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Towards multireference equivalents of the G2 and G3 methods

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The effect of replacing the standard single-determinant reference wave functions in variants of G2 and G3 theory by multireference (MR) wave functions based on a full-valence complete active space has been investigated. Twelve methods of this type have been introduced and comparisons, based on a slightly reduced G2-1 test set, are made both internally and with the equivalent single-reference methods. We use CASPT2 as the standard MR-MP2 method and MRCI+Q as the higher correlation procedure in these calculations. We find that MR-G2(MP2,SVP), MR-G2(MP2), and MR-G3(MP2) perform comparably with their single-reference analogs, G2(MP2,SVP), G2(MP2), and G3(MP2), with mean absolute deviations (MADs) from the experimental data of 1.41, 1.54, and 1.23 kcal mol^{-1}, compared with 1.60, 1.59, and 1.19 kcal mol^{-1}, respectively. The additivity assumptions in the MR-Gn methods have been tested by carrying out MR-G2/MRCI+Q and MR-G3/MRCI+Q calculations, which correspond to large-basis-set MRCI+Q+ZPVE+HLC calculations. These give MADs of 1.84 and 1.58 kcal mol^{-1}, respectively, i.e., the agreement with experiment is somewhat worse than that obtained with the MR-G2(MP2) and MR-G3(MP2) methods. In a third series of calculations, we have examined pure MP2 and MR-MP2 analogs of the G2 and G3 procedures by carrying out large-basis-set MP2 and CASPT2(+ZPVE+HLC) calculations. The resultant methods, which we denote G2/MP2, G3/MP2, MR-G2/MP2, and MR-G3/MP2, give MADs of 4.19, 3.36, 2.01, and 1.66 kcal mol^{-1}, respectively. Finally, we have examined the effect of using MCQDPT2 in place of CASPT2 in five of our MR-Gn procedures, and find that there is a small but consistent deterioration in performance. Our calculations suggest that the MR-G3(MP2) and MR-G3/MP2 procedures may be useful in situations where a multireference approach is desirable. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1411998]

I. INTRODUCTION

The prediction of thermodynamic properties, such as atomization energies, ionization energies, electron affinities, and heats of formation, to "chemical accuracy" has long been a goal of quantum chemists, and there has been great progress in this direction in recent years.[1] Methods that have been developed in an attempt to achieve this goal, include the Gaussian series (Gn, $n = 1$, 2 or 3) of model chemistries developed by Curtiss, Raghavachari, Pople, and co-workers,[2–4] the complete-basis-set (CBS) methods of Petersson and co-workers,[5] the BAC-MPX (X=2 or 4) methods due to Melius and co-workers,[6] the W1, W2 and related methods of Martin,[7] and the extrapolation procedures due to Dunning, Feller, Dixon, Peterson, and co-workers.[8] The G2 and G3 methods and their variants,[3,4] in particular, have become very popular among both theoreticians and experimentalists, because of their ability to predict accurate thermodynamics for a wide variety of chemical compounds.

One potential drawback of the Gn approaches is that they are based on the presumption that the chemical species of interest can be well described by a single configuration, i.e., it can be well represented by a single Lewis structure.

There are, however, many systems for which this assumption may not be appropriate.[9] Important examples include transition structures for many chemical reactions, regions of potential energy surfaces in which bonds are dissociating or forming near conical intersections, as well as the vast majority of electronic excited states.[9] In addition, first-row transition metal complexes and unsaturated compounds that contain transition metals are also often not well described by a single-determinant wave function. For such species with pronounced multireference character, the Gn methods may not provide accurate thermodynamic quantities.[9]

The aim of the various Gn models is generally to estimate energies at a high correlation level, typically quadratic configuration interaction (QCISD(T)),[10] with a large basis set. This is achieved by starting with a modest-basis-set QCISD(T) calculation and estimating the effect of moving to a larger basis set at the MP2 and /or MP4 levels, i.e., assuming the additivity of basis set and correlation effects. In addition, a zero-point vibrational energy correction is incorporated, as well as a "higher level correction," which is intended to account for any remaining deficiencies in level of theory and basis set. In a multireference (MR) Gn approach, the analog of MP2 would be MR-MP2 while the analog of QCI would ideally be MR-QCI. Unfortunately, codes for carrying out MR-QCI [or related coupled cluster (MR-CC)] cal-

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TABLE I. Higher-level-correction parameters (in mHartrees) for the MR-G2 and G2-type methods.

