Error cancellation in atomization and chemical reaction energies

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G2 benchmark set of atomization energies

- 55 selected molecules

  [Curtiss, Raghavachari, Trucks, and & Pople, J. Chem. Phys. **94**, 7221 (1991)]

- 1st and 2nd row atoms
- E_{atmz}: experimental heat of formation (0K)

  [e.g. Feller & Peterson, J. Chem. Phys. **110**, 8384 (1999)]

- reference bond energies

$$E_{\mathrm{bond}} = E_{\mathrm{atomz}} + E_{\mathrm{ZPE}} + \Delta E_{\mathrm{SR\&SO}}$$

- obtained from computational method (here: CASINO DMC)

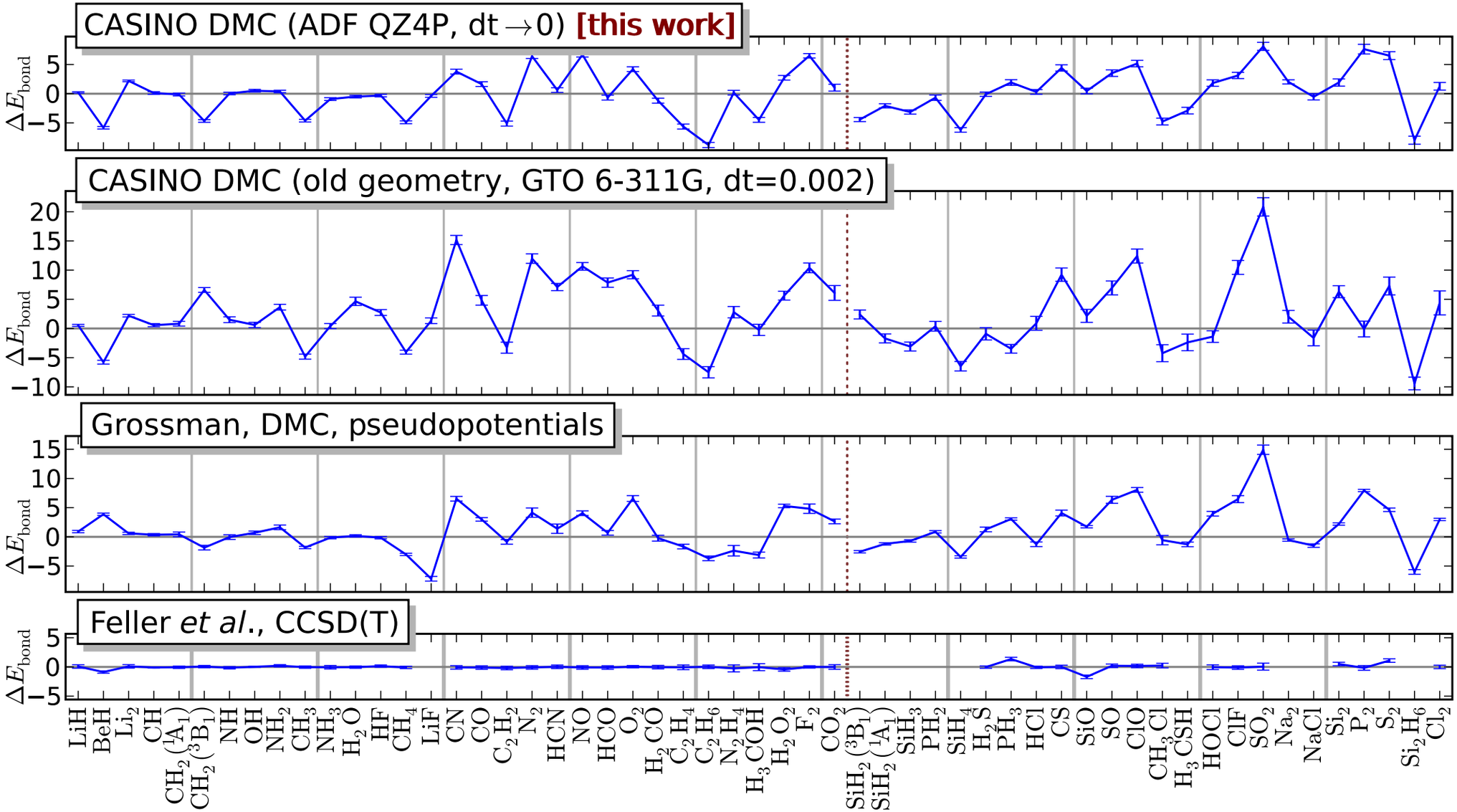
$$E_{\mathrm{bond}} = \left(\sum E_{\mathrm{total}}^{\mathrm{atom}} \right) - E_{\mathrm{total}}^{\mathrm{molecule}}$$

