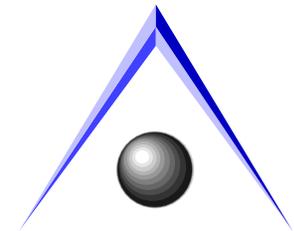


COMPOSITE METHODS

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COMPOSITE METHODS

- Based on additivity of
 - Basis set improvements
 - Level of theory improvements
 - High level = H
 - Low level = L
 - Big basis = B
 - Small basis = S
 - $\Delta_1 = L(B) - L(S)$: Basis set improvement
 - $\Delta_2 = H(S) - L(S)$: Level of theory improvement
 - $H(B) = H(S) + \Delta_1 + \Delta_2$
 - Approximate additivity avoids direct calc of H(B)
 - Mostly applicable to thermodynamics

G2 and G3 Methods

G2: L.A. Curtiss, K. Raghavachari, G.W. Trucks, and J.A. Pople, *J. Chem. Phys.*, **94**, 7221 (1991)

Based on additivity (independence) of basis set improvements and correlation improvements.

Geometries taken from MP2/6-31G(d) optimizations (**Full Core**)

$$E_0(\text{G2}) = E_0(\text{G1}) + \Delta + 1.14 \text{ npair}$$

🍏 npair = number of electron pairs (empirical modification)

$$E_0(\text{G1}) = E[\text{MP4/6-311G(d,p)}] + \Delta E(+)+\Delta E(2\text{df})+\Delta E(\text{QCI}) + \Delta E(\text{HLC}) + \Delta E(\text{ZPE})$$

🍏 $\Delta E(+)$ = correction for adding diffuse functions to the 6-311G(d,p) basis set

🍏 $\Delta E(2\text{df})$ = correction for adding 2df to the 6-311G(d,p) basis set

🍏 QCI = quadratic CI = QCISD(T) = (poor approximation to CCSD(T))

$$\Delta E(\text{QCI}) = E[\text{QCI/6-311G(d,p)}] - E[\text{MP4/6-311G(d,p)}]$$

🍏 HLC = higher level correction: “slightly empirical” fitted parameter

🍏 $\Delta E(\text{ZPE})$ = correction for vibrational zero point energy (ZPE) obtained from HF/6-31G(d), scaled using appropriate scale factor: A.P. Scott and L. Radom, *J. Phys. Chem.*, **100**, 16502–16513 (1996).

$$\Delta = \Delta_1 + \Delta_2$$

$$\Delta_1 = \Delta E(+2\text{df}) - \Delta E(+)- \Delta E(2\text{df}) \text{ (don't separate latter two)}$$

$$\Delta_2 = E(\text{MP2/6-311+G(3df,2p)}) - E[\text{MP2/6-311+G(2df,p)}]: \text{ further basis set improvement}$$

Other versions:

G2 (MP2): eliminate MP4 – replace with MP2

G2 (MP2, SVP): based entirely on 6-31G(d,p), not 6-311G(d,p)

G3: J. Chem. Phys., 109, 7764 (1999)

$$E_0(\text{G3}) = E[\text{MP4/6-31G(d)} + \Delta E(+)+\Delta E(2\text{df,p})] + \Delta E(\text{QCI}) + \Delta E(\text{G3Large}) + \Delta E(\text{SOC}) + \Delta E(\text{ZPE}) + \Delta E(\text{HLC})$$

🍏 Initial geometries from HF/6-31G(d) → Hessian run, ZPE correction

🍏 Final geometries from MP2/6-31G(d)

$$\text{🍏 } \Delta E(+)=E[\text{MP4/6-31+G(d)}] - E[\text{MP4/6-31G(d)}]$$

$$\text{🍏 } \Delta E(2\text{df,p})=E[\text{MP4/6-31G(2df,p)}] - E[\text{MP4/6-31G(d)}]$$

$$\text{🍏 } \Delta E(\text{QCI}) = E[\text{QCI/6-31G(d,p)}] - E[\text{MP4/6-31G(d,p)}]$$

$$\text{🍏 } \Delta E(\text{G3Large}) = E[\text{MP2/6-311+G(3df,2p)}] - E[\text{MP2/6-31G(2df,p)}] - E[\text{MP2/6-31+G(d)}] - E[\text{MP2/6-31G(d)}]$$

🍏 $\Delta E(\text{SOC})$: spin-orbit coupling from atoms

🍏 Modification: G2(MP2) – replace MP4 with MP2

**Predicts heats of formation to ~ 1kcal/mol
Not good for barrier heights, rxn paths**

In GAMESS (Sean Nedd)

G2 (MP2)
G3 (MP2)
QCI replaced by CR-CC(2,3)
Currently closed shell only

GAMESS G3 input file

RUNTYP=G3MP2

See EXAM43.inp

OTHER COMPOSITE METHODS

- Weizman Wn methods (n=1,2,3,4)
 - Jan Martin at Weizman Institute, now UNT
 - A. Karton, E. Rabinovich, and J. M. L. Martin, J. Chem. Phys. **125** (144108), 144108 (2006).
 - Uses cc basis sets up to aug-cc-pV5Z
 - No empirical parameters, very time-consuming
 - Extrapolation to complete basis set limit
- Not yet in GAMESS

**Predicts heats of formation to ~ 1kcal/mol
Not good for barrier heights, rxn paths**

OTHER COMPOSITE METHODS

- ccCA Methods (Angela Wilson, UNT)
 - N. J. De Yonker, B. R. Wilson, A. W. Pierpont, T. R. Cundari, and A. K. Wilson, *Molecular Physics* **107** (20), 1107 (2009): ccCA-S4
 - Uses cc basis sets through aug-cc-pVQZ
 - Extrapolation to complete basis set limit
 - No empirical parameters
 - Modified version in GAMESS
 - Replaces CCSD(T) with CR-CC(2,3)
 - Thermodynamics as reliable as ccCA-S4
 - Accurate for diradical reaction paths due to CR-CC(2,3)
 - Better than Gn; less demanding than Wn