Method	A
MR-G2(MP2.SVP)	8.250
MR(QD)-G2(MP2.SVP)	8.731
MR-G2(MP2)	7.542
MR(QD)-G2(MP2)	7.820
MR-G2/MRCI+Q	6.469
MR-G2/MP2	8.802
MR(QD)-G2/MP2	9.437
G2/MP2	4.246

TABLE II. Higher-level-correction parameters (in mHartrees) for the MR-G3 and G3-type methods.

Method	A	B	C	D
MR-G3(MP2)	11.086	2.493	10.368	1.713
MR(QD)-G3(MP2)	11.575	2.705	10.697	1.822
MR-G3/MRCI+Q	11.158	3.605	9.564	2.912
MR-G3/MP2	12.900	1.799	13.099	1.915
MR(QD)-G3/MP2	13.135	1.819	13.177	1.749
G3/MP2	7.579	4.157	9.970	0.573

culations are not widely available at the present time. We have selected multireference configuration interaction with single and double substitutions (MR-CISD) as the best current alternative.

The present multireference analogs of both the G2 and G3 methods are described in Sec. II. It is important as a first step in developing MR-Gn procedures that may be usefully applied to problems requiring a multireference approach, to examine the performance of such procedures for systems that are reasonably described by single-reference treatments. That is the principal aim of the present study and the G2-1 test set is well suited for this purpose. Accordingly, since the new multireference procedures are essentially untested with respect to their ability to reliably predict accurate thermodynamic quantities in the manner of the Gn methods, Sec. III contains a detailed assessment of their performance on a slightly modified G2-1 test set. We also examine the performance of pure MP2 and MR-MP2 analogs of G2 and G3 theory. Finally, conclusions that emerge from our study are presented in Sec. IV.

II. METHODS

A. Relationship between the Gn and MR-Gn methods

The simplest version of the G2 method, referred to as G2(MP2,SVP),[3(e),3(f)] is based on the following additivity approximation to estimate the QCISD(T) energy for the extended 6-311+G($3df,2p$) basis set,

$$E[QCISD(T)/6\text{-}311+G(3df,2p)]$$
$$\approx E[QCISD(T)/6\text{-}31G(d)]$$
$$+ E[MP2/6\text{-}311+G(3df,2p)] - E[MP2/6\text{-}31G(d)].$$
$$(1)$$

The G2(MP2,SVP) energy is derived by adding to this, firstly a zero-point vibrational energy (ZPVE) obtained from scaled (by 0.8929) HF/6-31G(d) vibrational frequencies, and secondly a "higher level correction" (HLC). The HLC is an empirical correction which is determined by minimizing the mean absolute deviation (MAD) between experiment and theory for the thermochemical quantities in a test set of molecules (see below).

The multireference versions of the Gn schemes are based on the same premise as the single-reference version, namely, that the effects of improvements in the basis set and treatment of electron correlation are additive. In our initial

set of MR-Gn procedures, we retain the same geometries [MP2(full)/6-31G(d)] and ZPVEs [scaled HF/6-31G(d)] as in the Gn methods and these are thus taken from the G2 data base.[11] This makes it easier to identify inherent MR-Gn differences. The current single-configuration levels of theory are replaced by multireference analogs as follows:

$$SCF \Rightarrow MCSCF, \qquad (2)$$

$$MP2 \Rightarrow MR\text{-}MP2, \qquad (3)$$

$$QCISD(T) \Rightarrow MR\text{-}CISD. \qquad (4)$$

MCSCF refers to multiconfiguration (MC) self-consistent-field (SCF) calculations based on the CASSCF (Ref. 12) or FORS (Ref. 13) prescription. We include all valence electrons and valence orbitals in the "active space." For example, the active spaces for methane, ammonia, and water are [8, 8], [8, 7], and [8, 6], respectively, where the first number is the number of active electrons and the second number refers to the number of active orbitals. By choosing a full-valence CASSCF approach, we obtain a procedure that is well-defined for any species, but the downside is that the cost rises very rapidly with molecular size. Our standard MR-MP2 multireference second-order perturbation theory method is the CASPT2 procedure developed by Roos and co-workers.[14,15] We also examine results obtained with the multiconfiguration quasidegenerate second-order perturbation theory method, MCQDPT2, developed by Nakano.[16] We note that analytic gradients for MCQDPT2 have been derived, also by Nakano,[17] and are currently being implemented into the electronic structure code GAMESS.[18] This may be important in more refined versions of MR-Gn in which the geometries are reoptimized at MR-MP2 (rather than simply using the MP2 geometries of Gn theory).

The remaining step in the MR-Gn model requires a multi-reference energy calculation at a level of theory that is comparable to QCISD(T). The obvious choice would be MR-QCISD(T). While several groups have worked on multireference coupled cluster methods,[19] there are no efficient, general MR-CCSD(T) codes available at the present time. So, while in the long term it is desirable to use MR-QCISD(T) or MR-CCSD(T) for this step of the method, in the short term we will use the internally-contracted MR-CISD (of Werner and Knowles)[20] with the Davidson cluster correction (Q). We will refer to this method as MRCI+Q throughout the present work.

In this manner, we have constructed the MR-G2-type and MR-G3-type methods defined by Eqs. (5), (6), and (7),

TABLE III. MR-G2(MP2,SVP) heat of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G2(MP2,SVP) values.[a]

