Supplemental Material to: Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction

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DERIVATIVE DISCONTINUITY FROM THE PERSPECTIVE OF PERTURBATION THEORY

As discussed in our paper, we aim to express $\epsilon_{N+1}(N+1)$ in terms of $\{\epsilon_i(N), \psi_i(\mathbf{r})\}$, based on perturbation theory [1]. Here, we provide the full derivation (the notations used here are the same as those used in the paper). As Eq. (12) of our paper gives

$$\begin{aligned}&(H_{\rm KS} + \lambda H^{'(0)} + \lambda^2 H^{'(1)} + \cdots)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \cdots) \\ &= (\epsilon_i^{(0)} + \lambda\epsilon_i^{(1)} + \lambda^2\epsilon_i^{(2)} + \cdots)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \cdots),\end{aligned} \tag{1}$$

expanding Eq. (1) and comparing coefficients of each power of λ yields an infinite series of simultaneous equations.

Zeroth-Order Theory

To zeroth order (λ^0) in Eq. (1), the equation is

$$H_{\rm KS}\psi_i^{(0)}(\mathbf{r}) = \epsilon_i^{(0)}\psi_i^{(0)}(\mathbf{r}), \tag{2}$$

which is simply the KS equation for the N-electron system (i.e., the unperturbed system). We then have $\psi_i^{(0)}(\mathbf{r}) = \psi_i(\mathbf{r})$ and $\epsilon_i^{(0)} = \epsilon_i(N)$. Therefore, $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) \approx \epsilon_{N+1}^{(0)} = \epsilon_{N+1}(N)$. Correspondingly, $\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \approx \epsilon_{N+1}(N) - \epsilon_{N+1}(N) = 0$, and $E_g = \Delta_{\rm KS} + \Delta_{xc} \approx \Delta_{\rm KS}$. Therefore, to obtain a nonvanishing Δ_{xc}, it is necessary to go beyond the zeroth-order theory.

First-Order Theory

To first order (λ^1) in Eq. (1), the equation is

$$H_{\rm KS}\psi_i^{(1)}(\mathbf{r}) + H^{'(0)}\psi_i^{(0)}(\mathbf{r}) = \epsilon_i^{(0)}\psi_i^{(1)}(\mathbf{r}) + \epsilon_i^{(1)}\psi_i^{(0)}(\mathbf{r}). \tag{3}$$

Taking the inner product of Eq. (3) with $\psi_i^{(0)}$,

$$\begin{aligned}&\langle\psi_i^{(0)} \mid H_{\rm KS} \mid \psi_i^{(1)}\rangle + \langle\psi_i^{(0)} \mid H^{'(0)} \mid \psi_i^{(0)}\rangle \\ &= \epsilon_i^{(0)}\langle\psi_i^{(0)} \mid \psi_i^{(1)}\rangle + \epsilon_i^{(1)}\langle\psi_i^{(0)} \mid \psi_i^{(0)}\rangle.\end{aligned} \tag{4}$$

As $H_{\rm KS}$ is Hermitian, the first term on the left-hand side is the same as that on the right-hand side. Moreover, we have $\langle\psi_i^{(0)} \mid \psi_i^{(0)}\rangle = \langle\psi_i \mid \psi_i\rangle = 1$, so the first-order correction to the orbital energy is

$$\epsilon_i^{(1)} = \langle\psi_i^{(0)} \mid H^{'(0)} \mid \psi_i^{(0)}\rangle = \langle\psi_i \mid H'_{\lambda=0} \mid \psi_i\rangle. \tag{5}$$

Rewriting Eq. (3), we have

$$(H_{\rm KS} - \epsilon_i^{(0)})\psi_i^{(1)}(\mathbf{r}) = -(H^{'(0)} - \epsilon_i^{(1)})\psi_i^{(0)}(\mathbf{r}). \tag{6}$$

Since $\{\psi_j^{(0)}(\mathbf{r})\}$ constitute a complete set, $\psi_i^{(1)}(\mathbf{r})$ can be expressed as a linear combination of them:

$$\psi_i^{(1)}(\mathbf{r}) = \sum_{j\neq i} a_j^{(i)}\psi_j^{(0)}(\mathbf{r}). \tag{7}$$

Note that it is unnecessary to include $j = i$ in the sum, for if $\psi_i^{(1)}(\mathbf{r})$ satisfies Eq. (6), so too does $(\psi_i^{(1)}(\mathbf{r}) + \alpha\psi_i^{(0)}(\mathbf{r}))$, for any constant α, and we can use this freedom to subtract off the $\psi_i^{(0)}(\mathbf{r})$ term so that $\tilde{\psi}_i^{\lambda}(\mathbf{r})$ is normalized at first order in λ. Inserting Eq. (7) into Eq. (6), we have

$$\sum_{j\neq i}(\epsilon_j^{(0)} - \epsilon_i^{(0)})a_j^{(i)}\psi_j^{(0)}(\mathbf{r}) = -(H^{'(0)} - \epsilon_i^{(1)})\psi_i^{(0)}(\mathbf{r}). \tag{8}$$