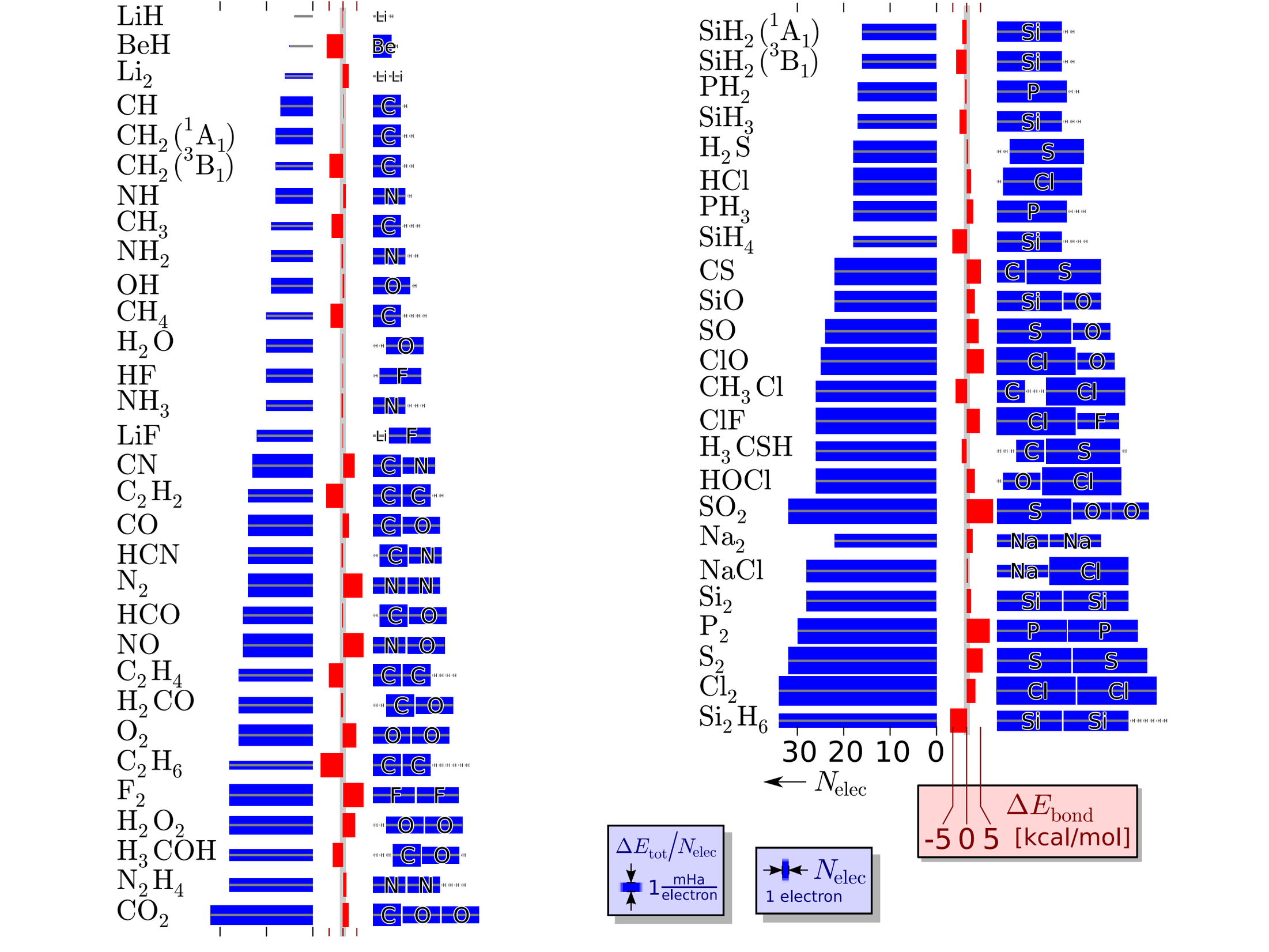
  (E_{total}: non-relativistic electronic groundstate energy - static nuclei)