	Species		Species		Species	
Heats of formation	LiH	30.3 (+3.0)	PH_3	3.1 (−1.8)	F_2	0.5 (−0.5)
	BeH	84.2 (−2.5)	H_2S	−5.2 (+0.3)	CO_2	−96.5 (+2.4)
	CH	141.6 (+0.9)	HCl	−23.2 (+1.1)	Na_2	29.4 (+4.6)
	$CH_2\,{}^3B_1$	94.9 (−1.2)	Li_2	47.4 (+4.2)	Si_2	139.7 (+0.2)
	$CH_2\,{}^1A_1$	100.8 (+2.0)	LiF	−80.5 (+0.4)	P_2	35.3 (−1.0)
	CH_3	34.5 (+0.5)	C_2H_2	54.4 (−0.2)	S_2	32.6 (−1.9)
	CH_4	−20.0 (+2.1)	C_2H_4	15.2 (−2.7)	Cl_2	1.1 (−1.1)
	NH	85.9 (−0.7)	CN	106.8 (−1.9)	NaCl	−46.1 (+2.5)
	NH_2	44.7 (+0.4)	HCN	31.6 (−0.1)	SiO	−22.5 (−2.1)
	NH_3	−9.1 (−1.9)	CO	−28.5 (+2.1)	CS	64.5 (+2.4)
	OH	8.7 (+0.7)	HCO	9.5 (+0.5)	SO	3.5 (−2.3)
	H_2O	−57.7 (−0.1)	HCHO	−26.4 (+0.4)	ClO	26.2 (−2.0)
	HF	−65.6 (+0.5)	CH_3OH	−48.4 (+0.4)	ClF	−12.5 (+0.7)
	$SiH_2\,{}^1A_1$	62.9 (+2.3)	N_2	−0.2 (+0.2)	CH_3Cl	−21.4 (+1.8)
	$SiH_2\,{}^3B_1$	87.2 (−1.0)	N_2H_4	23.8 (−1.0)	CH_3SH	−7.4 (+1.9)
	SiH_3	48.2 (−0.3)	NO	20.6 (+1.0)	HOCl	−17.8 (+0.0)
	SiH_4	7.5 (+0.7)	O_2	1.2 (−1.2)	SO_2	−65.8 (−5.2)
	PH_2	33.5 (−0.4)	H_2O_2	−32.5 (+0.0)		
Ionization energies	Li	123.4 (+0.9)	Cl	296.2 (+2.9)	HCl	293.2 (+0.8)
	Be	219.3 (−4.4)	CH_4	293.0 (−2.0)	C_2H_2	262.3 (+0.6)
	B	189.2 (+2.2)	NH_3	233.0 (+1.8)	C_2H_4	240.8 (+1.5)
	C	257.8 (+1.9)	OH	300.1 (−0.1)	CO	324.1 (−1.0)
	N	334.1 (+1.2)	OH_2	291.2 (−0.2)	$N_2\,{}^2\Sigma_g^+$	359.0 (+0.3)
	O	313.0 (+0.8)	HF	371.1 (−1.2)	$N_2\,{}^2\Pi_u$	384.1 (+1.0)
	F	402.4 (−0.7)	SiH_4	253.5 (+0.2)	O_2	279.8 (−1.5)
	Na	114.1 (+4.4)	PH	233.0 (+1.1)	P_2	243.2 (−0.4)
	Mg	178.7 (−2.4)	PH_2	224.8 (+1.6)	S_2	213.1 (+2.7)
	Al	137.2 (+0.8)	PH_3	228.4 (−0.8)	Cl_2	265.0 (+0.2)
	Si	186.9 (+1.0)	SH	237.7 (+1.4)	ClF	291.6 (+0.3)
	P	241.4 (+0.5)	$H_2S\,{}^2B_1$	240.4 (+1.0)	CS	262.9 (−1.6)
	S	234.4 (+4.5)	$H_2S\,{}^2A_1$	294.0 (+0.7)		
Electron affinities	C	31.6 (−2.5)	CH_3	−1.7 (+3.5)	SH	53.2 (+1.2)
	O	33.6 (+0.1)	NH	7.9 (+0.9)	O_2	11.1 (−1.0)
	F	81.0 (−2.6)	NH_2	17.5 (+0.3)	NO	−0.9 (+1.4)
	Si	32.2 (−0.3)	OH	42.9 (−0.7)	CN	91.7 (−2.7)
	P	14.2 (+3.0)	SiH	27.7 (+1.7)	PO	24.5 (+0.6)
	S	46.3 (+1.6)	SiH_2	23.2 (+2.7)	S_2	37.5 (+0.8)
	Cl	83.9 (−0.5)	SiH_3	33.6 (−1.1)	Cl_2	53.9 (+1.2)
	CH	27.4 (+1.2)	PH	22.0 (+1.8)		
	CH_2	16.0 (−1.0)	PH_2	28.7 (+0.6)		
Proton affinities	NH_3	205.4 (−2.9)	SiH_4	153.5 (+0.5)	HCl	133.1 (+0.5)
	H_2O	160.8 (+4.3)	PH_3	185.3 (+1.8)		
	C_2H_2	153.5 (−1.2)	H_2S	167.6 (+1.2)		

[a]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

$$E[\text{MR-G2(MP2,SVP)}]$$
$$= E[\text{MRCI}+\text{Q}/6\text{-}31\text{G}(d)]$$
$$+ (E[\text{CASPT2}/6\text{-}311+\text{G}(3df,2p)]$$
$$- E[\text{CASPT2}/6\text{-}31\text{G}(d)]) + \text{ZPVE} + \text{HLC}, \qquad (5)$$

$$E[\text{MR-G2(MP2)}]$$
$$= E[\text{MRCI}+\text{Q}/6\text{-}311\text{G}(d,p)]$$
$$+ (E[\text{CASPT2}/6\text{-}311+\text{G}(3df,2p)]$$
$$- E[\text{CASPT2}/6\text{-}311\text{G}(d,p)]) + \text{ZPVE} + \text{HLC}, \qquad (6)$$

$$E[\text{MR-G3(MP2)}]$$
$$= E[\text{MRCI}+\text{Q}/6\text{-}31\text{G}(d)] + (E[\text{CASPT2}/\text{G3MP2large}]$$
$$- E[\text{CASPT2}/6\text{-}31\text{G}(d)]) + \Delta E(\text{SO}) + \text{ZPVE} + \text{HLC}. \qquad (7)$$

The spin–orbit correction $[\Delta E(\text{SO})]$ used in our MR-G3(MP2) calculations [Eq. (7)] is the same as that used in G3 theory.[4]