Taking the inner product of Eq. (8) with $\psi_k^{(0)}$, we get

$$\begin{aligned}&\sum_{j\neq i}(\epsilon_j^{(0)} - \epsilon_i^{(0)})a_j^{(i)}\langle\psi_k^{(0)} \mid \psi_j^{(0)}\rangle \\ &= -\langle\psi_k^{(0)} \mid H^{'(0)} \mid \psi_i^{(0)}\rangle + \epsilon_i^{(1)}\langle\psi_k^{(0)} \mid \psi_i^{(0)}\rangle.\end{aligned} \tag{9}$$

If $k = i$, the left-hand side is zero, we recover Eq. (5); If $k \neq i$, we get $(\epsilon_k^{(0)} - \epsilon_i^{(0)})a_k^{(i)} = -\langle\psi_k^{(0)} \mid H^{'(0)} \mid \psi_i^{(0)}\rangle$, or $a_j^{(i)} = \frac{\langle\psi_j^{(0)}|H^{'(0)}|\psi_i^{(0)}\rangle}{\epsilon_i^{(0)} - \epsilon_j^{(0)}}$, so the first-order correction to the orbital is

$$\psi_i^{(1)}(\mathbf{r}) = \sum_{j\neq i} \frac{\langle\psi_j^{(0)} \mid H^{'(0)} \mid \psi_i^{(0)}\rangle}{\epsilon_i^{(0)} - \epsilon_j^{(0)}}\psi_j^{(0)}(\mathbf{r}). \tag{10}$$

Note that $\tilde{\rho}_{\lambda=0}(\mathbf{r}) = \sum_{i=1}^{N+1}|\tilde{\psi}_i^{\lambda=0}(\mathbf{r})|^2 = \sum_{i=1}^{N+1}|\psi_i^{(0)}(\mathbf{r})|^2 = \sum_{i=1}^{N+1}|\psi_i(\mathbf{r})|^2 = \rho(\mathbf{r}) + \rho_{\rm L}(\mathbf{r})$, where $\rho_{\rm L}(\mathbf{r}) \equiv |\psi_{N+1}(\mathbf{r})|^2$ is the KS LUMO density of the N-electron system. Consequently, we have

$$H'_{\lambda=0} = e^2\int \frac{\rho_{\rm L}(\mathbf{r}')}{|\ \mathbf{r}\ -\ \mathbf{r}\ '|}d\mathbf{r}' + v_{xc}([\rho+\rho_{\rm L}];\mathbf{r}) - v_{xc}([\rho];\mathbf{r}). \tag{11}$$

As $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) \approx \epsilon_{N+1}^{(0)} + \epsilon_{N+1}^{(1)}$, we have

$$\begin{aligned}
\Delta_{xc} &= \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \\
&\approx \epsilon_{N+1}^{(1)} = \langle \psi_{N+1} \mid H'_{\lambda=0} \mid \psi_{N+1} \rangle \\
&= e^2 \iint \frac{\rho_{\rm L}(\mathbf{r})\rho_{\rm L}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
&\quad + \int \rho_{\rm L}(\mathbf{r}) \Big\{ v_{xc}([\rho+\rho_{\rm L}];\mathbf{r}) - v_{xc}([\rho];\mathbf{r}) \Big\} d\mathbf{r},
\end{aligned} \tag{12}$$

and $E_g = \Delta_{\rm KS} + \Delta_{xc} \approx \Delta_{\rm KS} + \epsilon_{N+1}^{(1)}$. Eq. (12) is a key result, showing that the DD can be approximately expressed as an explicit universal functional of $\rho(\mathbf{r})$ and $\rho_{\rm L}(\mathbf{r})$, and can be calculated in the standard KS method without extra computational cost.

Second-Order Theory

To second order (λ^2) in Eq. (1), the equation is

$$\begin{aligned}
&H_{\rm KS}\psi_i^{(2)}(\mathbf{r}) + H'^{(0)}\psi_i^{(1)}(\mathbf{r}) + H'^{(1)}\psi_i^{(0)}(\mathbf{r}) \\
&= \epsilon_i^{(0)}\psi_i^{(2)}(\mathbf{r}) + \epsilon_i^{(1)}\psi_i^{(1)}(\mathbf{r}) + \epsilon_i^{(2)}\psi_i^{(0)}(\mathbf{r}).
\end{aligned} \tag{13}$$

Taking the inner product of Eq. (13) with $\psi_i^{(0)}$, we get

$$\begin{aligned}
&\langle \psi_i^{(0)} \mid H_{\rm KS} \mid \psi_i^{(2)} \rangle + \langle \psi_i^{(0)} \mid H'^{(0)} \mid \psi_i^{(1)} \rangle + \langle \psi_i^{(0)} \mid H'^{(1)} \mid \psi_i^{(0)} \rangle \\
&= \epsilon_i^{(0)} \langle \psi_i^{(0)} \mid \psi_i^{(2)} \rangle + \epsilon_i^{(1)} \langle \psi_i^{(0)} \mid \psi_i^{(1)} \rangle + \epsilon_i^{(2)} \langle \psi_i^{(0)} \mid \psi_i^{(0)} \rangle.
\end{aligned} \tag{14}$$

