	1.18	0.93	0.77	0.56	0.59

Table B.14: The frontier orbital energies (in eV) of the EA131 database calculated from vertical EA. The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	0.75	0.65	0.63	0.65	0.73	0.79	0.75	1.31	0.63	0.64
He	-2.63	-3.81	-3.92	-4.18	-4.12	-4.02	-4.05	-3.75	-3.92	-4.13
Li	0.62	0.52	-0.33	0.40	0.48	0.51	0.47	0.78	0.48	0.40
Be	-0.36	-0.16	-0.27	-0.55	-0.45	-0.35	-0.40	-0.08	-0.28	-0.53
B	0.25	0.54	0.41	0.09	0.22	0.32	0.27	0.63	0.40	0.11

C	1.25	1.55	1.45	1.11	1.23	1.31	1.27	1.72	1.43	1.14
N	-0.22	0.17	-0.02	-0.10	-0.10	-0.11	-0.12	0.31	-0.05	-0.13
O	1.45	1.66	1.54	1.47	1.46	1.44	1.44	1.90	1.46	1.43
F	3.44	3.54	3.48	3.44	3.38	3.35	3.35	3.81	3.30	3.35
Ne	-5.31	-6.61	-6.84	-7.21	-7.09	-6.99	-7.03	-6.41	-6.81	-7.15
Na	0.54	0.55	0.46	0.52	0.57	0.52	0.49	0.75	0.46	0.46
Mg	-0.23	-0.15	-0.21	-0.49	-0.43	-0.33	-0.37	-0.10	-0.22	-0.46
Al	0.45	0.50	0.46	0.14	0.23	0.32	0.28	0.58	0.44	0.17
Si	1.42	1.46	1.44	1.14	1.21	1.29	1.26	1.60	1.42	1.16
P	0.74	0.85	0.75	0.71	0.82	0.87	0.83	1.17	0.73	0.70
S	2.10	2.14	2.06	2.03	2.12	2.16	2.13	2.49	2.04	2.04
Cl	3.69	3.65	3.60	3.60	3.66	3.68	3.66	4.05	3.58	3.60
Ar	-2.81	-2.98	-3.29	-3.58	-3.43	-3.31	-3.37	-2.90	-3.27	-3.56
CH_3	-0.07	-0.04	-0.30	-0.23	-0.17	-0.14	-0.16	0.15	-0.31	-0.23
CH_4	-0.62	-0.72	-0.92	-1.12	-1.07	-0.98	-1.02	-0.71	-0.92	-1.09
NH	0.33	0.46	0.28	0.27	0.29	0.29	0.28	0.70	0.26	0.26
NH_2	0.74	0.75	2.57	0.59	0.61	0.62	0.61	1.01	0.53	0.59
NH_3	-0.56	-0.69	-0.89	-1.10	-1.05	-0.96	-1.00	-0.65	-0.89	-1.07
OH	1.83	1.85	1.70	1.71	1.69	1.68	1.67	2.11	1.62	1.68
H_2O	-0.56	-0.72	-0.87	-1.09	-1.04	-0.95	-0.98	-0.61	-0.87	-1.06
HF	-0.63	-0.77	-0.87	-1.10	-1.05	-0.96	-0.99	-0.61	-0.87	-1.06
SiH_3	0.93	0.91	0.76	0.81	0.88	0.91	0.89	1.17	0.75	0.81
SiH_4	-1.11	-0.78	-1.08	-1.28	-1.22	-1.13	-1.17	-0.84	-1.07	-1.25
PH_3	-1.21	-0.64	-0.89	-1.12	-1.04	-0.94	-0.99	-0.64	-0.88	-1.08
SH_2	-0.49	-0.59	-0.81	-1.04	-0.96	-0.87	-0.91	-0.57	-0.81	-1.01
HCl	-0.52	-0.62	-0.77	-0.99	-0.92	-0.82	-0.87	-0.52	-0.77	-0.97
HCCH	-1.90	-0.69	-0.96	-1.13	-1.09	-1.00	-1.04	-0.77	-0.96	-1.10
CH_2CH_2	-1.86	-0.82	-1.83	-1.29	-1.25	-1.15	-1.19	-0.89	-1.09	-1.26
CH_3CH_3	-0.62	-0.68	-0.96	-1.14	-1.10	-1.02	-1.05	-0.74	-0.96	-1.11
HCN	-0.48	-0.69	-1.86	-0.90	-0.85	-0.78	-0.81	-0.50	-0.71	-0.87
CO	-1.50	-1.30	-1.52	-1.75	-1.66	-1.56	-1.61	-1.22	-1.54	-1.74
HCO	0.02	-0.02	-0.07	-0.07	-0.01	0.01	-0.01	0.43	-0.09	-0.06
CH_2O	-0.55	-0.56	-0.88	-1.09	-1.03	-0.97	-1.00	-0.54	-0.91	-1.08
CH_3OH	-0.55	-0.59	-0.83	-1.01	-0.97	-0.89	-0.92	-0.61	-0.83	-0.98
N_2	-2.24	-2.05	-2.07	-2.25	-2.20	-2.16	-2.18	-1.70	-2.11	-2.26
NH_2NH_2	-0.45	-0.55	-0.77	-0.98	-0.93	-0.84	-0.88	-0.53	-0.77	-0.95
NO	-0.42	-0.26	-0.13	-0.29	-0.25	-0.23	-0.24	0.30	-0.17	-0.29
O_2	-0.08	-0.20	0.00	-0.10	-0.07	-0.08	-0.09	0.46	-0.07	-0.12
HOOH	-0.92	-0.76	-1.33	-1.23	-1.19	-1.09	-1.13	-0.76	-1.02	-1.20
F_2	0.42	0.48	0.72	0.63	0.63	0.62	0.61	1.26	0.66	0.62
CO_2	-0.65	-0.87	-1.14	-1.33	-1.28	-1.19	-1.23	-0.82	-1.14	-1.31
P_2	0.48	0.57	0.81	0.64	0.65	0.63	0.63	1.08	0.78	0.64
S_2	1.53	1.35	1.58	1.48	1.51	1.49	1.49	1.98	1.54	1.49
Cl_2	0.75	0.87	0.86	0.72	0.76	0.77	0.76	1.24	0.84	0.73
NaCl	0.65	0.79	0.76	0.56	0.57	0.64	0.62	1.01	0.76	0.60
SiO	0.03	0.10	0.17	-0.07	-0.01	0.04	0.01	0.42	0.14	-0.06

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CS	-0.09	0.07	0.26	0.06	0.10	0.09	0.08	0.58	0.23	0.06
ClO	2.19	1.93	2.14	2.09	2.08	2.05	2.06	2.59	2.09	2.08
ClF	0.44	0.55	0.57	0.45	0.47	0.47	0.47	0.98	0.55	0.45
SiH_3SiH_3	-0.69	-0.72	-1.20	-1.21	-1.16	-1.06	-1.11	-0.77	-1.01	-1.18
CH_3Cl	-0.51	-0.55	-0.78	-0.96	-0.91	-0.82	-0.86	-0.55	-0.78	-0.93
CH_3SH	-0.50	-0.54	-0.82	-1.01	-0.96	-0.87	-0.91	-0.59	-0.82	-0.99
SO_2	0.81	0.73	1.12	0.96	0.97	0.94	0.95	1.54	1.08	0.97
BF_3	-1.04	-0.82	-1.12	-1.35	-1.31	-1.23	-1.25	-0.81	-1.12	-1.31
BCl_3	-0.17	-0.10	-1.01	-0.16	-0.11	-0.13	-0.14	0.36	0.06	-0.18
$AlCl_3$	0.06	0.24	-0.14	-0.35	-0.23	-0.14	-0.20	0.18	-0.13	-0.35
CF_4	-1.33	-1.40	-1.82	-2.03	-2.01	-1.92	-1.95	-1.50	-1.81	-1.99
CCl_4	-0.46	0.22	-0.43	-0.48	-0.38	-0.25	-0.33	-0.08	-0.43	-0.45
OCS	-0.74	-0.88	-1.23	-1.28	-1.24	-1.21	-1.25	-0.94	-1.11	-1.28
CS_2	0.01	0.00	0.37	0.16	0.17	0.12	0.14	0.69	0.34	0.17
CF_2O	-2.37	-1.01	-1.36	-1.56	-1.52	-2.11	-1.47	-1.03	-1.35	-1.53
SiF_4	-0.81	-0.71	-1.16	-1.37	-1.32	-1.24	-1.27	-0.79	-1.15	-1.33
N_2O	-2.01	-1.46	-1.78	-2.16	-2.12	-2.12	-2.13	-1.46	-1.77	-1.97
NF_3	-2.06	-2.24	-2.73	-2.92	-2.84	-2.78	-2.84	-2.39	-2.74	-2.93
PF_3	-1.23	-1.07	-1.44	-1.66	-1.60	-1.48	-1.53	-1.20	-1.46	-1.63
O_3	1.93	1.88	2.64	2.52	2.53	2.46	2.48	3.28	2.62	2.54
F_2O	-0.31	-0.28	-0.14	-0.23	-0.21	-0.21	-0.22	0.37	-0.20	-0.24
ClF_3	1.20	1.02	1.32	1.21	1.22	1.19	1.20	1.83	1.29	1.23
CF_2CF_2	-1.65	-1.07	-1.49	-1.72	-1.68	-1.59	-1.62	-1.16	-1.49	-1.69
CF_3CN	-0.96	-0.98	-1.39	-1.60	-1.55	-1.51	-1.54	-1.11	-1.39	-1.55
CH_3CCH	-1.13	-0.56	-0.84	-0.99	-0.97	-0.89	-0.92	-0.63	-0.84	-0.97
CH_2CCH_2	-0.56	-0.67	-1.49	-1.16	-1.13	-1.04	-1.08	-0.78	-1.00	-1.13
$cylC_3H_4$	-1.82	-0.75	-1.82	-1.19	-1.16	-1.07	-1.11	-0.83	-1.02	-1.17
$cylC_3H_6$	-0.65	-0.77	-1.09	-1.27	-1.24	-1.15	-1.19	-0.88	-1.09	-1.24
$CH_3CH_2CH_3$	-0.60	-0.63	-0.96	-1.15	-1.11	-1.02	-1.06	-0.73	-0.96	-1.11
CH_3CCCH_3	-0.67	-0.52	-0.90	-1.06	-1.03	-0.95	-0.98	-0.67	-0.90	-1.03
$cylC_4H_6$	-1.41	-0.69	-1.00	-1.20	-1.17	-1.08	-1.11	-0.81	-1.02	-1.17
isobutane	-0.56	-0.56	-0.92	-1.10	-1.07	-0.98	-1.02	-0.70	-0.92	-1.07
benzene	-0.71	-0.52	-1.37	-1.12	-1.08	-0.99	-1.03	-0.72	-0.94	-1.09
CH_2F_2	-0.58	-0.68	-0.88	-1.07	-1.03	-0.94	-0.98	-0.67	-0.88	-1.04
CF_3H	-0.60	-0.82	-0.90	-1.11	-1.06	-0.99	-1.02	-0.69	-0.91	-1.08
CH_2Cl_2	-0.49	-0.48	-0.77	-0.96	-0.89	-0.80	-0.85	-0.54	-0.77	-0.94
CCl_3H	-0.83	-0.32	-0.77	-0.96	-0.87	-0.75	-0.82	-0.53	-0.77	-0.95
CH_3NO_2	-0.37	-0.06	-0.10	-0.24	-0.23	-0.24	-0.24	0.35	-0.14	-0.25
CH_3SiH_3	-0.53	-0.59	-0.87	-1.05	-1.01	-0.92	-0.96	-0.66	-0.87	-1.03
HCOOH	-0.57	-0.70	-1.88	-1.13	-1.08	-0.99	-1.03	-0.69	-0.92	-1.11
CH_3CONH_2	-0.31	-0.33	-0.57	-0.77	-0.72	-0.63	-0.67	-0.34	-0.57	-0.74
$cylNHC_2H_4$	-0.56	-0.63	-0.87	-1.06	-1.02	-0.93	-0.97	-0.67	-0.87	-1.03
NCCN	-0.19	0.14	0.24	0.06	0.11	0.12	0.11	0.59	0.21	0.07
CH_3NHCH_3	-0.56	-0.57	-0.87	-1.04	-1.01	-0.93	-0.96	-0.66	-0.87	-1.01
CH_2CO	-0.51	-0.72	-1.22	-1.08	-1.31	-1.17	-1.25	-0.68	-0.90	-1.05
$cylOC_2H_4$	-0.86	-0.69	-0.95	-1.13	-1.09	-1.01	-1.04	-0.75	-0.96	-1.10

