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Short Communication

Application of Second Order BWEN Perturbation Theory to Some Simple Reactions

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The second order Brillouin-Wigner perturbation expansion with the Epstein–Nesbet partitioning is applied to some isomerization and insertion reactions, using the 6-31G* basis set. BWEN2 is found to be comparable in accuracy with RSMP2 for predictions of energy barriers and isomerization energies.

Key words: Perturbation theory – Isomerization reactions.

In recent years it has become feasible to include significant levels of correlation corrections in *ab initio* calculations on chemical processes. Among the approaches commonly used for ground states, the least expensive computationally is second order many body perturbation theory [1, 2]. The Rayleigh–Schrödinger (RS) approach as applied to Hartree-Fock wavefunctions [3] has been popularized by Pople and co-workers [1, 4–6] and has been applied with considerable success to many phenomena. As noted by Ostlund and Bowen [7], this RSMP2 method is theoretically pleasing since it is invariant to an arbitrary mixing of degenerate orbitals.

Recently, an alternative perturbation expansion, a Brillouin–Wigner expansion with an "Epstein–Nesbet" partitioning of the Hamiltonian, has been used with the semi-empirical MNDO method to predict the barriers in some isomerization reactions [8]. While this BWEN2 method does not have the invariance property noted above, it does recover a larger portion of the correlation error than does RSMP2 [7]. Furthermore, since the relationship between BWEN perturbation theory and configuration interaction is clear [9], there is a possibility of using this approach for both ground and excited states [10].

Table 1. Total energies (hartree)[a]

	HF	MP2	MP3	MP4(DQ)	MP4(SDQ)	BWEN2
HCCH	−76.81783	−77.06457	−77.07502	−77.07652	−77.07995	−77.08835
HC(H)C	−76.73717	−76.98034	−76.99381	−76.99541	−77.00009	−76.99521
H_2CC	−76.76340	−76.98518	−77.00704	−77.00983	−77.01299	−77.00275
HCN	−92.87520	−93.15461	−93.15701	−93.15980	−93.16376	−93.16588
C(H)N	−92.79195	−93.06709	−93.07371	−93.07639	−93.08213	−93.08858
CNH	−92.85523	−93.12306	−93.13082	−93.13301	−93.13707	−93.14063
H_2CO	−113.86633	−114.16523	−114.17168	−114.17529	−114.17947	−114.18327
HC(H)O	−113.69964	−114.01801	−114.01823	−114.02333	−114.03024	−114.02974
HCOH(trans)	−113.78351	−114.06882	−114.08153	−114.08553	−114.08925	−114.07718
HNNH(trans)	−109.99476	−110.31108	−110.32275	−110.32576	−110.32863	−110.33427
HN(H)N	−109.84629	−110.18300	−110.18641	−110.19048	−110.19641	−110.20126
H_2NN	−109.96357	−110.26728	−110.28098	−110.28401	−110.28817	−110.28518
HSiCH	−327.76488	−327.99291	−327.99805			−328.00962
HSi(H)C	−327.77969	−327.96988	−327.99087			−327.98377
H_2SiC	−327.85455	−328.05678	−328.07549			−328.07102
SiH_4	−291.22444	−291.30780	−291.32653			−291.31521
$SiH_4^{\ddagger}$	−291.09738	−291.20052	−291.22294			−291.21361
SiH_2+H_2	−291.12673	−291.21345	−291.23634			−291.22855

[a] The MP results have been taken from Refs. [6] and [11].

Table 2. Relative energies (kcal/mol)[a]

	HF	MP2	MP3	MP4(DQ)	MP4(SDQ)	BWEN2
HCCH	0.0	0.0	0.0	0.0	0.0	0.0
HC(H)C	50.6	52.9	51.0	50.9	50.1	58.4
H_2CC	34.2	49.8	42.7	41.9	42.0	53.7
HCN	0.0	0.0	0.0	0.0	0.0	0.0
C(H)N	52.2	54.9	52.3	52.3	51.2	48.5
CNH	12.5	19.8	16.4	16.8	16.7	15.8
H_2CO	0.0	0.0	0.0	0.0	0.0	0.0
HC(H)O	104.6	92.4	96.3	95.4	93.7	96.2
HCOH(trans)	52.0	60.5	56.6	56.3	56.6	66.5
HNNH(trans)	0.0	0.0	0.0	0.0	0.0	0.0
HN(H)N	93.2	80.4	85.6	84.9	83.0	83.5
H_2NN	19.6	27.5	26.2	26.2	25.4	30.8
HSiCH	47.0	40.1	48.6			38.5
HSi(H)C	56.3	54.5	53.1			54.7
H_2SiC	0.0	0.0	0.0			0.0
SiH_4	0.0	0.0	0.0			0.0
$SiH_4^{\ddagger}$	79.7	67.3	65.0			63.8
SiH_2+H_2	61.3	59.2	56.6			54.4

[a] The MP results have been taken from Refs. [6] and [11].

To our knowledge, the two perturbation approaches discussed above have not been extensively compared for the prediction of isomerization or reaction barriers. In the present note the ability of these two methods to predict such barriers in a series of 1,2 hydrogen shifts and the insertion of SiH_2 into H_2 is compared. The RSMP calculations on 1,2-shifts are taken from the work of Pople and coworkers [6, 11], while SiH_2 insertion [12] and BWEN2 [13] calculations were performed in this laboratory. All calculations were performed using the 6-31G* basis set [14, 15]. In all calculations the inner shells have been excluded from the perturbation calculations.

The calculated total and relative energies are compared in Tables 1 and 2, respectively. Third and fourth order MP results have been included in both tables. The BWEN2 total energies are consistently lower than the MP2 values and are frequently lower than those from MP3. If one can assume that the MP4 (SDQ) results are the closest to experiment, then the ability of the two second order methods to predict the barriers from the processes considered here appears to be roughly comparable. Thus, BWEN2 may be a reasonable alternative for such processes, particularly if one is interested in comparing similar processes in ground and excited states.

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