As $H_{\rm KS}$ is Hermitian, the first term on the left-hand side is the same as that on the right-hand side. Moreover, we have $\langle \psi_i^{(0)} \mid \psi_i^{(0)} \rangle = 1$ and $\langle \psi_i^{(0)} \mid \psi_i^{(1)} \rangle = 0$ (see Eq. (10)), so the second-order correction to the orbital energy is

$$\begin{aligned}
\epsilon_i^{(2)} &= \langle \psi_i^{(0)} \mid H'^{(0)} \mid \psi_i^{(1)} \rangle + \langle \psi_i^{(0)} \mid H'^{(1)} \mid \psi_i^{(0)} \rangle \\
&= \sum_{j \neq i} \frac{|\langle \psi_j \mid H'_{\lambda=0} \mid \psi_i \rangle|^2}{\epsilon_i(N) - \epsilon_j(N)} + \langle \psi_i \mid H'^{(1)} \mid \psi_i \rangle,
\end{aligned} \tag{15}$$

where

$$
\begin{aligned}
H^{'(1)} &= \left.\frac{\partial H^{'}_{\lambda}}{\partial \lambda}\right|_{\lambda=0} \\
&= \int \left\{ \frac{e^2}{\mid \mathbf{r} \; - \; \mathbf{r}^{\,\prime} \mid} + \frac{\delta v_{xc}([\tilde{\rho}_{\lambda}];\mathbf{r})}{\delta \tilde{\rho}_{\lambda}(\mathbf{r}')} \right\} \left.\frac{\partial \tilde{\rho}_{\lambda}(\mathbf{r}^{'})}{\partial \lambda}\right|_{\lambda=0} d\mathbf{r}^{'} \\
&= \int \left\{ \frac{e^2}{\mid \mathbf{r} \; - \; \mathbf{r}^{\,\prime} \mid} + f_{xc}([\rho+\rho_{\mathrm{L}}];\mathbf{r},\mathbf{r}') \right\} \\
&\quad \times \left\{ 2 \sum_{i=1}^{N+1} \Re(\psi_i^{*}(\mathbf{r}')\psi_i^{(1)}(\mathbf{r}')) \right\} d\mathbf{r}^{'}.
\end{aligned}
\tag{16}
$$

Here $f_{xc}([\rho];\mathbf{r},\mathbf{r}') \equiv \delta v_{xc}([\rho];\mathbf{r})/\delta\rho(\mathbf{r}')$ is the XC kernel, the asterisk (*) denotes complex conjugate, and $\Re(\cdots)$ denotes the real part of $(\cdots)$. From Eq. (15), we have

$$
\epsilon^{(2)}_{N+1} = \sum_{j \neq N+1} \frac{|\langle \psi_j \mid H^{'}_{\lambda=0} \mid \psi_{N+1} \rangle|^2}{\epsilon_{N+1}(N) - \epsilon_j(N)} + \langle \psi_{N+1} \mid H^{'(1)} \mid \psi_{N+1} \rangle. \tag{17}
$$

Correspondingly, $\epsilon_{N+1}(N+1) = \epsilon^{\lambda=1}_{N+1}(N+1) \approx \epsilon^{(0)}_{N+1} + \epsilon^{(1)}_{N+1} + \epsilon^{(2)}_{N+1}$. This gives $\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \approx \epsilon^{(1)}_{N+1} + \epsilon^{(2)}_{N+1}$ and $E_g = \Delta_{\mathrm{KS}} + \Delta_{xc} \approx \Delta_{\mathrm{KS}} + (\epsilon^{(1)}_{N+1} + \epsilon^{(2)}_{N+1})$.

TABLES

TABLE I. Fundamental gaps (in eV) of the FG115 database [2], calculated by three schemes (see text for details) using the LDA [3] and LB94 [4] functionals.