OCHCHO	0.69	1.04	1.01	0.84	0.90	0.94	0.91	1.36	0.98	0.84
CH_3CH_2OH	-0.53	-0.55	-0.82	-1.00	-0.96	-0.88	-0.91	-0.60	-0.82	-0.97
CH_3OCH_3	-0.58	-0.60	-0.90	-1.09	-1.05	-0.96	-1.00	-0.69	-0.90	-1.06
cylSC_2H_4	-0.78	-0.66	-0.94	-1.12	-1.08	-1.00	-1.03	-0.74	-0.94	-1.10
CH_3SOCH_3	-0.40	-0.43	-0.67	-0.87	-0.82	-0.74	-0.78	-0.45	-0.67	-0.84
CH_2CHF	-0.88	-0.76	-1.92	-1.16	-1.12	-1.03	-1.07	-0.77	-0.97	-1.13
CH_3CH_2Cl	-0.51	-0.56	-0.82	-1.00	-0.96	-0.87	-0.91	-0.60	-0.82	-0.98
CH_2CHCl	-1.11	-0.68	-0.90	-1.09	-1.04	-0.96	-1.00	-0.70	-0.90	-1.06
CH_3CClO	-0.85	-0.36	-0.71	-0.89	-0.84	-0.76	-0.79	-0.48	-0.71	-0.86
prplCl	-0.48	-0.47	-0.79	-0.98	-0.93	-0.84	-0.88	-0.57	-0.79	-0.95
NC_3H_9	-0.54	-0.52	-0.88	-1.06	-1.02	-0.94	-0.98	-0.66	-0.88	-1.03
cylOC_4H_4	-0.74	-0.60	-1.88	-1.12	-1.08	-0.99	-1.02	-0.73	-0.93	-1.09
cylNHC_4H_4	-0.51	-0.46	-0.71	-0.91	-0.86	-0.77	-0.81	-0.50	-0.71	-0.88
NO_2	1.44	1.13	4.32	1.41	1.43	1.38	1.39	2.03	1.40	1.41
SF_6	-1.05	-0.50	-1.05	-1.15	-1.10	-1.02	-1.06	-0.55	-1.03	-1.07
$CFCl_3$	-0.68	-0.16	-0.68	-0.78	-0.68	-0.57	-0.64	-0.33	-0.69	-0.76
$CClF_3$	-1.06	-1.07	-1.49	-1.73	-1.63	-1.50	-1.56	-1.20	-1.48	-1.68
$CBrF_3$	-0.81	-0.76	-1.02	-1.26	-1.16	-1.06	-1.11	-0.67	-1.03	-1.23
HCCF	-0.55	-0.61	-0.81	-0.98	-0.94	-0.87	-0.90	-0.62	-0.81	-0.96
HCCCN	-0.36	-0.12	-0.36	-0.54	-0.49	-0.46	-0.48	-0.03	-0.38	-0.53
NCCCCN	0.68	1.08	1.15	0.97	1.01	1.03	1.02	1.47	1.12	0.98
C_2N_2	-0.19	0.14	0.24	0.06	0.11	0.12	0.11	0.59	0.21	0.07
C_3O_2	-0.74	-0.68	-0.38	-0.58	-0.56	-0.59	-0.58	0.00	-0.42	-0.57
FCN	-0.66	-0.59	-0.87	-1.07	-1.01	-0.91	-0.95	-0.53	-0.86	-1.04
HCCCCH	-0.64	-0.46	-0.99	-0.93	-1.12	-0.85	-1.09	-0.63	-0.80	-0.90
H_2CS	0.28	0.39	-0.88	0.41	0.42	0.40	0.40	0.90	0.56	0.40
$HCONH_2$	-0.35	-0.47	-0.63	-0.84	-0.78	-0.69	-0.73	-0.40	-0.63	-0.81
CH_2CHCHO	-0.46	0.02	0.03	-0.14	-0.11	-0.09	-0.11	0.34	0.00	-0.15
CH_2CCl_2	-1.07	-0.64	-0.92	-1.11	-1.06	-1.07	-1.02	-0.72	-0.92	-1.09
$CHFCF_2$	-0.54	-0.73	-0.92	-1.12	-1.08	-1.00	-1.03	-0.70	-0.92	-1.09
CH_2CF_2	-1.03	-0.73	-0.97	-1.15	-1.12	-1.03	-1.07	-0.76	-0.97	-1.12
CH_3F	-0.58	-0.66	-0.87	-1.04	-1.01	-0.92	-0.96	-0.66	-0.87	-1.01
CF_2Cl_2	-0.90	-0.65	-1.21	-1.36	-1.26	-1.12	-1.20	-0.85	-1.21	-1.34
SiF_2	0.10	0.18	0.26	0.02	0.08	0.12	0.10	0.51	0.23	0.02
MSE		0.10	-0.11	-0.24	-0.19	-0.14	-0.16	0.23	-0.08	-0.22
MAE		0.21	0.36	0.34	0.31	0.26	0.29	0.33	0.27	0.32
rms		0.34	0.54	0.44	0.41	0.36	0.39	0.45	0.35	0.42

Table B.15: The frontier orbital energies (in eV) of the EA131 database calculated from -HOMO(N+1). The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3

H	0.75	-1.97	1.34	1.37	1.21	0.85	1.05	1.77	1.35	1.35
He	-2.63	-6.06	-3.84	-4.10	-4.15	-4.26	-4.15	-3.74	-3.84	-4.05
Li	0.62	-0.88	0.17	0.69	0.73	0.70	0.71	0.97	0.79	0.68
Be	-0.36	-1.89	-0.06	-0.44	-0.34	-0.40	-0.37	0.11	-0.07	-0.43
B	0.25	-2.14	0.81	0.45	0.42	0.15	0.30	1.09	0.80	0.47
C	1.25	-2.06	1.64	1.28	1.16	0.74	0.98	2.09	1.64	1.32
N	-0.22	-3.49	0.26	0.11	-0.12	-0.62	-0.35	0.71	0.27	0.09
O	1.45	-2.91	1.48	1.43	1.16	0.55	0.88	2.22	1.50	1.45
F	3.44	-1.96	2.85	2.87	2.59	1.94	2.29	3.92	2.91	2.96
Ne	-5.31	-9.77	-6.70	-7.28	-7.29	-7.53	-7.35	-6.48	-6.67	-7.17
Na	0.54	-0.85	0.75	0.67	0.71	0.67	0.68	0.94	0.76	0.64
Mg	-0.23	-1.38	-0.03	-0.42	-0.35	-0.31	-0.31	0.02	-0.05	-0.38
Al	0.45	-1.58	0.82	0.48	0.47	0.31	0.41	0.95	0.80	0.50
Si	1.42	-1.26	1.78	1.46	1.35	1.07	1.24	2.00	1.76	1.48
P	0.74	-1.90	1.23	1.01	0.92	0.63	0.79	1.60	1.21	1.01
S	2.10	-1.20	2.43	2.34	2.15	1.71	1.95	2.91	2.42	2.33
Cl	3.69	-0.31	3.74	3.73	3.46	2.92	3.21	4.34	3.73	3.72
Ar	-2.81	-5.19	-3.06	-3.59	-3.46	-3.48	-3.43	-2.86	-3.03	-3.51
CH_3	-0.07	-2.78	0.38	0.36	0.20	-0.17	0.03	0.83	0.38	0.35
CH_4	-0.62	-1.97	-0.83	-1.05	-0.99	-0.92	-0.95	-0.67	-0.83	-1.03
NH	0.33	-3.16	0.67	0.60	0.37	-0.14	0.13	1.24	0.68	0.60
NH_2	0.74	-2.84	1.04	1.03	0.78	0.27	0.55	1.66	1.04	1.03
NH_3	-0.56	-2.18	-0.78	-1.02	-0.97	-0.90	-0.92	-0.61	-0.78	-1.00
OH	1.83	-2.56	1.83	1.84	1.56	0.96	1.28	2.65	1.85	1.88
H_2O	-0.56	-2.44	-0.76	-1.02	-0.97	-0.94	-0.94	-0.57	-0.76	-1.00
HF	-0.63	-2.65	-0.76	-1.04	-1.00	-1.00	-0.98	-0.56	-0.77	-1.01
SiH_3	0.93	-1.61	1.27	1.18	1.09	0.81	0.96	1.63	1.26	1.19
SiH_4	-1.11	-2.02	-0.97	-1.20	-1.13	-1.05	-1.09	-0.80	-0.96	-1.17
PH_3	-1.21	-1.95	-0.77	-1.05	-0.97	-0.88	-0.92	-0.60	-0.76	-1.01
SH_2	-0.49	-2.05	-0.69	-0.95	-0.88	-0.82	-0.84	-0.51	-0.68	-0.93
HCl	-0.52	-2.37	-0.63	-0.91	-0.85	-0.85	-0.83	-0.43	-0.63	-0.88
HCCH	-1.90	-1.81	-0.88	-1.10	-1.04	-0.96	-0.99	-0.73	-0.88	-1.08
CH_2CH_2	-1.86	-2.05	-1.59	-1.22	-1.17	-1.09	-1.12	-0.85	-1.00	-1.20
CH_3CH_3	-0.62	-1.89	-0.87	-1.09	-1.03	-0.95	-0.99	-0.70	-0.87	-1.07
HCN	-0.48	-2.32	-1.75	-0.81	-0.77	-0.79	-0.76	-0.39	-0.57	-0.78
CO	-1.50	-3.73	-1.45	-1.77	-1.79	-1.93	-1.83	-1.11	-1.46	-1.75
HCO	0.02	-2.94	0.24	0.22	0.06	-0.33	-0.12	0.84	0.24	0.23
CH_2O	-0.55	-2.45	-0.76	-1.02	-1.12	-1.40	-1.25	-0.31	-0.77	-0.99
CH_3OH	-0.55	-1.89	-0.73	-0.94	-0.90	-0.84	-0.86	-0.56	-0.73	-0.93
N_2	-2.24	-5.45	-2.13	-2.35	-2.50	-2.88	-2.67	-1.61	-2.16	-2.33
NH_2NH_2	-0.45	-2.11	-0.64	-0.89	-0.84	-0.81	-0.81	-0.46	-0.64	-0.87
NO	-0.42	-4.30	-0.24	-0.40	-0.61	-1.12	-0.84	0.49	-0.23	-0.37
O_2	-0.08	-4.58	-0.18	-0.26	-0.50	-1.08	-0.77	0.65	-0.17	-0.22
HOOH	-0.92	-2.40	-1.25	-1.17	-1.11	-1.06	-1.07	-0.72	-0.92	-1.15
F_2	0.42	-4.43	0.05	0.01	-0.17	-0.73	-0.43	1.27	0.20	0.18
CO_2	-0.65	-2.60	-1.03	-1.28	-1.22	-1.19	-1.19	-0.77	-1.02	-1.26