- $E_{\mathrm{atmz}}, E_{\mathrm{bond}}, E_{\mathrm{ZPE}} > 0$

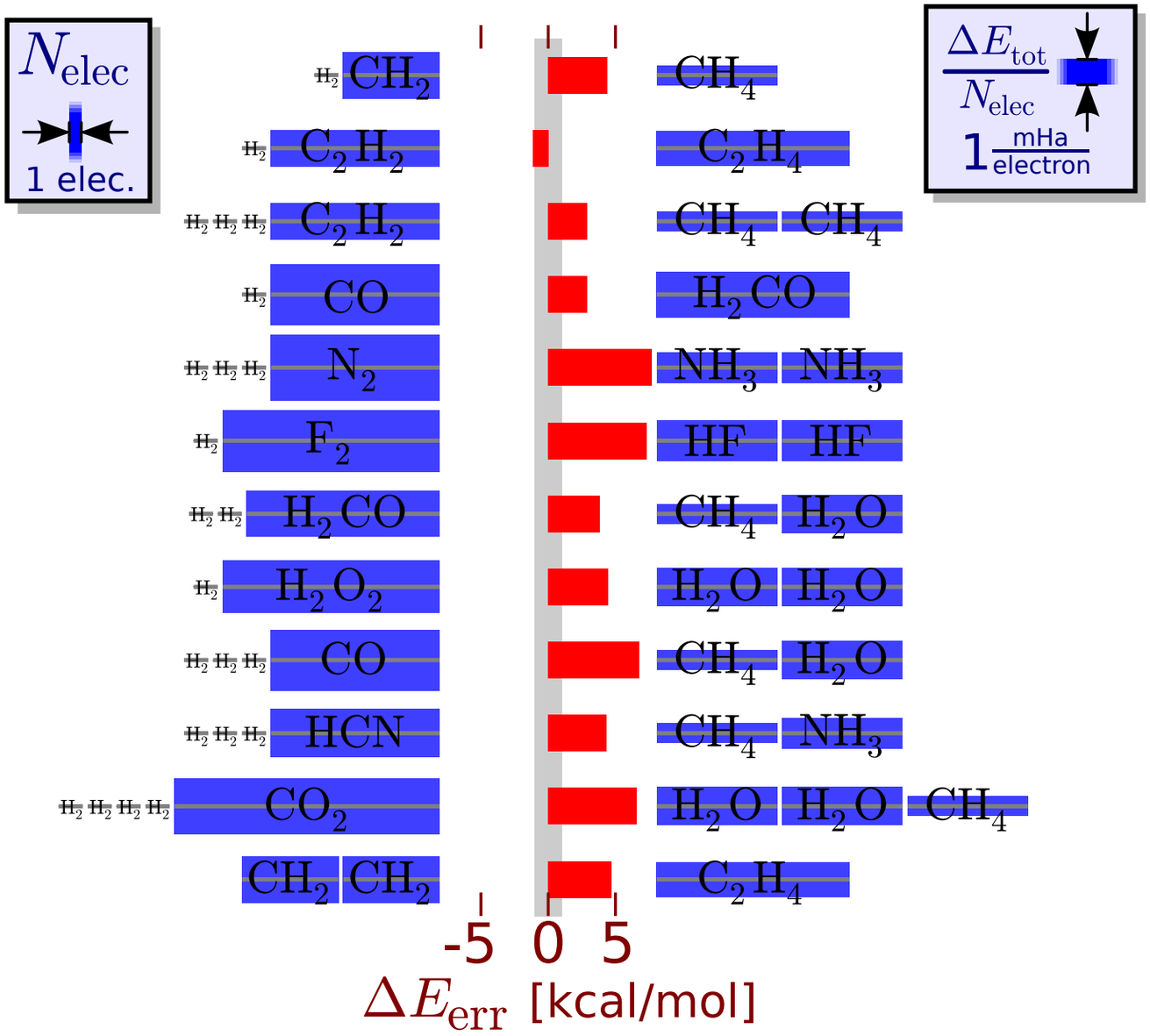
Comparing benchmark data

$$\Delta E_{\mathrm{bond}} = E_{\mathrm{bond}}^{\mathrm{computed}} - E_{\mathrm{bond}}^{\mathrm{reference}}$$




LiH
BeH
Li_2
CH
CH_2 ($^1A_1$)
CH_2 ($^3B_1$)
NH
CH_3
NH_2
OH
CH_4
H_2O
HF
NH_3
LiF
CN
C_2H_2
CO
HCN
N_2
HCO
NO
C_2H_4
H_2CO
O_2
C_2H_6
F_2
H_2O_2
H_3COH
N_2H_4
CO_2
SiH_2 ($^1A_1$)
SiH_2 ($^3B_1$)
PH_2
SiH_3
H_2S
HCl
PH_3
SiH_4
CS
SiO
SO
ClO
CH_3Cl
ClF
H_3CSH
HOCl
SO_2
Na_2
NaCl
Si_2
P_2
S_2
Cl_2
Si_2H_6
30 20 10 0
N_{elec}
ΔE_{bond}
-5 0 5 [kcal/mol]
$\Delta E_{tot}/N_{elec}$
1 $\frac{mHa}{electron}$
N_{elec}
1 electron

Chemical reaction energies



[selected molecules from Helgaker test set]