		LDA			LB94		
Molecule	Reference	$\Delta_{\rm KS}$	$\Delta_{\rm KS}+\Delta_{xc}$	E_g	$\Delta_{\rm KS}$	$\Delta_{\rm KS}+\Delta_{xc}$	E_g
H (Hydrogen atom)	12.86	4.71	11.05	9.19	9.48	14.26	11.16
He (Helium atom)	27.23	18.01	22.01	21.81	20.71	27.60	27.40
Li (Lithium atom)	4.22	1.13	5.49	3.98	-2.55	6.13	4.72
Be (Beryllium atom)	9.66	3.50	10.44	7.51	3.34	12.05	8.93
B (Boron atom)	7.99	0.19	10.30	6.19	-0.16	11.09	7.74
C (Carbon atom)	9.97	0.08	13.38	8.08	-0.52	14.28	9.59
N (Nitrogen atom)	14.74	4.02	14.02	11.94	3.28	17.01	13.15
O (Oxygen atom)	12.14	0.29	14.44	10.27	-0.28	17.79	12.20
F (Fluorine atom)	13.98	0.12	18.95	12.13	-0.81	22.36	13.99
Ne (Neon atom)	26.91	17.25	23.74	23.40	18.77	27.98	27.69
Na (Sodium atom)	4.14	0.91	5.44	3.88	-1.92	6.86	4.93
Mg (Magnesium atom)	7.76	3.39	8.15	6.20	3.68	9.71	8.04
Al (Aluminum atom)	5.53	0.09	6.74	4.54	-0.41	7.26	5.68
Si (Silicon atom)	6.73	-0.02	8.37	5.76	-0.52	8.91	6.52
P (Phosphorus atom)	9.78	2.16	9.56	8.13	0.65	10.87	8.49
S (Sulfur atom)	8.23	0.04	9.85	7.25	-0.64	11.79	8.34
Cl (Chlorine atom)	9.30	-0.07	12.47	8.38	-0.76	13.29	9.35
Ar (Argon atom)	18.65	11.23	15.78	15.52	11.85	18.38	18.23
CH_3 (Methyl radical)	9.86	1.79	8.25	8.04	0.67	11.21	9.35
CH_4 (Methane)	15.06	9.21	12.19	11.47	10.08	15.55	14.78
NH (Imidogen) ($^3\Sigma^-$)	13.17	3.10	11.72	11.04	1.99	15.71	12.11
NH_2 (Amino radical)	11.34	1.97	10.56	9.87	1.17	14.46	11.27
NH_3 (Ammonia)	11.54	5.64	9.42	8.47	6.59	12.96	11.91

OH (Hydroxyl radical)	11.27	0.16	11.52	9.79	-0.63	16.50	11.38
H_2O (Water)	13.35	6.57	11.03	9.85	7.65	15.08	13.66
HF (Hydrogen fluoride)	16.91	9.00	14.23	12.50	10.40	19.39	17.10
SiH_3 (Silyl)	7.95	1.32	8.48	6.80	0.15	9.91	7.49
SiH_4 (Silane)	14.03	8.14	11.36	10.55	8.43	13.69	13.11
PH_3 (Phosphine)	11.82	6.13	9.63	8.72	6.32	14.08	11.34
H_2S (Hydrogen sulfide)	11.00	5.57	9.69	8.44	5.56	14.12	11.06
HCl (Hydrogen sulfide)	13.36	7.02	13.00	10.49	7.06	15.89	13.30
C_2H_2 (Acetylene)	13.43	6.78	14.94	9.23	6.70	16.23	13.61
C_2H_4 (Ethylene)	12.57	5.60	14.41	9.01	5.46	15.42	12.30
C_2H_6 (Ethane)	13.41	7.80	10.79	10.06	8.61	13.93	13.24
HCN (Hydrogen cyanide)	14.31	7.87	17.57	11.53	7.71	18.65	15.17
CO (Carbon monoxide)	15.57	6.87	18.28	12.93	6.54	19.07	15.35
HCO (Formyl radical)	9.56	1.31	12.24	7.99	0.97	12.83	9.56
H_2CO (Formaldehyde)	11.56	3.41	14.51	8.94	3.27	15.37	11.86
CH_3OH (Methyl alcohol)	11.67	5.75	9.76	8.28	6.70	13.87	12.07
N_2 (Nitrogen diatomic)	17.88	8.21	20.51	15.84	7.85	20.94	17.30
N_2H_4 (Hydrazine)	10.29	4.43	8.49	7.44	5.33	11.80	10.74
NO (Nitric oxide)	10.11	-0.04	13.79	8.76	-0.24	14.38	10.15
O_2 (Oxygen diatomic) ($^3\Sigma_g$)	12.52	2.06	13.55	11.42	1.81	16.91	12.44
H_2O_2 (Hydrogen peroxide)	12.65	4.66	17.70	8.99	4.57	19.47	13.08
F_2 (Fluorine diatomic)	15.53	3.42	20.95	14.02	3.24	21.51	15.40
CO_2 (Carbon dioxide)	14.58	8.41	13.44	11.90	8.51	20.97	15.64
P_2 (Phosphorus diatomic)	10.19	3.71	11.25	9.37	3.46	11.58	9.96
S_2 (Sulfur diatomic) ($^3\Sigma_g$)	7.96	1.05	9.64	7.40	0.55	9.65	7.75
Cl_2 (Chlorine diatomic)	10.93	2.96	12.67	9.55	2.85	13.00	10.55
NaCl (Sodium Chloride)	8.64	3.30	7.55	6.24	3.35	11.30	8.95
SiO (Silicon monoxide)	11.60	4.61	12.44	9.96	4.74	13.48	11.67
CS (Carbon monosulfide)	11.58	3.85	13.59	10.42	3.62	13.77	11.26
ClO (Monochlorine monoxide)	8.85	-0.03	12.41	8.16	-0.26	12.58	8.86