P_2	0.48	-2.13	1.05	0.89	0.72	0.35	0.55	1.37	1.03	0.87
S_2	1.53	-1.67	1.83	1.72	1.54	1.12	1.35	2.31	1.81	1.72
Cl_2	0.75	-2.20	0.99	0.86	0.68	0.28	0.49	1.50	0.99	0.87
NaCl	0.65	-0.83	0.87	0.62	0.65	0.65	0.67	1.10	0.88	0.65
SiO	0.03	-2.35	0.33	0.07	-0.01	-0.25	-0.11	0.60	0.31	0.07
CS	-0.09	-3.00	0.46	0.26	0.11	-0.32	-0.09	0.90	0.44	0.25
ClO	2.19	-1.97	2.23	2.18	1.95	1.41	1.71	3.00	2.24	2.22
ClF	0.44	-2.95	0.53	0.41	0.22	-0.23	0.02	1.16	0.56	0.45
SiH_3SiH_3	-0.69	-1.95	-1.10	-1.14	-1.07	-1.00	-1.03	-0.73	-0.91	-1.12
CH_3Cl	-0.51	-1.96	-0.65	-0.87	-0.81	-0.76	-0.78	-0.47	-0.65	-0.85
CH_3SH	-0.50	-1.90	-0.70	-0.93	-0.86	-0.80	-0.83	-0.53	-0.70	-0.91
SO_2	0.81	-2.78	1.17	1.01	0.80	0.29	0.57	1.76	1.16	1.03
BF_3	-1.04	-2.44	-1.01	-1.31	-1.24	-1.18	-1.20	-0.78	-1.01	-1.28
BCl_3	-0.17	-2.98	-0.90	0.23	0.10	-0.31	-0.10	0.90	0.48	0.22
$AlCl_3$	0.06	-1.61	0.13	-0.13	-0.07	-0.12	-0.09	0.41	0.15	-0.15
CF_4	-1.33	-2.98	-1.72	-1.96	-1.90	-1.83	-1.86	-1.47	-1.71	-1.94
CCl_4	-0.46	-2.11	-0.09	-0.14	-0.19	-0.35	-0.26	0.33	-0.08	-0.12
OCS	-0.74	-2.47	-1.10	-1.13	-1.27	-1.37	-1.42	-0.89	-0.94	-1.13
CS_2	0.01	-2.59	0.66	0.45	0.30	-0.10	0.12	1.08	0.64	0.45
CF_2O	-2.37	-2.74	-1.24	-1.51	-1.44	-2.41	-1.41	-0.98	-1.23	-1.48
SiF_4	-0.81	-2.48	-1.05	-1.36	-1.27	-1.23	-1.24	-0.75	-1.04	-1.33
N_2O	-2.01	-3.27	-1.62	-2.18	-2.34	-2.74	-2.52	-1.40	-1.61	-1.87
NF_3	-2.06	-4.45	-2.61	-2.82	-2.81	-3.05	-2.97	-2.30	-2.62	-2.86
PF_3	-1.23	-2.59	-1.31	-1.60	-1.54	-1.49	-1.50	-1.13	-1.34	-1.58
O_3	1.93	-2.29	2.49	2.39	2.16	1.55	1.88	3.47	2.54	2.47
F_2O	-0.31	-4.52	-0.41	-0.44	-0.63	-1.16	-0.87	0.62	-0.33	-0.33
ClF_3	1.20	-2.61	1.35	1.25	1.02	0.51	0.79	2.14	1.38	1.31
CF_2CF_2	-1.65	-2.65	-1.38	-1.67	-1.60	-1.54	-1.56	-1.12	-1.38	-1.65
CF_3CN	-0.96	-2.69	-1.28	-1.45	-1.60	-1.90	-1.74	-1.06	-1.28	-1.49
CH_3CCH	-1.13	-1.66	-0.74	-0.94	-0.89	-0.82	-0.85	-0.57	-0.74	-0.92
CH_2CCH_2	-0.56	-1.82	-1.39	-1.10	-1.06	-0.98	-1.01	-0.75	-0.91	-1.08
$cylC_3H_4$	-1.82	-1.88	-1.54	-1.12	-1.07	-1.00	-1.03	-0.77	-0.92	-1.10
$cylC_3H_6$	-0.65	-1.97	-1.00	-1.22	-1.17	-1.09	-1.12	-0.84	-1.00	-1.20
$CH_3CH_2CH_3$	-0.60	-1.77	-0.87	-1.10	-1.04	-0.96	-1.00	-0.70	-0.87	-1.08
CH_3CCCH_3	-0.67	-1.61	-0.82	-1.01	-0.97	-0.89	-0.93	-0.64	-0.82	-0.99
$cylC_4H_6$	-1.41	-1.81	-0.88	-1.14	-1.08	-1.01	-1.04	-0.77	-0.92	-1.12
isobutane	-0.56	-1.69	-0.83	-1.04	-0.99	-0.91	-0.95	-0.66	-0.83	-1.02
benzene	-0.71	-1.60	-1.00	-1.08	-1.03	-0.94	-0.98	-0.68	-0.87	-1.06
CH_2F_2	-0.58	-2.09	-0.78	-1.00	-0.95	-0.91	-0.92	-0.61	-0.78	-0.98
CF_3H	-0.60	-2.43	-0.78	-1.02	-0.99	-1.01	-0.98	-0.60	-0.79	-1.00
CH_2Cl_2	-0.49	-2.07	-0.61	-0.84	-0.78	-0.74	-0.75	-0.43	-0.61	-0.82
CCl_3H	-0.83	-2.25	-0.57	-0.82	-0.75	-0.74	-0.74	-0.37	-0.57	-0.80
CH_3NO_2	-0.37	-2.09	0.13	-0.01	-0.21	-0.66	-0.43	0.84	0.12	0.02
CH_3SiH_3	-0.53	-1.88	-0.76	-0.97	-0.91	-0.84	-0.87	-0.60	-0.76	-0.96
HCOOH	-0.57	-2.06	-1.70	-1.02	-0.98	-1.00	-0.96	-0.57	-0.76	-0.99
CH_3CONH_2	-0.31	-1.66	-0.42	-0.66	-0.60	-0.55	-0.57	-0.24	-0.42	-0.64

cylNHC$_2$H$_4$	-0.56	-1.90	-0.74	-0.97	-0.92	-0.87	-0.88	-0.58	-0.75	-0.95
NCCN	-0.19	-3.15	0.36	0.17	0.01	-0.39	-0.17	0.84	0.34	0.18
CH$_3$NHCH$_3$	-0.56	-1.71	-0.78	-0.98	-0.93	-0.86	-0.89	-0.61	-0.78	-0.96
CH$_2$CO	-0.51	-2.45	-1.07	-1.00	-1.33	-1.29	-1.31	-0.61	-0.79	-0.98
cylOC$_2$H$_4$	-0.86	-1.94	-0.86	-1.06	-1.01	-0.95	-0.97	-0.69	-0.86	-1.04
OCHCHO	0.69	-2.24	1.22	1.05	0.90	0.50	0.72	1.73	1.21	1.06
CH$_3$CH$_2$OH	-0.53	-1.82	-0.70	-0.92	-0.87	-0.81	-0.83	-0.53	-0.70	-0.90
CH$_3$OCH$_3$	-0.58	-1.77	-0.81	-1.02	-0.97	-0.90	-0.93	-0.64	-0.81	-1.00
cylSC$_2$H$_4$	-0.78	-1.93	-0.82	-1.03	-0.98	-0.91	-0.94	-0.66	-0.82	-1.02
CH$_3$SOCH$_3$	-0.40	-1.67	-0.53	-0.77	-0.71	-0.68	-0.68	-0.35	-0.53	-0.75
CH$_2$CHF	-0.88	-2.03	-1.70	-1.08	-1.03	-0.99	-1.00	-0.70	-0.86	-1.06
CH$_3$CH$_2$Cl	-0.51	-1.86	-0.69	-0.91	-0.86	-0.80	-0.82	-0.52	-0.69	-0.89
CH$_2$CHCl	-1.11	-1.91	-0.77	-1.00	-0.94	-0.90	-0.91	-0.61	-0.77	-0.98
CH$_3$CClO	-0.85	-1.99	-0.57	-0.79	-0.73	-0.68	-0.70	-0.39	-0.57	-0.77
prplCl	-0.48	-1.73	-0.67	-0.88	-0.83	-0.76	-0.79	-0.50	-0.67	-0.87
NC$_3$H$_9$	-0.54	-1.64	-0.80	-1.00	-0.95	-0.88	-0.91	-0.63	-0.79	-0.98
cylOC$_4$H$_4$	-0.74	-1.68	-1.58	-1.03	-0.98	-0.91	-0.94	-0.66	-0.81	-1.01
cylNHC$_4$H$_4$	-0.51	-1.70	-0.53	-0.78	-0.72	-0.69	-0.69	-0.36	-0.53	-0.76
NO$_2$	1.44	-2.44	1.52	1.51	1.31	0.77	1.05	2.34	1.53	1.53
SF$_6$	-1.05	-2.85	-0.94	-1.03	-1.10	-1.29	-1.18	-0.30	-0.90	-0.94
CFCl$_3$	-0.68	-2.43	-0.39	-0.50	-0.55	-0.73	-0.63	0.05	-0.39	-0.47
CClF$_3$	-1.06	-2.76	-1.31	-1.60	-1.54	-1.56	-1.53	-1.07	-1.30	-1.56
CBrF$_3$	-0.81	-2.73	-0.82	-1.11	-1.13	-1.27	-1.18	-0.42	-0.83	-1.07
HCCF	-0.55	-1.91	-0.70	-0.90	-0.86	-0.82	-0.83	-0.55	-0.70	-0.88
HCCCN	-0.36	-1.90	-0.16	-0.36	-0.49	-0.80	-0.62	0.25	-0.17	-0.35
NCCCCN	0.68	-1.75	1.40	1.20	1.06	0.72	0.91	1.82	1.38	1.22
C$_2$N$_2$	-0.19	-3.15	0.36	0.17	0.01	-0.39	-0.17	0.84	0.34	0.18
C$_3$O$_2$	-0.74	-3.04	-0.28	-0.48	-0.67	-1.11	-0.86	0.26	-0.30	-0.46
FCN	-0.66	-2.50	-0.71	-0.99	-0.93	-0.93	-0.91	-0.43	-0.71	-0.97
HCCCCH	-0.64	-1.62	-0.73	-0.88	-1.04	-0.80	-1.14	-0.59	-0.73	-0.86
H$_2$CS	0.28	-2.64	-0.73	0.65	0.47	0.04	0.27	1.26	0.83	0.64
HCONH$_2$	-0.35	-1.94	-0.48	-0.72	-0.67	-0.65	-0.65	-0.29	-0.48	-0.70
CH$_2$CHCHO	-0.46	-2.88	0.33	0.15	-0.01	-0.38	-0.17	0.77	0.32	0.15
CH$_2$CCl$_2$	-1.07	-1.96	-0.77	-0.99	-0.93	-1.16	-0.90	-0.61	-0.77	-0.97
CHFCF$_2$	-0.54	-2.22	-0.79	-1.03	-0.99	-0.98	-0.97	-0.60	-0.79	-1.00
CH$_2$CF$_2$	-1.03	-2.08	-0.86	-1.07	-1.02	-0.97	-0.98	-0.68	-0.86	-1.05
CH$_3$F	-0.58	-1.99	-0.77	-0.98	-0.93	-0.87	-0.89	-0.61	-0.77	-0.96
CF$_2$Cl$_2$	-0.90	-2.64	-1.01	-1.19	-1.21	-1.29	-1.25	-0.59	-1.00	-1.16
SiF$_2$	0.10	-2.36	0.46	0.19	0.09	-0.19	-0.03	0.73	0.44	0.18
MSE		-2.03	0.00	-0.13	-0.17	-0.32	-0.23	0.40	0.08	-0.10
MAE		2.03	0.34	0.34	0.32	0.39	0.33	0.47	0.30	0.33
rms		2.30	0.43	0.43	0.41	0.51	0.44	0.62	0.38	0.41

Table B.16: The frontier orbital energies (in eV) of the EA131 database calculated from -LUMO(N). The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	0.75	-0.51	-0.53	-0.52	-0.53	-0.53	-0.53	-0.50	-0.53	-0.52
He	-2.63	-2.29	-4.17	-4.55	-4.64	-4.30	-4.37	-3.79	-4.17	-4.36
Li	0.62	1.34	1.28	-0.28	-0.27	0.35	-0.24	1.47	-0.23	-0.27
Be	-0.36	2.02	-0.49	-0.67	-0.54	-0.29	-0.43	-0.22	-0.50	-0.63
B	0.25	3.62	0.13	-0.15	0.12	0.57	0.32	0.38	0.11	-0.13
C	1.25	5.59	1.41	1.00	1.38	1.98	1.65	1.58	1.36	1.03
N	-0.22	4.15	-0.15	-0.15	0.06	0.51	0.22	0.26	-0.20	-0.20
O	1.45	6.50	1.76	1.70	1.94	2.48	2.16	1.93	1.60	1.63
F	3.44	9.33	4.27	4.13	4.32	4.90	4.56	4.09	3.91	3.94
Ne	-5.31	-3.59	-6.98	-7.25	-7.18	-6.84	-7.00	-6.31	-6.95	-7.16
Na	0.54	1.45	0.04	-0.29	-0.29	-0.24	-0.27	1.28	0.03	-0.29
Mg	-0.23	1.34	-0.41	-0.59	-0.54	-0.38	-0.45	-0.20	-0.42	-0.54
Al	0.45	2.76	0.12	-0.08	0.07	0.36	0.20	0.33	0.10	-0.06
Si	1.42	4.37	1.12	0.87	1.11	1.55	1.31	1.30	1.10	0.90
P	0.74	3.73	0.35	0.55	0.84	1.21	0.97	1.04	0.32	0.54
S	2.10	5.64	1.76	2.01	2.34	2.79	2.51	2.28	1.72	2.00
Cl	3.69	7.75	3.51	3.65	4.03	4.58	4.26	3.93	3.47	3.66
Ar	-2.81	-0.84	-3.49	-3.74	-3.61	-3.41	-3.51	-2.90	-3.47	-3.65
CH_3	-0.07	2.95	-0.74	-0.55	-0.29	0.04	-0.19	-0.11	-0.75	-0.58
CH_4	-0.62	0.31	-1.07	-1.26	-1.36	-1.16	-1.20	-0.79	-1.07	-1.17
NH	0.33	4.32	0.03	0.12	0.38	0.83	0.55	0.49	-0.02	0.09
NH_2	0.74	4.54	2.17	0.36	0.64	1.11	0.82	0.67	0.16	0.34
NH_3	-0.56	0.66	-1.05	-1.28	-1.35	-1.12	-1.17	-0.71	-1.05	-1.17
OH	1.83	6.46	1.70	1.72	1.98	2.53	2.20	1.91	1.55	1.67
H_2O	-0.56	0.85	-1.04	-1.28	-1.35	-1.10	-1.16	-0.68	-1.04	-1.17
HF	-0.63	0.87	-1.03	-1.27	-1.36	-1.11	-1.17	-0.69	-1.04	-1.16
SiH_3	0.93	3.54	0.34	1.11	1.18	1.31	1.15	1.01	0.34	0.97
SiH_4	-1.11	0.37	-1.23	-1.45	-1.48	-1.28	-1.33	-0.89	-1.22	-1.35
PH_3	-1.21	0.61	-1.04	-1.27	-1.28	-1.09	-1.14	-0.70	-1.04	-1.17
SH_2	-0.49	0.79	-0.99	-1.22	-1.23	-1.03	-1.08	-0.65	-0.99	-1.12
HCl	-0.52	1.08	-0.98	-1.19	-1.20	-0.99	-1.06	-0.65	-0.98	-1.10
HCCH	-1.90	0.40	-1.10	-1.27	-1.38	-1.21	-1.23	-0.87	-1.10	-1.19
CH_2CH_2	-1.86	1.12	-1.25	-1.46	-1.55	-1.35	-1.38	-0.95	-1.25	-1.36
CH_3CH_3	-0.62	0.38	-1.09	-1.29	-1.38	-1.18	-1.22	-0.80	-1.09	-1.20
HCN	-0.48	1.11	-0.96	-1.14	-1.26	-1.08	-1.10	-0.71	-0.96	-1.05
CO	-1.50	2.01	-1.57	-1.77	-1.54	-1.08	-1.34	-1.28	-1.61	-1.75
HCO	0.02	3.46	-0.22	-0.14	0.12	0.57	0.31	0.26	-0.25	-0.15
CH_2O	-0.55	2.68	-0.98	-1.16	-0.92	-0.46	-0.72	-0.71	-1.03	-1.15
CH_3OH	-0.55	0.61	-0.99	-1.18	-1.28	-1.08	-1.12	-0.70	-0.99	-1.09
N_2	-2.24	1.96	-1.92	-2.10	-1.81	-1.29	-1.58	-1.70	-1.98	-2.11

NH_2NH_2	-0.45	0.91	-0.96	-1.20	-1.25	-1.01	-1.07	-0.61	-0.96	-1.09
NO	-0.42	4.25	0.14	-0.03	0.29	0.87	0.54	0.29	0.04	-0.07
O_2	-0.08	4.53	0.35	0.24	0.56	1.13	0.79	0.47	0.21	0.17
HOOH	-0.92	1.68	-1.18	-1.42	-1.50	-1.25	-1.31	-0.83	-1.18	-1.31
F_2	0.42	5.87	1.56	1.37	1.59	2.15	1.82	1.41	1.30	1.19
CO_2	-0.65	0.86	-1.29	-1.50	-1.55	-1.30	-1.37	-0.88	-1.29	-1.40
P_2	0.48	3.43	0.58	0.42	0.62	0.95	0.75	0.83	0.55	0.43
S_2	1.53	4.53	1.36	1.29	1.54	1.94	1.70	1.73	1.32	1.31
Cl_2	0.75	4.27	0.77	0.63	0.89	1.34	1.08	1.03	0.73	0.65
NaCl	0.65	2.26	0.58	0.38	0.28	0.45	0.42	0.87	0.58	0.47
SiO	0.03	2.86	-0.03	-0.20	-0.01	0.33	0.14	0.27	-0.06	-0.18
CS	-0.09	3.42	0.07	-0.12	0.12	0.55	0.30	0.29	0.03	-0.11
ClO	2.19	5.98	2.11	2.04	2.28	2.79	2.49	2.29	1.99	2.00
ClF	0.44	4.46	0.66	0.53	0.79	1.27	0.99	0.87	0.59	0.51
SiH_3SiH_3	-0.69	0.61	-1.16	-1.38	-1.38	-1.19	-1.25	-0.82	-1.16	-1.29
CH_3Cl	-0.51	0.87	-0.96	-1.15	-1.22	-1.02	-1.07	-0.66	-0.96	-1.06
CH_3SH	-0.50	0.83	-0.99	-1.19	-1.24	-1.03	-1.09	-0.68	-0.99	-1.10
SO_2	0.81	4.42	1.10	0.95	1.20	1.66	1.40	1.37	1.03	0.95
BF_3	-1.04	0.75	-1.25	-1.49	-1.56	-1.32	-1.37	-0.86	-1.25	-1.37
BCl_3	-0.17	2.74	-0.41	-0.67	-0.43	-0.03	-0.27	-0.20	-0.45	-0.68
$AlCl_3$	0.06	2.23	-0.43	-0.51	-0.39	-0.18	-0.32	-0.01	-0.42	-0.50
CF_4	-1.33	0.04	-1.96	-2.23	-2.31	-2.04	-2.10	-1.54	-1.95	-2.09
CCl_4	-0.46	2.76	-0.73	-0.79	-0.56	-0.14	-0.38	-0.42	-0.73	-0.76
OCS	-0.74	1.94	-1.25	-1.45	-1.21	-0.81	-1.05	-0.98	-1.29	-1.44
CS_2	0.01	2.85	0.06	-0.13	0.05	0.37	0.18	0.31	0.02	-0.12
CF_2O	-2.37	1.79	-1.50	-1.73	-1.79	-1.37	-1.60	-1.09	-1.50	-1.62
SiF_4	-0.81	1.15	-1.27	-1.49	-1.49	-1.24	-1.32	-0.83	-1.26	-1.38
N_2O	-2.01	1.57	-1.91	-2.10	-1.84	-1.37	-1.64	-1.52	-1.96	-2.08
NF_3	-2.06	1.03	-2.82	-3.05	-2.85	-2.36	-2.64	-2.45	-2.86	-3.02
PF_3	-1.23	0.88	-1.62	-1.82	-1.82	-1.54	-1.65	-1.30	-1.62	-1.73
O_3	1.93	6.24	2.89	2.74	3.00	3.48	3.20	3.18	2.80	2.71
F_2O	-0.31	4.32	0.19	0.02	0.28	0.82	0.50	0.21	0.01	-0.10
ClF_3	1.20	4.88	1.30	1.18	1.43	1.91	1.63	1.56	1.21	1.16
CF_2CF_2	-1.65	0.50	-1.63	-1.87	-1.91	-1.67	-1.74	-1.20	-1.63	-1.76
CF_3CN	-0.96	1.96	-1.55	-1.73	-1.48	-1.03	-1.29	-1.15	-1.55	-1.68
CH_3CCH	-1.13	0.45	-0.98	-1.16	-1.25	-1.07	-1.10	-0.71	-0.98	-1.07
CH_2CCH_2	-0.56	0.85	-1.14	-1.33	-1.42	-1.22	-1.26	-0.84	-1.14	-1.24
cylC_3H_4	-1.82	1.10	-1.18	-1.38	-1.49	-1.30	-1.33	-0.92	-1.18	-1.28
cylC_3H_6	-0.65	0.27	-1.24	-1.45	-1.54	-1.33	-1.37	-0.94	-1.23	-1.35
$CH_3CH_2CH_3$	-0.60	0.42	-1.08	-1.29	-1.36	-1.17	-1.21	-0.79	-1.08	-1.19
CH_3CCCH_3	-0.67	0.48	-1.02	-1.20	-1.29	-1.09	-1.13	-0.72	-1.02	-1.12
cylC_4H_6	-1.41	0.66	-1.15	-1.36	-1.45	-1.25	-1.29	-0.86	-1.15	-1.27
isobutane	-0.56	0.51	-1.05	-1.25	-1.32	-1.13	-1.17	-0.75	-1.05	-1.16
benzene	-0.71	1.23	-1.06	-1.26	-1.34	-1.15	-1.19	-0.77	-1.06	-1.17
CH_2F_2	-0.58	0.34	-1.07	-1.27	-1.38	-1.18	-1.22	-0.80	-1.08	-1.18
CF_3H	-0.60	0.30	-1.14	-1.34	-1.45	-1.26	-1.29	-0.86	-1.15	-1.25

CH_2Cl_2	-0.49	1.46	-0.99	-1.17	-1.20	-0.98	-1.06	-0.68	-0.99	-1.09
CCl_3H	-0.83	2.07	-1.04	-1.17	-1.08	-0.75	-0.94	-0.71	-1.04	-1.12
CH_3NO_2	-0.37	3.18	-0.28	-0.44	-0.20	0.26	-0.01	-0.06	-0.36	-0.47
CH_3SiH_3	-0.53	0.64	-1.04	-1.24	-1.30	-1.10	-1.15	-0.74	-1.04	-1.15
HCOOH	-0.57	1.51	-1.17	-1.39	-1.47	-1.25	-1.30	-0.86	-1.17	-1.29
CH_3CONH_2	-0.31	0.91	-0.78	-0.98	-1.05	-0.85	-0.90	-0.47	-0.78	-0.89
cylNHC_2H_4	-0.56	0.50	-1.07	-1.27	-1.36	-1.16	-1.20	-0.78	-1.07	-1.18
NCCN	-0.19	3.54	0.16	0.00	0.26	0.69	0.44	0.39	0.12	0.00
CH_3NHCH_3	-0.56	0.51	-1.02	-1.21	-1.29	-1.10	-1.14	-0.73	-1.01	-1.12
CH_2CO	-0.51	2.14	-1.10	-1.29	-1.33	-0.87	-1.13	-0.78	-1.09	-1.20
cylOC_2H_4	-0.86	0.32	-1.13	-1.33	-1.43	-1.23	-1.26	-0.84	-1.13	-1.24
OCHCHO	0.69	4.44	0.84	0.69	0.96	1.43	1.15	1.05	0.78	0.67
CH_3CH_2OH	-0.53	0.62	-0.99	-1.19	-1.28	-1.08	-1.12	-0.70	-0.99	-1.10
CH_3OCH_3	-0.58	0.45	-1.06	-1.26	-1.34	-1.14	-1.18	-0.76	-1.06	-1.17
cylSC_2H_4	-0.78	0.97	-1.13	-1.34	-1.41	-1.21	-1.25	-0.84	-1.13	-1.24
CH_3SOCH_3	-0.40	0.67	-0.88	-1.08	-1.16	-0.97	-1.00	-0.57	-0.88	-0.99
CH_2CHF	-0.88	1.02	-1.17	-1.38	-1.48	-1.28	-1.31	-0.89	-1.17	-1.28
CH_3CH_2Cl	-0.51	0.67	-1.01	-1.20	-1.28	-1.08	-1.12	-0.71	-1.01	-1.11
CH_2CHCl	-1.11	1.45	-1.10	-1.30	-1.39	-1.20	-1.23	-0.82	-1.10	-1.21
CH_3CClO	-0.85	2.34	-0.91	-1.10	-1.09	-0.64	-0.90	-0.59	-0.91	-1.01
prplCl	-0.48	0.81	-0.97	-1.17	-1.23	-1.03	-1.08	-0.67	-0.97	-1.08
NC_3H_9	-0.54	0.55	-1.02	-1.22	-1.28	-1.09	-1.13	-0.72	-1.02	-1.13
cylOC_4H_4	-0.74	0.87	-1.10	-1.29	-1.39	-1.20	-1.23	-0.82	-1.10	-1.20
cylNHC_4H_4	-0.51	0.57	-0.95	-1.15	-1.24	-1.04	-1.08	-0.67	-0.95	-1.05
NO_2	1.44	5.08	2.84	1.45	1.71	2.18	1.90	1.87	1.41	1.43
SF_6	-1.05	2.43	-1.14	-1.31	-1.13	-0.69	-0.93	-0.74	-1.14	-1.22
$CFCl_3$	-0.68	2.49	-0.95	-1.06	-0.82	-0.40	-0.65	-0.64	-0.96	-1.02
$CClF_3$	-1.06	1.32	-1.71	-1.97	-1.88	-1.52	-1.70	-1.31	-1.70	-1.85
$CBrF_3$	-0.81	1.92	-1.25	-1.46	-1.25	-0.86	-1.08	-0.88	-1.27	-1.41
HCCF	-0.55	0.67	-1.00	-1.16	-1.26	-1.09	-1.12	-0.75	-1.00	-1.09
HCCCN	-0.36	2.67	-0.54	-0.69	-0.46	-0.07	-0.30	-0.28	-0.57	-0.68
NCCCCN	0.68	3.97	0.92	0.76	0.99	1.37	1.15	1.16	0.88	0.77
C_2N_2	-0.19	3.54	0.16	0.00	0.26	0.69	0.44	0.39	0.12	0.00
C_3O_2	-0.74	2.55	-0.49	-0.68	-0.44	-0.05	-0.28	-0.24	-0.54	-0.68
FCN	-0.66	1.51	-1.03	-1.23	-1.23	-0.95	-1.06	-0.62	-1.03	-1.14
HCCCCH	-0.64	1.84	-0.95	-1.10	-1.18	-0.82	-1.03	-0.72	-0.95	-1.03
H_2CS	0.28	3.62	0.35	0.19	0.41	0.81	0.57	0.60	0.32	0.20
$HCONH_2$	-0.35	0.77	-0.87	-1.08	-1.17	-0.95	-1.00	-0.55	-0.87	-0.98
CH_2CHCHO	-0.46	3.07	-0.26	-0.40	-0.18	0.23	-0.01	-0.03	-0.30	-0.41
CH_2CCl_2	-1.07	1.70	-1.16	-1.35	-1.33	-0.99	-1.19	-0.85	-1.15	-1.26
$CHFCF_2$	-0.54	0.77	-1.15	-1.35	-1.45	-1.25	-1.29	-0.85	-1.15	-1.26
CH_2CF_2	-1.03	0.75	-1.18	-1.38	-1.47	-1.27	-1.31	-0.87	-1.18	-1.28
CH_3F	-0.58	0.35	-1.04	-1.23	-1.34	-1.14	-1.18	-0.76	-1.04	-1.14
CF_2Cl_2	-0.90	1.97	-1.40	-1.57	-1.35	-0.93	-1.17	-1.05	-1.40	-1.51
SiF_2	0.10	3.01	0.02	-0.13	0.07	0.43	0.22	0.33	-0.01	-0.13

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MSE		2.43	-0.19	-0.38	-0.31	0.01	-0.15	0.10	-0.25	-0.34
MAE		2.45	0.42	0.49	0.52	0.54	0.49	0.30	0.39	0.44
rms		2.72	0.51	0.59	0.62	0.63	0.57	0.40	0.47	0.53