ClF (Chlorine monofluoride)	12.43	3.28	14.96	10.86	3.08	15.57	12.07
Si_2H_6 (Disilane)	11.33	6.56	10.09	9.12	6.37	13.13	11.05
CH_3Cl (Methyl chloride)	12.01	6.25	12.16	9.16	6.28	15.05	12.09
CH_3SH (Methanethiol)	10.01	4.76	9.10	7.53	4.89	11.62	10.14
SO_2 (Sulfur dioxide)	11.74	3.64	13.66	10.99	3.51	13.95	11.78
BF_3 (Borane, trifluoro-)	17.22	9.55	13.80	12.70	10.04	21.46	18.10
BCl_3 (Borane, trichloro-)	12.07	4.85	13.24	10.80	4.68	14.44	11.31
$AlCl_3$ (Aluminum trichloride)	12.13	5.66	11.57	9.67	5.73	12.73	11.27
CF_4 (Carbon tetrafluoride)	17.85	10.68	14.18	13.60	12.60	18.35	18.12
CCl_4 (Carbon tetrachloride)	11.97	4.90	11.90	9.86	4.86	12.23	10.54
OCS (Carbonyl sulfide)	12.13	5.51	15.04	10.09	5.20	15.17	12.69
CS_2 (Carbon disulfide)	10.19	3.94	12.06	9.50	3.74	12.83	10.21
CF_2O (Carbonic difluoride)	16.08	6.63	18.68	11.46	6.39	19.13	15.78
SiF_4 (Silicon tetrafluoride)	16.95	9.66	14.84	13.30	10.87	18.38	17.03
N_2O (Nitrous oxide)	15.01	6.81	18.48	11.89	6.56	18.74	15.49
NF_3 (Nitrogen trifluoride)	15.76	7.28	21.00	13.00	7.17	21.65	16.54
PF_3 (Phosphorus trifluoride)	13.00	6.43	14.13	10.16	6.72	16.22	13.48
O_3 (Ozone)	11.06	1.72	14.19	10.40	1.46	14.27	10.95
F_2O (Difluorine monoxide)	13.82	3.22	17.96	12.34	3.13	18.16	13.52
ClF_3 (Chlorine trifluoride)	11.79	3.02	14.48	10.69	3.02	14.98	11.72
C_2F_4 (Tetrafluoroethylene)	12.45	5.88	16.43	9.13	5.72	16.80	13.97
CH_3CCH (Propyne)	11.69	6.21	9.29	8.32	6.49	15.16	11.54
CH_2CCH_2 (Allene)	10.83	5.69	13.81	8.55	5.55	14.75	11.89
C_3H_4 (Cyclopropene)	11.87	4.90	13.67	8.13	4.79	14.78	11.94
C_3H_6 (Cyclopropane)	11.64	6.97	9.91	9.21	7.64	12.86	12.25
CH_2F_2 (Methane, difluoro-)	14.15	7.94	11.27	10.37	9.39	18.17	14.57
CHF_3 (Methane, trifluoro-)	15.44	9.23	12.97	11.94	10.78	17.62	16.11
CH_2Cl_2 (Methylene chloride)	12.18	5.86	13.28	9.52	5.80	14.27	11.91
$CHCl_3$ (Chloroform)	12.38	5.31	12.67	9.75	5.26	12.92	11.20
CH_3NO_2 (Methane, nitro-)	11.94	3.67	15.16	9.24	3.44	15.25	11.52

CH_3SiH_3 (Methyl silane)	12.35	7.30	11.00	9.87	7.60	13.18	12.42
HCOOH (Formic acid)	11.98	5.13	16.09	9.03	4.95	16.84	13.35
CH_3CONH_2 (Acetamide)	10.05	4.98	11.35	7.59	4.89	15.37	10.91
C_2N_2 (Cyanogen)	13.90	5.83	14.73	12.67	5.74	14.98	13.28
CH_2CO (Ketene)	10.32	3.72	14.32	8.11	3.42	14.70	11.32
C_2H_4O (Ethylene oxide)	11.68	6.10	9.16	8.37	7.34	13.25	12.10
$C_2H_2O_2$ (Ethanedial)	10.04	1.80	11.15	8.63	1.57	11.37	9.16
CH_3CH_2OH (Ethanol)	11.38	5.64	9.37	8.07	6.63	13.30	11.60
CH_3OCH_3 (Dimethyl ether)	10.79	5.47	8.59	7.71	6.64	12.29	11.31
C_2H_4S (Thiirane)	9.93	4.34	11.64	7.41	4.13	12.53	10.12
CH_2CHF (Ethene, fluoro-)	11.55	5.46	14.50	8.78	5.41	15.41	12.73
CH_3CH_2Cl (Ethyl chloride)	11.74	6.31	11.37	8.90	6.36	15.13	11.85
CH_2CHCl (Ethene, chloro-)	11.35	4.92	13.61	8.50	4.76	14.23	11.59
CH_3COCl (Acetyl Chloride)	11.97	4.72	15.12	9.29	4.48	15.16	11.79
NO_2 (Nitrogen dioxide)	9.79	1.13	12.94	8.85	0.93	13.37	10.08
$CFCl_3$ (Trichloromonofluoromethane)	12.61	5.21	12.99	10.26	5.11	13.32	11.26
CF_3Cl (Methane, chlorotrifluoro-)	14.27	7.18	16.96	11.44	6.89	17.67	14.30
HCCF (Fluoroacetylene)	12.04	6.50	11.49	9.12	6.98	14.93	12.64
HCCCN (Cyanoacetylene)	12.20	5.16	13.29	11.03	5.05	13.63	12.00
C_4N_2 (2-Butynedinitrile)	11.52	4.44	11.76	10.28	4.37	11.94	10.70
C_2N_2 (Cyanogen)	13.90	5.83	14.73	12.67	5.74	14.98	13.28
C_3O_2 (Carbon suboxide)	11.64	4.67	13.37	11.42	4.47	13.53	11.82
FCN (Cyanogen fluoride)	14.33	7.31	14.25	11.41	7.76	17.03	14.59
C_4H_2 (Diacetylene)	11.00	4.77	12.17	9.94	4.69	12.67	11.09
H_2CS (Thioformaldehyde)	9.18	1.80	11.02	8.20	1.48	11.27	8.87
$CHONH_2$ (Formamide)	10.81	5.15	15.38	8.13	5.00	16.16	11.67
CH_2CCl_2 (Ethene, 1,1-dichloro-)	11.17	4.69	13.08	8.66	4.58	14.11	11.01
C_2HF_3 (Trifluoroethylene)	11.11	5.39	15.16	8.62	5.31	15.96	13.10
CH_2CF_2 (Ethene, 1,1-difluoro-)	11.81	5.77	15.06	8.87	5.66	15.99	13.12
CH_3F (Methyl fluoride)	14.09	7.88	11.02	10.21	9.02	17.02	14.36