Table B.17: The fundamental gaps (in eV) of the FG131 database calculated from vertical IP - vertical EA. The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	12.86	12.95	13.15	13.00	12.92	12.90	12.91	12.60	13.14	13.02
He	27.23	28.27	28.55	28.85	28.78	28.73	28.74	28.94	28.47	28.75
Li	4.22	5.06	4.07	4.91	4.81	4.85	4.88	5.05	5.10	4.99
Be	9.66	9.16	9.30	9.46	9.31	9.18	9.24	9.63	9.33	9.50
B	7.99	8.13	8.35	8.30	8.29	8.23	8.25	8.41	8.34	8.29
C	9.97	9.99	10.23	10.19	10.17	10.13	10.14	10.27	10.21	10.18
N	14.74	14.57	14.91	14.63	14.69	14.74	14.72	14.90	14.86	14.67
O	12.14	12.41	12.58	12.36	12.37	12.38	12.37	12.40	12.57	12.36
F	13.98	14.14	14.30	14.07	14.15	14.19	14.17	14.21	14.28	14.09
Ne	26.91	28.32	28.65	28.82	28.68	28.60	28.61	28.45	28.33	28.60
Na	4.14	4.80	4.75	4.35	4.30	4.44	4.45	4.83	4.76	4.49
Mg	7.76	7.76	7.68	8.14	8.03	7.81	7.85	8.14	7.72	8.03
Al	5.53	5.57	5.74	5.75	5.72	5.67	5.70	5.79	5.73	5.74
Si	6.73	6.74	6.89	6.89	6.86	6.82	6.84	6.92	6.87	6.89
P	9.78	9.64	9.87	9.69	9.58	9.54	9.58	9.66	9.86	9.71
S	8.23	8.28	8.46	8.38	8.34	8.33	8.35	8.46	8.45	8.40
Cl	9.30	9.33	9.47	9.36	9.35	9.35	9.37	9.47	9.46	9.40
Ar	18.65	18.70	19.11	19.33	19.19	19.09	19.15	19.18	19.05	19.34
CH_3	9.86	10.05	10.40	9.94	9.92	9.90	9.92	10.18	10.39	9.96
CH_4	15.06	14.68	15.16	15.31	15.26	15.15	15.20	15.42	15.15	15.30
NH	13.17	13.33	13.64	13.29	13.31	13.34	13.33	13.50	13.60	13.31
NH_2	11.34	11.43	7.60	11.55	11.48	11.47	11.49	11.64	11.63	11.59
NH_3	11.54	11.66	11.87	12.05	11.98	11.88	11.93	12.10	11.84	12.05
OH	11.27	11.45	11.65	11.47	11.49	11.50	11.49	11.58	11.64	11.48
H_2O	13.35	13.52	13.71	13.85	13.77	13.68	13.71	13.87	13.63	13.81
HF	16.91	17.12	17.26	17.36	17.28	17.20	17.22	17.35	17.10	17.27
SiH_3	7.95	8.04	8.35	7.96	7.97	7.96	7.97	8.19	8.34	7.98
SiH_4	14.03	12.92	13.90	14.02	13.90	13.71	13.80	14.10	13.84	14.01
PH_3	11.82	11.12	11.41	11.60	11.57	11.50	11.54	11.63	11.41	11.62
SH_2	11.00	11.00	11.27	11.43	11.39	11.32	11.36	11.44	11.24	11.43
HCl	13.36	13.34	13.56	13.71	13.67	13.60	13.63	13.75	13.53	13.71
HCCH	13.43	12.10	12.31	12.35	12.35	12.28	12.31	12.51	12.29	12.34
CH_2CH_2	12.57	11.44	12.33	11.67	11.67	11.60	11.63	11.77	11.58	11.67
CH_3CH_3	13.41	12.59	13.55	13.70	13.60	13.40	13.49	13.83	13.55	13.69

HCN	14.31	14.44	15.57	14.43	14.42	14.36	14.38	14.59	14.37	14.42
CO	15.57	15.16	15.69	15.95	15.82	15.68	15.75	16.06	15.72	16.01
HCO	9.56	9.80	10.21	9.98	9.98	9.96	9.98	10.13	10.21	10.01
CH_2O	11.56	11.31	11.83	11.94	11.88	11.82	11.85	11.91	11.80	11.94
CH_3OH	11.67	11.27	11.87	11.96	11.90	11.78	11.83	12.09	11.81	11.94
N_2	17.88	17.45	18.13	18.17	18.13	18.06	18.10	18.41	18.16	18.24
NH_2NH_2	10.29	9.95	10.57	10.72	10.65	10.51	10.57	10.83	10.56	10.73
NO	10.11	10.17	10.41	10.32	10.37	10.38	10.37	10.45	10.42	10.35
O_2	12.52	12.78	13.07	12.99	13.04	13.08	13.06	13.21	13.10	13.04
HOOH	12.65	12.07	13.17	12.96	12.92	12.79	12.84	13.15	12.81	12.96
F_2	15.53	14.91	15.31	15.27	15.34	15.37	15.36	15.45	15.31	15.31
CO_2	14.58	14.54	15.14	15.20	15.13	15.02	15.06	15.27	15.06	15.18
P_2	10.19	9.96	9.62	9.66	9.73	9.82	9.79	9.62	9.61	9.69
S_2	7.96	8.12	8.40	8.33	8.24	8.20	8.23	8.31	8.39	8.34
Cl_2	10.93	10.34	10.90	10.95	10.86	10.78	10.83	10.98	10.88	10.95
NaCl	8.64	8.56	8.52	8.67	8.69	8.65	8.66	8.71	8.49	8.65
SiO	11.60	11.22	11.51	11.61	11.58	11.51	11.55	11.72	11.50	11.64
CS	11.58	11.22	12.70	11.48	11.40	11.40	11.43	11.49	11.29	11.54
ClO	8.85	8.84	9.09	8.99	9.01	9.01	9.01	9.10	9.09	9.02
ClF	12.43	11.87	12.28	12.30	12.29	12.29	12.30	12.39	12.26	12.32
SiH_3SiH_3	11.33	11.00	11.80	11.69	11.65	11.55	11.61	11.74	11.59	11.69
CH_3Cl	12.01	11.65	12.20	12.30	12.25	12.14	12.19	12.41	12.17	12.30
CH_3SH	10.01	9.80	10.26	10.36	10.33	10.25	10.29	10.43	10.22	10.37
SO_2	11.74	11.40	12.49	11.62	11.62	11.61	11.61	11.73	11.60	11.66
BF_3	17.22	15.29	16.89	16.98	16.90	16.69	16.78	17.39	16.87	17.00
BCl_3	12.07	10.90	13.05	12.11	11.90	11.68	11.81	12.18	11.95	12.15
$AlCl_3$	12.13	10.64	12.43	12.55	12.26	11.89	12.10	12.62	12.39	12.57
CF_4	17.85	15.96	17.86	17.91	17.87	17.66	17.74	18.43	17.82	17.96
CCl_4	11.97	10.34	12.38	12.35	12.06	11.65	11.87	12.56	12.35	12.33
OCS	12.13	12.13	12.57	12.51	12.52	12.52	12.55	12.68	12.41	12.54
CS_2	10.19	10.04	9.73	9.83	9.86	9.96	9.92	9.77	9.73	9.86
CF_2O	16.08	14.19	14.99	15.06	15.02	15.60	14.95	15.14	14.90	15.03
SiF_4	16.95	15.18	17.32	17.36	17.23	16.94	17.08	17.81	17.28	17.41
N_2O	15.01	14.37	14.73	14.97	14.96	14.99	14.98	14.81	14.66	14.79
NF_3	15.76	15.19	16.31	16.41	16.36	16.27	16.33	16.59	16.27	16.44
PF_3	13.00	12.36	13.07	13.25	13.23	13.11	13.17	13.48	13.10	13.29
O_3	11.06	10.76	10.74	10.77	10.77	10.77	10.77	10.32	10.73	10.79
F_2O	13.82	13.01	13.66	13.62	13.66	13.66	13.66	13.81	13.67	13.67
ClF_3	11.79	10.98	11.71	11.72	11.70	11.64	11.68	11.89	11.71	11.74
CF_2CF_2	12.45	11.17	12.05	12.13	12.16	12.07	12.10	12.29	12.01	12.13
CF_3CN	15.39	14.47	15.49	15.52	15.49	15.43	15.47	15.66	15.45	15.50
CH_3CCH	11.69	10.77	11.20	11.22	11.22	11.13	11.17	11.38	11.17	11.22
CH_2CCH_2	10.83	10.76	11.65	11.20	11.20	11.11	11.15	11.33	11.13	11.20
cylC_3H_4	11.87	10.46	11.68	10.92	10.89	10.79	10.84	11.07	10.86	10.91
cylC_3H_6	11.64	11.51	12.05	12.11	12.07	11.96	12.01	12.23	12.03	12.10
$CH_3CH_2CH_3$	12.72	11.73	12.90	13.06	12.93	12.70	12.81	13.19	12.90	13.04

CH_3CCCH_3	10.46	9.82	10.46	10.50	10.48	10.37	10.42	10.62	10.44	10.49
cylC_4H_6	11.14	10.10	10.50	10.57	10.55	10.46	10.50	10.67	10.49	10.56
isobutane	12.28	11.30	12.44	12.61	12.50	12.28	12.38	12.68	12.40	12.59
benzene	10.16	9.79	10.76	10.38	10.36	10.26	10.30	10.46	10.31	10.37
CH_2F_2	14.15	13.11	14.11	14.23	14.19	14.04	14.10	14.57	14.11	14.24
CF_3H	15.44	14.36	15.38	15.51	15.46	15.31	15.37	15.89	15.37	15.52
CH_2Cl_2	12.18	11.19	12.51	12.59	12.41	12.13	12.27	12.75	12.45	12.59
CCl_3H	12.38	10.85	12.46	12.57	12.33	11.98	12.16	12.72	12.43	12.57
CH_3NO_2	11.94	11.07	11.67	11.97	11.91	11.82	11.87	12.05	11.94	12.00
CH_3SiH_3	12.35	11.85	12.64	12.71	12.66	12.54	12.60	12.84	12.62	12.71
HCOOH	11.98	11.81	13.22	12.37	12.31	12.21	12.24	12.46	12.19	12.35
CH_3CONH_2	10.05	9.99	11.12	10.64	10.57	10.44	10.49	10.71	10.46	10.61
cylNHC_2H_4	10.44	10.26	10.71	10.82	10.76	10.65	10.70	10.94	10.69	10.82
NCCN	13.90	13.00	13.33	13.34	13.27	13.20	13.23	13.41	13.33	13.36
CH_3NHCH_3	9.65	9.34	9.88	10.01	9.96	9.84	9.89	10.11	9.86	10.00
CH_2CO	10.32	10.43	11.02	10.78	11.05	10.92	10.99	10.93	10.68	10.79
cylOC_2H_4	11.68	11.15	11.69	11.77	11.72	11.61	11.66	11.89	11.64	11.75
OCHCHO	10.04	8.95	9.82	9.92	9.83	9.67	9.75	10.07	9.84	9.94
CH_3CH_2OH	11.38	10.74	11.53	11.65	11.58	11.44	11.50	11.78	11.49	11.63
CH_3OCH_3	10.79	10.33	11.00	11.11	11.05	10.92	10.97	11.21	10.95	11.08
cylSC_2H_4	9.93	9.59	10.01	10.11	10.09	10.01	10.05	10.19	9.98	10.11
CH_3SOCH_3	9.54	9.25	9.73	9.85	9.80	9.69	9.73	9.94	9.70	9.84
CH_2CHF	11.55	11.13	12.38	11.49	11.49	11.42	11.45	11.66	11.40	11.49
CH_3CH_2Cl	11.74	11.23	11.97	12.08	12.03	11.89	11.96	12.19	11.94	12.07
CH_2CHCl	11.35	10.51	11.02	11.09	11.03	10.90	10.96	11.22	10.99	11.08
CH_3CClO	11.97	11.11	12.69	11.98	11.90	11.76	11.83	12.07	11.83	11.95
prplCl	11.63	10.83	11.81	11.92	11.85	11.68	11.76	12.03	11.78	11.91
NC_3H_9	9.10	8.77	9.34	9.48	9.43	9.31	9.36	9.55	9.32	9.46
cylOC_4H_4	9.82	9.51	10.87	9.97	9.95	9.85	9.89	10.10	9.90	9.96
cylNHC_4H_4	8.89	8.73	9.02	9.10	9.07	8.98	9.02	9.18	9.00	9.09
NO_2	9.79	10.05	4.69	10.28	10.31	10.32	10.32	10.48	10.48	10.33
SF_6	16.98	14.22	16.57	16.59	16.50	16.24	16.37	17.03	16.60	16.59
$CFCl_3$	12.61	11.00	12.75	12.76	12.51	12.16	12.35	12.91	12.72	12.75
$CClF_3$	14.27	13.64	14.59	14.75	14.67	14.52	14.59	14.81	14.55	14.73
$CBrF_3$	12.97	12.45	13.07	13.16	13.11	13.02	13.08	13.24	13.07	13.22
HCCF	12.04	11.78	12.11	12.14	12.15	12.09	12.11	12.37	12.09	12.14
HCCCN	12.20	11.48	12.03	12.06	12.01	11.93	11.97	12.12	12.03	12.07
NCCCCN	11.52	10.42	10.92	10.94	10.86	10.77	10.82	11.02	10.92	10.95
C_2N_2	13.90	13.00	13.33	13.34	13.27	13.20	13.23	13.41	13.33	13.36
C_3O_2	11.64	11.44	11.23	11.30	11.33	11.40	11.37	11.29	11.23	11.32
FCN	14.33	13.91	14.36	14.39	14.38	14.30	14.33	14.49	14.32	14.40
HCCCCH	11.00	10.38	11.18	10.97	11.16	10.86	11.12	11.22	10.97	10.97
H_2CS	9.18	8.87	10.23	8.85	8.88	8.93	8.92	8.85	8.76	8.88
$HCONH_2$	10.81	10.70	11.54	11.13	11.07	10.97	11.01	11.20	10.94	11.11
CH_2CHCHO	10.70	9.79	10.10	10.18	10.13	10.07	10.10	10.20	10.08	10.19
CH_2CCl_2	11.17	10.20	10.92	10.99	10.91	10.86	10.84	11.13	10.89	10.98