CF_2Cl_2 (Difluorodichloromethane)	13.33	6.06	14.58	10.86	5.87	15.08	12.56
SiF_2 (Silicon difluoride)	11.04	4.09	12.17	9.62	4.26	13.40	11.50
MSE		-7.22	0.78	-2.33	-7.20	2.73	0.03
MAE		7.22	2.11	2.33	7.20	2.74	0.47
rms		7.44	2.45	2.57	7.48	3.13	0.63

TABLE II. Comparison of errors (in eV) of the 115 derivative discontinuities (in eV) of the FG115 database [2], calculated by the DD(0th) and DD(1st), using the LDA [3] and LB94 [4] functionals. Here DD(0th) = 0 is obtained from the zeroth-order perturbation theory, and DD(1st), which is calculated by the difference between the $\Delta_{\rm KS} + \Delta_{xc}$ and $\Delta_{\rm KS}$ gaps, is obtained from the first-order perturbation theory (i.e., "frozen orbital approximation"). The reference (DD) values are calculated by the difference between the E_g and $\Delta_{\rm KS}$ gaps, using the respective functionals. Note that since LB94 yields very accurate E_g, and possibly accurate $\Delta_{\rm KS}$ (due to the correct asymptote of the LB94 potential), the reference DD values calculated by LB94 should be more accurate than those calculated by LDA.

	LDA			LB94		
Molecule	DD	DD(0th)	DD(1st)	DD	DD(0th)	DD(1st)
H (Hydrogen atom)	4.48	-4.48	1.86	1.68	-1.68	3.10
He (Helium atom)	3.80	-3.80	0.20	6.70	-6.70	0.20
Li (Lithium atom)	2.85	-2.85	1.51	7.27	-7.27	1.40
Be (Beryllium atom)	4.01	-4.01	2.93	5.58	-5.58	3.12
B (Boron atom)	6.00	-6.00	4.12	7.90	-7.90	3.36
C (Carbon atom)	8.01	-8.01	5.29	10.11	-10.11	4.69
N (Nitrogen atom)	7.92	-7.92	2.08	9.87	-9.87	3.86
O (Oxygen atom)	9.98	-9.98	4.17	12.48	-12.48	5.59
F (Fluorine atom)	12.02	-12.02	6.82	14.80	-14.80	8.37
Ne (Neon atom)	6.15	-6.15	0.33	8.92	-8.92	0.30
Na (Sodium atom)	2.97	-2.97	1.56	6.85	-6.85	1.93
Mg (Magnesium atom)	2.81	-2.81	1.95	4.36	-4.36	1.67
Al (Aluminum atom)	4.44	-4.44	2.20	6.10	-6.10	1.58