$CHFCF_2$	11.11	10.75	11.25	11.32	11.34	11.27	11.29	11.56	11.23	11.32
CH_2CF_2	11.81	11.11	11.55	11.61	11.62	11.54	11.57	11.82	11.52	11.61
CH_3F	14.09	13.38	14.12	14.22	14.17	14.04	14.09	14.44	14.08	14.20
CF_2Cl_2	13.33	12.16	13.67	13.74	13.54	13.25	13.41	13.81	13.64	13.73
SiF_2	11.04	10.66	10.74	11.07	11.02	10.96	10.99	11.13	10.79	11.11
MSE		-0.46	0.10	0.13	0.08	-0.01	0.03	0.23	0.05	0.13
MAE		0.57	0.44	0.32	0.29	0.27	0.28	0.39	0.30	0.32
rms		0.76	0.74	0.42	0.40	0.38	0.39	0.47	0.39	0.41

Table B.18: The fundamental gaps (in eV) of the FG131 database calculated from HOMO(N+1) - HOMO(N). The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	12.86	9.56	10.86	10.54	10.41	10.21	10.34	10.92	10.87	10.63
He	27.23	21.82	25.03	25.22	25.05	24.53	24.77	26.15	25.15	25.34
Li	4.22	4.10	3.61	4.63	4.57	4.51	4.59	4.86	4.82	4.69
Be	9.66	7.50	8.98	9.21	8.97	8.69	8.86	9.22	9.01	9.23
B	7.99	6.31	7.41	7.46	7.32	7.09	7.21	7.57	7.40	7.44
C	9.97	8.16	9.05	9.08	8.98	8.83	8.90	9.22	9.04	9.08
N	14.74	11.81	13.01	12.83	12.84	12.76	12.82	13.41	13.03	12.94
O	12.14	10.51	11.11	10.95	10.96	10.94	10.95	11.17	11.13	10.98
F	13.98	12.28	12.73	12.55	12.64	12.68	12.67	12.84	12.76	12.61
Ne	26.91	23.15	25.53	26.01	25.92	25.61	25.74	26.96	25.73	26.19
Na	4.14	3.88	4.49	4.14	4.20	4.20	4.24	4.63	4.50	4.22
Mg	7.76	6.08	7.53	7.77	7.66	7.39	7.53	7.90	7.57	7.75
Al	5.53	4.67	5.39	5.40	5.30	5.16	5.24	5.44	5.38	5.39
Si	6.73	5.87	6.45	6.47	6.37	6.24	6.32	6.50	6.44	6.47
P	9.78	8.20	9.10	9.07	8.86	8.63	8.77	9.09	9.09	9.08
S	8.23	7.35	7.88	7.74	7.67	7.59	7.66	7.92	7.87	7.79
Cl	9.30	8.45	8.86	8.72	8.69	8.64	8.68	8.90	8.85	8.76
Ar	18.65	15.49	18.06	18.48	18.01	17.40	17.71	18.63	18.04	18.47
CH_3	9.86	8.21	9.42	9.05	8.96	8.76	8.87	9.43	9.41	9.09
CH_4	15.06	11.42	14.83	14.96	14.59	13.91	14.27	15.36	14.84	14.97
NH	13.17	11.09	12.13	11.89	11.87	11.79	11.84	12.35	12.15	11.96
NH_2	11.34	10.05	8.83	10.63	10.57	10.48	10.54	10.86	10.77	10.69
NH_3	11.54	8.36	11.51	11.66	11.29	10.63	10.99	12.09	11.53	11.70
OH	11.27	9.94	10.47	10.32	10.33	10.30	10.32	10.56	10.49	10.36
H_2O	13.35	9.69	12.87	13.04	12.70	12.05	12.39	13.63	12.91	13.11
HF	16.91	12.30	15.58	15.77	15.50	14.89	15.21	16.62	15.69	15.91
SiH_3	7.95	6.98	7.87	7.60	7.50	7.35	7.44	7.83	7.86	7.63
SiH_4	14.03	10.54	13.73	13.86	13.51	12.87	13.22	14.14	13.72	13.86

PH_3	11.82	8.68	11.38	11.54	11.22	10.65	10.96	11.73	11.38	11.55
SH_2	11.00	8.36	11.11	11.25	10.89	10.29	10.62	11.45	11.09	11.26
HCl	13.36	10.43	13.09	13.28	12.90	12.30	12.61	13.53	13.08	13.28
HCCH	13.43	9.01	12.23	12.31	11.96	11.32	11.67	12.61	12.21	12.31
CH_2CH_2	12.57	8.79	12.29	11.77	11.45	10.84	11.17	12.03	11.69	11.77
CH_3CH_3	13.41	10.07	13.38	13.52	13.18	12.54	12.88	13.87	13.38	13.53
HCN	14.31	11.34	15.16	14.07	13.72	13.14	13.44	14.41	13.97	14.06
CO	15.57	12.77	15.29	15.52	15.23	14.74	14.99	15.80	15.33	15.57
HCO	9.56	8.09	9.38	9.17	9.11	8.97	9.05	9.48	9.39	9.23
CH_2O	11.56	8.71	11.44	11.60	11.48	11.23	11.37	11.82	11.48	11.65
CH_3OH	11.67	8.15	11.57	11.70	11.39	10.76	11.10	12.25	11.61	11.75
N_2	17.88	15.72	17.44	17.51	17.41	17.18	17.30	17.90	17.50	17.60
NH_2NH_2	10.29	7.41	10.37	10.55	10.21	9.61	9.93	10.94	10.40	10.59
NO	10.11	8.82	9.61	9.55	9.54	9.48	9.52	9.78	9.63	9.59
O_2	12.52	11.42	12.12	12.05	12.09	12.09	12.10	12.44	12.19	12.15
HOOH	12.65	8.85	12.59	12.41	12.09	11.44	11.79	13.03	12.30	12.49
F_2	15.53	13.92	14.70	14.63	14.65	14.63	14.65	14.82	14.67	14.65
CO_2	14.58	11.69	14.57	14.69	14.40	13.84	14.14	15.15	14.58	14.75
P_2	10.19	9.28	9.59	9.60	9.58	9.55	9.58	9.59	9.58	9.63
S_2	7.96	7.50	8.05	7.98	7.87	7.76	7.84	8.02	8.05	8.00
Cl_2	10.93	9.53	10.61	10.64	10.52	10.36	10.46	10.71	10.58	10.65
NaCl	8.64	6.13	8.46	8.63	8.31	7.75	8.04	8.85	8.46	8.62
SiO	11.60	9.83	11.26	11.37	11.26	11.02	11.16	11.64	11.29	11.44
CS	11.58	10.40	11.42	11.52	11.39	11.24	11.34	11.68	11.44	11.59
ClO	8.85	8.27	8.64	8.54	8.53	8.50	8.52	8.64	8.64	8.56
ClF	12.43	10.81	11.91	11.92	11.82	11.68	11.77	12.04	11.88	11.93
SiH_3SiH_3	11.33	9.14	12.04	11.96	11.66	11.13	11.43	12.14	11.83	11.96
CH_3Cl	12.01	9.07	12.05	12.18	11.82	11.19	11.53	12.49	12.04	12.18
CH_3SH	10.01	7.46	10.31	10.42	10.08	9.48	9.81	10.66	10.29	10.42
SO_2	11.74	10.86	11.31	11.34	11.34	11.31	11.33	11.53	11.34	11.40
BF_3	17.22	12.51	16.16	16.32	16.07	15.46	15.79	17.15	16.26	16.47
BCl_3	12.07	10.71	12.90	11.67	11.49	11.33	11.43	11.71	11.50	11.70
$AlCl_3$	12.13	9.63	12.14	12.29	11.93	11.42	11.70	12.46	12.11	12.34
CF_4	17.85	13.39	17.26	17.39	17.16	16.53	16.87	18.28	17.36	17.55
CCl_4	11.97	9.80	12.08	12.05	11.77	11.35	11.58	12.28	12.05	12.03
OCS	12.13	9.97	12.45	12.35	12.26	11.90	12.22	12.78	12.27	12.38
CS_2	10.19	9.41	9.65	9.74	9.67	9.66	9.69	9.67	9.65	9.76
CF_2O	16.08	11.26	14.57	14.71	14.41	14.80	14.12	15.28	14.60	14.78
SiF_4	16.95	13.17	16.78	16.97	16.69	16.08	16.41	17.67	16.86	17.10
N_2O	15.01	11.68	14.20	14.62	14.57	14.48	14.54	14.73	14.19	14.37
NF_3	15.76	12.90	15.82	15.95	15.71	15.38	15.61	16.50	15.85	16.07
PF_3	13.00	9.95	12.84	13.05	12.75	12.18	12.48	13.42	12.91	13.10
O_3	11.06	10.32	10.39	10.39	10.39	10.41	10.41	10.27	10.39	10.41
F_2O	13.82	12.24	13.32	13.25	13.25	13.18	13.22	13.50	13.32	13.28
ClF_3	11.79	10.61	11.43	11.43	11.42	11.37	11.40	11.60	11.42	11.46
CF_2CF_2	12.45	8.96	11.94	12.10	11.82	11.25	11.55	12.43	11.93	12.12

CF_3CN	15.39	12.27	15.33	15.35	15.20	14.90	15.07	15.78	15.31	15.41
CH_3CCH	11.69	8.15	11.29	11.35	11.03	10.42	10.75	11.64	11.27	11.35
CH_2CCH_2	10.83	8.39	11.90	11.48	11.17	10.58	10.90	11.77	11.41	11.49
cylC_3H_4	11.87	7.99	11.55	11.01	10.70	10.11	10.43	11.28	10.92	11.00
cylC_3H_6	11.64	9.04	12.25	12.33	12.00	11.37	11.71	12.67	12.24	12.33
$CH_3CH_2CH_3$	12.72	9.52	12.87	13.03	12.70	12.07	12.41	13.34	12.87	13.03
CH_3CCCH_3	10.46	7.54	10.71	10.79	10.48	9.88	10.21	11.05	10.70	10.78
cylC_4H_6	11.14	7.85	10.76	10.88	10.57	10.00	10.31	11.12	10.78	10.87
isobutane	12.28	9.27	12.57	12.72	12.40	11.78	12.12	13.04	12.57	12.72
benzene	10.16	7.93	10.83	10.78	10.51	10.00	10.28	10.94	10.68	10.77
CH_2F_2	14.15	10.24	13.63	13.76	13.49	12.88	13.20	14.40	13.68	13.83
CF_3H	15.44	11.78	14.88	15.03	14.78	14.23	14.51	15.68	14.92	15.09
CH_2Cl_2	12.18	9.45	12.28	12.42	12.07	11.45	11.78	12.72	12.27	12.43
CCl_3H	12.38	9.67	12.25	12.42	12.04	11.46	11.77	12.67	12.24	12.42
CH_3NO_2	11.94	9.01	11.51	11.54	11.51	11.39	11.47	11.75	11.56	11.61
CH_3SiH_3	12.35	9.79	12.81	12.91	12.58	11.97	12.30	13.23	12.80	12.92
HCOOH	11.98	8.79	12.96	12.17	11.89	11.36	11.63	12.70	12.04	12.23
CH_3CONH_2	10.05	7.46	10.66	10.82	10.51	9.91	10.23	11.33	10.69	10.87
cylNHC_2H_4	10.44	7.68	10.79	10.91	10.59	9.99	10.31	11.30	10.80	10.94
NCCN	13.90	12.54	13.16	13.18	13.06	12.93	13.00	13.27	13.16	13.19
CH_3NHCH_3	9.65	6.78	10.04	10.18	9.86	9.25	9.58	10.57	10.06	10.20
CH_2CO	10.32	8.36	10.93	10.72	10.83	10.30	10.59	11.06	10.64	10.74
cylOC_2H_4	11.68	8.21	11.65	11.76	11.47	10.85	11.19	12.34	11.70	11.83
OCHCHO	10.04	8.62	9.48	9.57	9.51	9.39	9.46	9.80	9.51	9.62
CH_3CH_2OH	11.38	7.97	11.40	11.54	11.23	10.61	10.94	12.06	11.43	11.59
CH_3OCH_3	10.79	7.60	11.02	11.16	10.87	10.26	10.59	11.66	11.05	11.21
cylSC_2H_4	9.93	7.30	10.20	10.29	9.96	9.37	9.69	10.56	10.18	10.30
CH_3SOCH_3	9.54	7.05	9.91	10.07	9.79	9.25	9.54	10.42	9.93	10.10
CH_2CHF	11.55	8.55	12.27	11.51	11.21	10.65	10.95	11.84	11.42	11.52
CH_3CH_2Cl	11.74	8.83	11.93	12.07	11.72	11.09	11.42	12.38	11.92	12.08
CH_2CHCl	11.35	8.34	11.07	11.18	10.86	10.31	10.61	11.43	11.06	11.17
CH_3CClO	11.97	9.12	11.94	12.06	11.77	11.20	11.51	12.51	11.95	12.09
prplCl	11.63	8.67	11.87	12.00	11.65	11.01	11.35	12.32	11.86	12.00
NC_3H_9	9.10	6.49	9.69	9.83	9.54	8.95	9.27	10.18	9.70	9.85
cylOC_4H_4	9.82	7.35	10.93	10.23	9.95	9.42	9.71	10.45	10.13	10.22
cylNHC_4H_4	8.89	6.83	9.24	9.36	9.08	8.61	8.86	9.51	9.22	9.35
NO_2	9.79	8.94	6.98	9.65	9.64	9.61	9.64	9.97	9.86	9.72
SF_6	16.98	12.98	16.18	16.14	16.06	15.70	15.89	16.80	16.24	16.23
$CFCl_3$	12.61	10.18	12.46	12.47	12.21	11.81	12.03	12.64	12.43	12.46
$CClF_3$	14.27	11.32	14.39	14.58	14.20	13.62	13.92	14.85	14.37	14.56
$CBrF_3$	12.97	10.55	12.91	12.99	12.77	12.40	12.60	13.15	12.91	13.02
HCCF	12.04	8.93	11.93	11.99	11.68	11.09	11.41	12.39	11.92	12.00
HCCCN	12.20	9.77	11.93	11.98	11.85	11.66	11.76	12.06	11.93	11.99
NCCCCN	11.52	10.19	10.84	10.87	10.77	10.64	10.71	10.97	10.84	10.88
C_2N_2	13.90	12.54	13.16	13.18	13.06	12.93	13.00	13.27	13.16	13.19
C_3O_2	11.64	10.30	11.23	11.29	11.30	11.33	11.32	11.29	11.23	11.31

FCN	14.33	11.23	13.89	14.01	13.67	13.09	13.39	14.31	13.87	14.03
HCCCCH	11.00	8.26	11.12	11.12	11.03	10.32	10.92	11.48	11.11	11.12
H_2CS	9.18	8.17	10.25	8.75	8.67	8.58	8.64	8.78	8.68	8.78
$HCONH_2$	10.81	7.96	10.94	11.11	10.82	10.24	10.55	11.63	10.98	11.17
CH_2CHCHO	10.70	8.89	10.13	10.23	10.15	9.96	10.07	10.53	10.18	10.29
CH_2CCl_2	11.17	8.40	11.07	11.16	10.85	10.59	10.60	11.42	11.04	11.15
$CHFCF_2$	11.11	8.44	11.16	11.26	11.01	10.50	10.76	11.67	11.16	11.28
CH_2CF_2	11.81	8.65	11.54	11.61	11.32	10.75	11.05	11.99	11.53	11.62
CH_3F	14.09	10.08	13.56	13.68	13.41	12.79	13.12	14.34	13.63	13.76
CF_2Cl_2	13.33	10.72	13.45	13.54	13.24	12.74	13.02	13.68	13.43	13.53
SiF_2	11.04	9.49	10.54	10.69	10.61	10.43	10.53	10.92	10.60	10.77
MSE		-2.48	-0.26	-0.22	-0.42	-0.80	-0.59	0.09	-0.27	-0.18
MAE		2.48	0.50	0.44	0.50	0.81	0.62	0.47	0.43	0.43
rms		2.69	0.70	0.59	0.65	0.93	0.77	0.57	0.57	0.57

Table B.19: The fundamental gaps (in eV) of the FG131 database calculated from KS gaps. The reference energies are taken from ref. 22 with experimental geometries.

Molecule	ref.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
H	12.86	8.11	12.74	12.43	12.15	11.59	11.91	13.18	12.74	12.50
He	27.23	18.05	25.36	25.68	25.54	24.57	24.98	26.19	25.48	25.65
Li	4.22	1.88	2.50	5.60	5.57	4.86	5.54	4.36	5.83	5.65
Be	9.66	3.59	9.41	9.43	9.17	8.58	8.92	9.55	9.44	9.44
B	7.99	0.55	8.08	8.07	7.61	6.67	7.19	8.28	8.08	8.04
C	9.97	0.52	9.28	9.37	8.75	7.59	8.23	9.73	9.32	9.38
N	14.74	4.17	13.42	13.09	12.67	11.64	12.24	13.86	13.49	13.23
O	12.14	1.10	10.84	10.68	10.18	9.01	9.67	11.46	11.03	10.80
F	13.98	0.99	11.31	11.30	10.91	9.73	10.40	12.68	11.76	11.63
Ne	26.91	16.97	25.81	25.98	25.81	24.91	25.39	26.79	26.00	26.18
Na	4.14	1.58	5.20	5.11	5.20	5.12	5.19	4.30	5.22	5.15
Mg	7.76	3.36	7.91	7.93	7.85	7.46	7.67	8.12	7.94	7.91
Al	5.53	0.33	6.09	5.96	5.70	5.11	5.46	6.06	6.08	5.95
Si	6.73	0.24	7.11	7.06	6.61	5.76	6.24	7.19	7.10	7.05
P	9.78	2.57	9.98	9.53	8.93	8.05	8.59	9.66	9.98	9.55
S	8.23	0.51	8.55	8.07	7.48	6.52	7.09	8.55	8.57	8.12
Cl	9.30	0.39	9.08	8.79	8.12	6.98	7.63	9.31	9.12	8.82
Ar	18.65	11.14	18.49	18.64	18.16	17.33	17.79	18.67	18.47	18.60
CH_3	9.86	2.48	10.54	9.96	9.44	8.55	9.09	10.37	10.54	10.02
CH_4	15.06	9.14	15.07	15.18	14.96	14.15	14.52	15.48	15.08	15.12
NH	13.17	3.60	12.78	12.36	11.86	10.81	11.42	13.10	12.84	12.47
NH_2	11.34	2.68	7.71	11.29	10.71	9.65	10.27	11.85	11.65	11.38
NH_3	11.54	5.52	11.78	11.92	11.68	10.85	11.24	12.20	11.79	11.87

OH	11.27	0.92	10.61	10.44	9.91	8.74	9.40	11.30	10.79	10.58
H_2O	13.35	6.39	13.15	13.30	13.08	12.21	12.61	13.74	13.19	13.28
HF	16.91	8.78	15.85	16.00	15.86	15.00	15.40	16.75	15.96	16.06
SiH_3	7.95	1.83	8.79	7.68	7.41	6.85	7.26	8.45	8.78	7.84
SiH_4	14.03	8.15	13.99	14.11	13.85	13.10	13.46	14.23	13.98	14.04
PH_3	11.82	6.11	11.65	11.77	11.54	10.85	11.18	11.84	11.66	11.71
SH_2	11.00	5.52	11.41	11.52	11.24	10.49	10.86	11.60	11.39	11.45
HCl	13.36	6.97	13.44	13.56	13.25	12.43	12.84	13.75	13.43	13.49
HCCH	13.43	6.80	12.45	12.48	12.30	11.58	11.91	12.75	12.44	12.42
CH_2CH_2	12.57	5.62	11.95	12.02	11.83	11.10	11.43	12.13	11.93	11.94
CH_3CH_3	13.41	7.80	13.60	13.72	13.53	12.77	13.11	13.97	13.61	13.66
HCN	14.31	7.91	14.37	14.39	14.20	13.42	13.78	14.72	14.35	14.33
CO	15.57	7.04	15.41	15.52	14.98	13.89	14.49	15.97	15.48	15.58
HCO	9.56	1.69	9.84	9.54	9.05	8.06	8.63	10.06	9.89	9.61
CH_2O	11.56	3.58	11.66	11.74	11.28	10.28	10.85	12.22	11.74	11.81
CH_3OH	11.67	5.65	11.83	11.93	11.77	11.00	11.36	12.39	11.86	11.92
N_2	17.88	8.32	17.22	17.27	16.72	15.58	16.21	18.00	17.33	17.39
NH_2NH_2	10.29	4.39	10.70	10.86	10.63	9.81	10.19	11.09	10.72	10.81
NO	10.11	0.28	9.24	9.18	8.64	7.48	8.13	9.97	9.36	9.30
O_2	12.52	2.31	11.60	11.55	11.03	9.88	10.54	12.62	11.81	11.76
HOOH	12.65	4.78	12.52	12.66	12.48	11.63	12.02	13.14	12.56	12.65
F_2	15.53	3.62	13.19	13.27	12.88	11.75	12.40	14.68	13.57	13.65
CO_2	14.58	8.23	14.84	14.91	14.73	13.95	14.32	15.26	14.84	14.89
P_2	10.19	3.71	10.06	10.06	9.69	8.95	9.39	10.13	10.05	10.06
S_2	7.96	1.30	8.52	8.41	7.87	6.94	7.48	8.60	8.53	8.40
Cl_2	10.93	3.06	10.83	10.87	10.31	9.30	9.87	11.18	10.84	10.87
NaCl	8.64	3.04	8.76	8.87	8.68	7.96	8.29	9.08	8.75	8.80
SiO	11.60	4.62	11.62	11.64	11.25	10.43	10.91	11.97	11.66	11.69
CS	11.58	3.98	11.82	11.90	11.37	10.37	10.94	12.28	11.85	11.95
ClO	8.85	0.32	8.76	8.69	8.20	7.13	7.74	9.35	8.89	8.79
ClF	12.43	3.40	11.77	11.80	11.26	10.19	10.79	12.34	11.85	11.87
SiH_3SiH_3	11.33	6.58	12.11	12.19	11.97	11.32	11.64	12.24	12.08	12.12
CH_3Cl	12.01	6.24	12.36	12.46	12.22	11.45	11.82	12.68	12.35	12.39
CH_3SH	10.01	4.74	10.59	10.69	10.45	9.72	10.07	10.80	10.58	10.62
SO_2	11.74	3.66	11.39	11.40	10.93	9.94	10.50	11.92	11.46	11.48
BF_3	17.22	9.32	16.40	16.50	16.40	15.59	15.97	17.24	16.50	16.56
BCl_3	12.07	4.98	12.41	12.58	12.02	11.05	11.60	12.80	12.43	12.60
$AlCl_3$	12.13	5.79	12.71	12.68	12.25	11.48	11.93	12.89	12.68	12.69
CF_4	17.85	10.37	17.50	17.66	17.57	16.74	17.11	18.35	17.60	17.70
CCl_4	11.97	4.93	12.72	12.69	12.15	11.14	11.71	13.03	12.70	12.67
OCS	12.13	5.56	12.60	12.67	12.21	11.34	11.84	12.87	12.62	12.69
CS_2	10.19	3.97	10.26	10.32	9.92	9.20	9.62	10.45	10.26	10.33
CF_2O	16.08	6.74	14.83	14.93	14.76	13.76	14.32	15.39	14.86	14.92
SiF_4	16.95	9.54	17.00	17.09	16.90	16.09	16.49	17.75	17.08	17.15
N_2O	15.01	6.84	14.49	14.54	14.07	13.11	13.66	14.85	14.54	14.58
NF_3	15.76	7.42	16.03	16.18	15.75	14.69	15.28	16.65	16.10	16.23