Si (Silicon atom)	5.78	-5.78	2.61	7.03	-7.03	2.40
P (Phosphorus atom)	5.96	-5.96	1.44	7.84	-7.84	2.38
S (Sulfur atom)	7.20	-7.20	2.60	8.98	-8.98	3.45
Cl (Chlorine atom)	8.46	-8.46	4.09	10.11	-10.11	3.93
Ar (Argon atom)	4.29	-4.29	0.26	6.38	-6.38	0.15
CH_3 (Methyl radical)	6.24	-6.24	0.21	8.67	-8.67	1.86
CH_4 (Methane)	2.26	-2.26	0.72	4.71	-4.71	0.77
NH (Imidogen) ($^3\Sigma^-$)	7.94	-7.94	0.68	10.12	-10.12	3.60
NH_2 (Amino radical)	7.90	-7.90	0.70	10.10	-10.10	3.19
NH_3 (Ammonia)	2.83	-2.83	0.95	5.32	-5.32	1.05
OH (Hydroxyl radical)	9.63	-9.63	1.74	12.01	-12.01	5.12
H_2O (Water)	3.28	-3.28	1.19	6.01	-6.01	1.41
HF (Hydrogen fluoride)	3.50	-3.50	1.73	6.70	-6.70	2.29
SiH_3 (Silyl)	5.48	-5.48	1.68	7.34	-7.34	2.42
SiH_4 (Silane)	2.41	-2.41	0.81	4.67	-4.67	0.58
PH_3 (Phosphine)	2.59	-2.59	0.92	5.01	-5.01	2.74
H_2S (Hydrogen sulfide)	2.88	-2.88	1.25	5.50	-5.50	3.06
HCl (Hydrogen sulfide)	3.47	-3.47	2.51	6.25	-6.25	2.59
C_2H_2 (Acetylene)	2.45	-2.45	5.71	6.91	-6.91	2.62
C_2H_4 (Ethylene)	3.41	-3.41	5.41	6.84	-6.84	3.12
C_2H_6 (Ethane)	2.26	-2.26	0.73	4.62	-4.62	0.69
HCN (Hydrogen cyanide)	3.66	-3.66	6.04	7.46	-7.46	3.48
CO (Carbon monoxide)	6.06	-6.06	5.35	8.81	-8.81	3.72
HCO (Formyl radical)	6.68	-6.68	4.25	8.59	-8.59	3.27
H_2CO (Formaldehyde)	5.52	-5.52	5.58	8.59	-8.59	3.51
CH_3OH (Methyl alcohol)	2.53	-2.53	1.48	5.37	-5.37	1.79
N_2 (Nitrogen diatomic)	7.63	-7.63	4.67	9.45	-9.45	3.64
N_2H_4 (Hydrazine)	3.00	-3.00	1.05	5.41	-5.41	1.06
NO (Nitric oxide)	8.80	-8.80	5.03	10.39	-10.39	4.23
O_2 (Oxygen diatomic) ($^3\Sigma_g$)	9.36	-9.36	2.13	10.63	-10.63	4.47

H_2O_2 (Hydrogen peroxide)	4.33	-4.33	8.71	8.51	-8.51	6.39
F_2 (Fluorine diatomic)	10.60	-10.60	6.94	12.16	-12.16	6.11
CO_2 (Carbon dioxide)	3.49	-3.49	1.53	7.14	-7.14	5.33
P_2 (Phosphorus diatomic)	5.66	-5.66	1.88	6.50	-6.50	1.61
S_2 (Sulfur diatomic) ($^3\Sigma_g$)	6.35	-6.35	2.24	7.20	-7.20	1.90
Cl_2 (Chlorine diatomic)	6.59	-6.59	3.12	7.70	-7.70	2.45
NaCl (Sodium Chloride)	2.94	-2.94	1.31	5.60	-5.60	2.35
SiO (Silicon monoxide)	5.35	-5.35	2.48	6.93	-6.93	1.81
CS (Carbon monosulfide)	6.56	-6.56	3.17	7.64	-7.64	2.51
ClO (Monochlorine monoxide)	8.19	-8.19	4.24	9.11	-9.11	3.73
ClF (Chlorine monofluoride)	7.58	-7.58	4.10	8.99	-8.99	3.50
Si_2H_6 (Disilane)	2.56	-2.56	0.98	4.69	-4.69	2.08
CH_3Cl (Methyl chloride)	2.91	-2.91	3.01	5.81	-5.81	2.96
CH_3SH (Methanethiol)	2.76	-2.76	1.58	5.25	-5.25	1.48
SO_2 (Sulfur dioxide)	7.36	-7.36	2.66	8.27	-8.27	2.17
BF_3 (Borane, trifluoro-)	3.15	-3.15	1.10	8.06	-8.06	3.35
BCl_3 (Borane, trichloro-)	5.95	-5.95	2.44	6.63	-6.63	3.12
$AlCl_3$ (Aluminum trichloride)	4.01	-4.01	1.89	5.55	-5.55	1.46
CF_4 (Carbon tetrafluoride)	2.91	-2.91	0.59	5.52	-5.52	0.23
CCl_4 (Carbon tetrachloride)	4.96	-4.96	2.04	5.68	-5.68	1.70
OCS (Carbonyl sulfide)	4.59	-4.59	4.95	7.49	-7.49	2.48
CS_2 (Carbon disulfide)	5.56	-5.56	2.56	6.47	-6.47	2.62
CF_2O (Carbonic difluoride)	4.83	-4.83	7.22	9.40	-9.40	3.35
SiF_4 (Silicon tetrafluoride)	3.64	-3.64	1.53	6.16	-6.16	1.35
N_2O (Nitrous oxide)	5.08	-5.08	6.59	8.93	-8.93	3.25
NF_3 (Nitrogen trifluoride)	5.72	-5.72	8.00	9.38	-9.38	5.11
PF_3 (Phosphorus trifluoride)	3.73	-3.73	3.96	6.75	-6.75	2.74
O_3 (Ozone)	8.68	-8.68	3.79	9.49	-9.49	3.33
F_2O (Difluorine monoxide)	9.12	-9.12	5.63	10.40	-10.40	4.64
ClF_3 (Chlorine trifluoride)	7.67	-7.67	3.79	8.70	-8.70	3.27