PF_3	13.00	6.48	13.16	13.26	13.04	12.24	12.64	13.59	13.19	13.26
O_3	11.06	1.79	9.99	10.04	9.55	8.49	9.09	10.57	10.13	10.18
F_2O	13.82	3.40	12.72	12.80	12.34	11.20	11.85	13.91	12.98	13.05
ClF_3	11.79	3.12	11.48	11.50	11.01	9.96	10.56	12.19	11.59	11.61
CF_2CF_2	12.45	5.81	12.20	12.30	12.13	11.38	11.73	12.51	12.19	12.23
CF_3CN	15.39	7.61	15.61	15.63	15.08	14.04	14.63	15.87	15.59	15.61
CH_3CCH	11.69	6.04	11.53	11.57	11.39	10.67	11.01	11.78	11.52	11.51
CH_2CCH_2	10.83	5.71	11.65	11.71	11.54	10.82	11.15	11.86	11.64	11.64
cylC_3H_4	11.87	5.01	11.20	11.26	11.11	10.41	10.73	11.43	11.18	11.18
cylC_3H_6	11.64	6.80	12.48	12.56	12.37	11.61	11.96	12.76	12.47	12.48
$CH_3CH_2CH_3$	12.72	7.33	13.08	13.22	13.02	12.28	12.62	13.44	13.08	13.15
CH_3CCCH_3	10.46	5.45	10.91	10.98	10.79	10.08	10.41	11.13	10.90	10.91
cylC_4H_6	11.14	5.38	11.03	11.10	10.94	10.24	10.55	11.21	11.01	11.02
isobutane	12.28	7.06	12.79	12.93	12.73	12.00	12.33	13.14	12.79	12.86
benzene	10.16	5.10	10.89	10.95	10.83	10.21	10.49	11.02	10.88	10.87
CH_2F_2	14.15	7.81	13.92	14.03	13.92	13.16	13.50	14.59	13.97	14.03
CF_3H	15.44	9.05	15.23	15.34	15.24	14.48	14.82	15.94	15.28	15.35
CH_2Cl_2	12.18	5.92	12.66	12.75	12.49	11.70	12.09	12.97	12.65	12.69
CCl_3H	12.38	5.36	12.73	12.76	12.37	11.47	11.97	13.01	12.71	12.73
CH_3NO_2	11.94	3.74	11.92	11.98	11.50	10.47	11.06	12.66	12.04	12.10
CH_3SiH_3	12.35	7.27	13.10	13.18	12.96	12.23	12.58	13.38	13.09	13.12
HCOOH	11.98	5.22	12.43	12.54	12.39	11.60	11.96	13.00	12.46	12.53
CH_3CONH_2	10.05	4.88	11.02	11.14	10.96	10.20	10.56	11.55	11.05	11.12
cylNHC_2H_4	10.44	5.28	11.11	11.21	11.03	10.28	10.63	11.49	11.12	11.17
NCCN	13.90	5.85	13.35	13.34	12.81	11.85	12.40	13.72	13.38	13.38
CH_3NHCH_3	9.65	4.55	10.28	10.40	10.22	9.49	9.83	10.69	10.29	10.36
CH_2CO	10.32	3.76	10.95	11.02	10.83	9.88	10.42	11.23	10.94	10.96
cylOC_2H_4	11.68	5.95	11.92	12.03	11.89	11.13	11.48	12.49	11.96	12.02
OCHCHO	10.04	1.94	9.87	9.93	9.45	8.46	9.02	10.48	9.95	10.01
CH_3CH_2OH	11.38	5.54	11.69	11.82	11.64	10.87	11.23	12.23	11.72	11.79
CH_3OCH_3	10.79	5.38	11.27	11.40	11.24	10.50	10.84	11.78	11.30	11.37
cylSC_2H_4	9.93	4.39	10.51	10.60	10.40	9.67	10.01	10.73	10.50	10.52
CH_3SOCH_3	9.54	4.71	10.26	10.38	10.23	9.54	9.86	10.64	10.28	10.34
CH_2CHF	11.55	5.50	11.74	11.80	11.66	10.94	11.27	12.03	11.73	11.74
CH_3CH_2Cl	11.74	6.31	12.25	12.37	12.14	11.37	11.73	12.56	12.24	12.30
CH_2CHCl	11.35	4.97	11.41	11.48	11.30	10.61	10.93	11.63	11.39	11.40
CH_3CClO	11.97	4.79	12.27	12.36	12.13	11.16	11.71	12.71	12.28	12.33
prplCl	11.63	6.14	12.17	12.29	12.05	11.28	11.64	12.48	12.16	12.22
NC_3H_9	9.10	4.30	9.91	10.05	9.87	9.16	9.49	10.28	9.92	10.00
cylOC_4H_4	9.82	4.80	10.44	10.49	10.36	9.71	10.00	10.62	10.42	10.40
cylNHC_4H_4	8.89	4.57	9.66	9.72	9.60	8.96	9.25	9.82	9.64	9.64
NO_2	9.79	1.42	5.65	9.70	9.23	8.20	8.79	10.43	9.98	9.82
SF_6	16.98	7.70	16.38	16.42	16.10	15.09	15.65	17.24	16.48	16.51
$CFCl_3$	12.61	5.26	13.02	13.03	12.48	11.48	12.04	13.34	13.01	13.01
$CClF_3$	14.27	7.24	14.79	14.94	14.55	13.59	14.10	15.09	14.77	14.86
$CBrF_3$	12.97	5.91	13.33	13.35	12.89	11.98	12.50	13.60	13.36	13.36

HCCF	12.04	6.35	12.24	12.25	12.08	11.36	11.70	12.59	12.23	12.21
HCCCN	12.20	5.19	12.31	12.31	11.83	10.94	11.44	12.59	12.32	12.32
NCCCCN	11.52	4.47	11.32	11.31	10.84	9.99	10.47	11.63	11.34	11.33
C_2N_2	13.90	5.85	13.35	13.34	12.81	11.85	12.40	13.72	13.38	13.38
C_3O_2	11.64	4.71	11.44	11.49	11.07	10.27	10.73	11.79	11.48	11.53
FCN	14.33	7.21	14.20	14.25	13.97	13.12	13.54	14.50	14.20	14.20
HCCCCH	11.00	4.80	11.34	11.34	11.18	10.34	10.81	11.61	11.32	11.29
H_2CS	9.18	1.91	9.17	9.21	8.73	7.81	8.34	9.45	9.19	9.23
$HCONH_2$	10.81	5.25	11.33	11.47	11.31	10.54	10.90	11.89	11.37	11.45
CH_2CHCHO	10.70	2.94	10.72	10.78	10.32	9.36	9.91	11.33	10.80	10.86
CH_2CCl_2	11.17	4.74	11.45	11.53	11.25	10.41	10.89	11.66	11.43	11.45
$CHFCF_2$	11.11	5.45	11.53	11.59	11.48	10.77	11.09	11.92	11.52	11.54
CH_2CF_2	11.81	5.81	11.86	11.92	11.77	11.05	11.38	12.17	11.85	11.86
CH_3F	14.09	7.74	13.83	13.93	13.81	13.05	13.40	14.49	13.89	13.95
CF_2Cl_2	13.33	6.12	13.84	13.92	13.39	12.39	12.95	14.14	13.82	13.88
SiF_2	11.04	4.13	10.98	11.02	10.63	9.81	10.28	11.32	11.05	11.08
MSE		-6.94	-0.07	0.04	-0.27	-1.12	-0.67	0.40	0.05	0.05
MAE		6.94	0.53	0.49	0.57	1.15	0.77	0.54	0.45	0.45
rms		7.15	0.80	0.65	0.77	1.40	1.02	0.63	0.59	0.60

Table B.20: The 19 valence and 23 Rydberg excitation energies (in eV) calculated by various methods. The experimental reference values are taken from ref. 91. The molecular geometries are obtained in ref. 33.

Molecule	State	Exp.	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
N_2	$V^1\Pi_g$	9.31	9.11	9.46	9.47	9.42	9.36	9.39	9.54	9.47	9.49
	$V^1\Sigma_u{}^-$	9.97	9.68	9.31	9.34	9.28	9.28	9.29	9.02	9.25	9.28
	$V^1\Delta_u$	10.27	10.10	9.89	9.83	9.80	9.80	9.80	9.73	9.89	9.83
	$V^3\Sigma_u{}^+$	7.75	7.53	6.99	7.12	7.12	7.15	7.13	6.99	7.00	7.13
	$V^3\Pi_g$	8.04	7.40	7.74	7.97	7.88	7.80	7.84	7.98	7.75	7.99
	$V^3\Delta_u$	8.88	8.35	7.95	8.28	8.20	8.21	8.21	8.07	7.94	8.28
	$V^3\Sigma_u{}^-$	9.67	9.68	9.31	9.34	9.28	9.28	9.29	9.02	9.25	9.28
	$V^3\Pi_u$	11.19	10.40	10.91	11.14	11.04	10.98	11.02	11.26	11.01	11.26
CO	$V^1\Pi$	8.51	8.23	8.52	8.55	8.50	8.45	8.48	8.59	8.54	8.58
	$V^1\Sigma^-$	9.88	9.81	9.80	9.83	9.75	9.73	9.75	9.64	9.74	9.79
	$V^3\Pi$	6.32	5.72	5.83	6.13	6.09	6.05	6.08	6.14	5.86	6.19
	$V^3\Sigma^+$	8.51	8.06	7.95	7.94	7.93	7.95	7.95	7.99	7.91	7.96
	$V^3\Delta$	9.36	8.73	8.71	8.92	8.84	8.83	8.85	8.86	8.68	8.93
	$V^3\Sigma^-$	9.88	9.81	9.80	9.83	9.75	9.73	9.74	9.64	9.74	9.79
H_2O	R^1B_1	7.4	6.31	7.42	7.51	7.43	7.21	7.28	7.64	7.43	7.49

	R^1A_2	9.1	7.44	9.06	9.18	9.07	8.62	8.80	9.46	9.08	9.16
	R^1A_1	9.7	8.18	9.54	9.64	9.56	9.20	9.35	9.84	9.58	9.66
	R^1B_1	10.0	7.83	9.70	9.81	9.68	9.16	9.37	10.30	9.73	9.80
	R^1A_1	10.17	8.50	9.91	10.04	9.91	9.50	9.64	10.50	9.95	10.03
	R^3B_1	7.2	5.98	6.96	7.09	7.06	6.87	6.92	7.18	6.95	7.07
C_2H_4	R^1B_{3u}	7.11	6.43	7.60	7.61	7.45	7.06	7.22	7.65	7.58	7.56
	V^1B_{1u}	7.60	7.34	7.74	7.69	7.66	7.58	7.62	7.70	7.74	7.69
	R^1B_{1g}	7.80	6.90	8.16	8.21	8.08	7.62	7.82	8.25	8.16	8.17
	R^1B_{2g}	8.01	6.86	8.35	8.37	8.20	7.70	7.91	8.48	8.33	8.31
	R^1A_g	8.29	7.21	8.57	8.59	8.43	7.92	8.13	8.82	8.56	8.53
	R^1B_{3u}	8.62	7.45	9.11	9.06	8.88	8.39	8.63	9.34	9.09	9.04
	V^3B_{1u}	4.36	4.33	3.68	4.03	4.10	4.20	4.16	3.88	3.69	4.05
	R^3B_{3u}	6.98	6.34	7.45	7.48	7.35	6.96	7.12	7.55	7.43	7.44
	R^3B_{1g}	7.79	6.86	8.14	8.16	8.01	7.53	7.77	8.26	8.12	8.11
	R^3B_{2g}	7.79	6.81	8.24	8.23	8.07	7.60	7.81	8.39	8.22	8.19
	R^3A_g	8.15	7.09	8.36	8.26	8.10	7.66	7.88	8.64	8.35	8.26
CH_2O	V^1A_2	4.07	3.86	3.96	4.03	4.00	4.00	4.01	3.96	3.94	4.02
	R^1B_2	7.11	5.76	7.29	7.39	7.31	6.92	7.07	7.64	7.32	7.38
	R^1B_2	7.97	6.53	8.03	8.11	8.05	7.62	7.79	8.42	8.06	8.10
	R^1A_1	8.14	7.09	9.34	9.34	9.22	8.71	8.96	9.64	9.36	9.36
	R^1A_2	8.37	6.68	8.29	8.36	8.29	7.80	8.01	8.86	8.33	8.37
	R^1B_2	8.88	6.80	9.15	9.10	8.95	8.48	8.73	9.78	9.19	9.16
	V^3A_2	3.50	3.13	3.19	3.39	3.34	3.34	3.35	3.29	3.17	3.37
	V^3A_1	5.86	5.90	5.44	5.63	5.61	5.64	5.63	5.47	5.38	5.62
	R^3B_2	6.83	5.60	7.08	7.17	7.12	6.75	6.90	7.49	7.10	7.17
	R^3B_2	7.79	6.47	7.82	7.87	7.83	7.47	7.62	8.22	7.84	7.88
	R^3A_1	7.96	6.34	7.99	8.01	7.94	7.52	7.71	8.52	8.03	8.03
valence	MSE		-0.30	-0.36	-0.23	-0.28	-0.29	-0.28	-0.32	-0.37	-0.23
(19)	MAE		0.31	0.39	0.27	0.30	0.30	0.29	0.37	0.40	0.27
	rms		0.38	0.47	0.34	0.37	0.37	0.37	0.46	0.48	0.35
Rydberg	MSE		-1.29	0.19	0.24	0.12	-0.30	-0.12	0.51	0.20	0.22
(23)	MAE		1.29	0.29	0.28	0.21	0.35	0.22	0.51	0.28	0.27
	rms		1.35	0.38	0.37	0.30	0.40	0.30	0.58	0.37	0.36

Table B.21: The lowest CT excitation energies (in eV) of $C_2H_4 \cdots C_2F_4$ dimers calculated by various methods. Geometries of C_2H_4 and C_2F_4 are obtained in ref. 33.

R(Å)	SAC-CI[93]	PBE	LC-ωPBE	ωB97	ωB97X	ωB97X-D	ωB97X-D3	SLC-LDA-D3	SLC-PBE-D3	SLC-B97-D3
5	11.49	5.00	10.03	10.02	9.62	8.74	9.24	10.62	10.08	10.12
6	12.00	5.04	10.54	10.54	10.14	9.22	9.75	11.13	10.59	10.63

7	12.36	5.06	10.90	10.90	10.50	9.58	10.11	11.50	10.95	11.00
8	12.63	5.08	11.17	11.16	10.77	9.84	10.38	11.77	11.22	11.26
9	12.83	5.08	11.37	11.37	10.97	10.05	10.59	11.97	11.43	11.47
10	12.99	5.09	11.54	11.53	11.14	10.22	10.75	12.14	11.59	11.63

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