C_2F_4 (Tetrafluoroethylene)	3.25	-3.25	7.30	8.25	-8.25	2.83
CH_3CCH (Propyne)	2.11	-2.11	0.97	5.06	-5.06	3.61
CH_2CCH_2 (Allene)	2.86	-2.86	5.26	6.34	-6.34	2.86
C_3H_4 (Cyclopropene)	3.23	-3.23	5.55	7.16	-7.16	2.83
C_3H_6 (Cyclopropane)	2.24	-2.24	0.70	4.62	-4.62	0.61
CH_2F_2 (Methane, difluoro-)	2.43	-2.43	0.89	5.18	-5.18	3.60
CHF_3 (Methane, trifluoro-)	2.71	-2.71	1.03	5.34	-5.34	1.51
CH_2Cl_2 (Methylene chloride)	3.67	-3.67	3.75	6.11	-6.11	2.36
$CHCl_3$ (Chloroform)	4.44	-4.44	2.92	5.94	-5.94	1.73
CH_3NO_2 (Methane, nitro-)	5.57	-5.57	5.92	8.08	-8.08	3.73
CH_3SiH_3 (Methyl silane)	2.57	-2.57	1.14	4.83	-4.83	0.76
HCOOH (Formic acid)	3.90	-3.90	7.07	8.40	-8.40	3.50
CH_3CONH_2 (Acetamide)	2.61	-2.61	3.76	6.01	-6.01	4.46
C_2N_2 (Cyanogen)	6.84	-6.84	2.06	7.54	-7.54	1.70
CH_2CO (Ketene)	4.39	-4.39	6.21	7.90	-7.90	3.38
C_2H_4O (Ethylene oxide)	2.27	-2.27	0.79	4.76	-4.76	1.16
$C_2H_2O_2$ (Ethanedial)	6.83	-6.83	2.52	7.59	-7.59	2.21
CH_3CH_2OH (Ethanol)	2.44	-2.44	1.29	4.97	-4.97	1.70
CH_3OCH_3 (Dimethyl ether)	2.24	-2.24	0.88	4.67	-4.67	0.99
C_2H_4S (Thiirane)	3.07	-3.07	4.23	5.99	-5.99	2.41
CH_2CHF (Ethene, fluoro-)	3.31	-3.31	5.73	7.32	-7.32	2.67
CH_3CH_2Cl (Ethyl chloride)	2.59	-2.59	2.47	5.49	-5.49	3.28
CH_2CHCl (Ethene, chloro-)	3.58	-3.58	5.10	6.83	-6.83	2.64
CH_3COCl (Acetyl Chloride)	4.57	-4.57	5.83	7.31	-7.31	3.36
NO_2 (Nitrogen dioxide)	7.72	-7.72	4.08	9.15	-9.15	3.29
$CFCl_3$ (Trichloromonofluoromethane)	5.05	-5.05	2.73	6.15	-6.15	2.06
CF_3Cl (Methane, chlorotrifluoro-)	4.27	-4.27	5.52	7.41	-7.41	3.37
HCCF (Fluoroacetylene)	2.62	-2.62	2.37	5.67	-5.67	2.28
HCCCN (Cyanoacetylene)	5.86	-5.86	2.26	6.94	-6.94	1.63
C_4N_2 (2-Butynedinitrile)	5.84	-5.84	1.47	6.34	-6.34	1.24

C_2N_2 (Cyanogen)	6.84	-6.84	2.06	7.54	-7.54	1.70
C_3O_2 (Carbon suboxide)	6.75	-6.75	1.95	7.35	-7.35	1.71
FCN (Cyanogen fluoride)	4.10	-4.10	2.84	6.83	-6.83	2.43
C_4H_2 (Diacetylene)	5.17	-5.17	2.23	6.40	-6.40	1.58
H_2CS (Thioformaldehyde)	6.40	-6.40	2.82	7.39	-7.39	2.40
$CHONH_2$ (Formamide)	2.98	-2.98	7.25	6.66	-6.66	4.49
CH_2CCl_2 (Ethene, 1,1-dichloro-)	3.97	-3.97	4.42	6.43	-6.43	3.10
C_2HF_3 (Trifluoroethylene)	3.23	-3.23	6.54	7.79	-7.79	2.86
CH_2CF_2 (Ethene, 1,1-difluoro-)	3.10	-3.10	6.19	7.46	-7.46	2.87
CH_3F (Methyl fluoride)	2.33	-2.33	0.81	5.34	-5.34	2.66
CF_2Cl_2 (Difluorodichloromethane)	4.80	-4.80	3.72	6.69	-6.69	2.52
SiF_2 (Silicon difluoride)	5.53	-5.53	2.55	7.24	-7.24	1.91
MSE		-4.89	3.11		-7.23	2.70
MAE		4.89	3.11		7.23	2.70
rms		5.36	3.73		7.48	3.01