In order to investigate the additivity assumptions in Eqs. (5)–(7), we have also constructed the multireference equiva-

TABLE IV. MR-G2(MP2) heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G2(MP2) values.[a]

	Species		Species		Species	
Heats of formation	LiH	30.6 (+2.7)	PH$_3$	1.3 (+0.0)	F$_2$	1.2 (−1.2)
	BeH	83.0 (−1.3)	H$_2$S	−5.9 (+1.0)	CO$_2$	−95.0 (+0.9)
	CH	141.4 (+1.1)	HCl	−23.5 (+1.4)	Na$_2$	29.8 (+4.2)
	CH$_2$ $^3B_1$	94.5 (−0.8)	Li$_2$	47.9 (+3.7)	Si$_2$	140.4 (−0.5)
	CH$_2$ $^1A_1$	100.0 (+2.8)	LiF	−81.3 (+1.2)	P$_2$	36.7 (−2.4)
	CH$_3$	33.8 (+1.2)	C$_2$H$_2$	55.9 (−1.7)	S$_2$	33.3 (−2.6)
	CH$_4$	−20.9 (+3.0)	C$_2$H$_4$	11.4 (+1.1)	Cl$_2$	1.5 (−1.5)
	NH	85.7 (−0.5)	CN	108.4 (−3.5)	NaCl	−45.7 (+2.1)
	NH$_2$	44.2 (+0.9)	HCN	32.9 (−1.4)	SiO	−22.4 (−2.2)
	NH$_3$	−9.8 (−1.2)	CO	−27.8 (+1.4)	CS	65.7 (+1.2)
	OH	8.5 (+0.9)	HCO	10.2 (−0.2)	SO	4.0 (−2.8)
	H$_2$O	−58.2 (+0.4)	HCHO	−26.3 (+0.3)	ClO	26.6 (−2.4)
	HF	−65.5 (+0.4)	CH$_3$OH	−48.9 (+0.9)	ClF	−11.9 (−1.3)
	SiH$_2$ $^1A_1$	61.4 (+3.8)	N$_2$	1.0 (−1.0)	CH$_3$Cl	−21.3 (+1.7)
	SiH$_2$ $^3B_1$	85.7 (+0.5)	N$_2$H$_4$	23.2 (−0.4)	CH$_3$SH	−5.2 (−0.3)
	SiH$_3$	45.8 (+2.1)	NO	21.3 (+0.3)	HOCl	−17.7 (−0.1)
	SiH$_4$	4.0 (+4.2)	O$_2$	1.5 (−1.5)	SO$_2$	−64.6 (−6.4)
	PH$_2$	32.4 (+0.7)	H$_2$O$_2$	−32.6 (+0.1)		
Ionization energies	Li	123.4 (+0.9)	Cl	295.5 (+3.6)	HCl	292.9 (+1.1)
	Be	218.9 (−4.0)	CH$_4$	293.4 (−2.4)	C$_2$H$_2$	262.0 (+0.9)
	B	190.2 (+1.2)	NH$_3$	232.9 (+1.9)	C$_2$H$_4$	244.6 (−2.3)
	C	258.5 (+1.2)	OH	299.5 (+0.5)	CO	324.1 (−1.0)
	N	334.1 (+1.2)	H$_2$O	291.0 (+0.0)	N$_2$ $^2\Sigma_g^+$	358.5 (+0.8)
	O	312.3 (+1.5)	HF	370.3 (−0.4)	N$_2$ $^2\Pi_u$	383.6 (+1.5)
	F	401.4 (+0.3)	SiH$_4$	254.6 (−0.9)	O$_2$	279.3 (−1.0)
	Na	114.1 (+4.4)	PH	232.9 (+1.2)	P$_2$	242.6 (+0.2)
	Mg	178.2 (−1.9)	PH$_2$	224.6 (+1.8)	S$_2$	212.9 (+2.9)
	Al	137.2 (+0.8)	PH$_3$	228.3 (−0.7)	Cl$_2$	264.4 (+0.8)
	Si	187.0 (+0.9)	SH	237.3 (+1.8)	ClF	290.9 (+1.0)
	P	241.2 (+0.7)	H$_2$S $^2B_1$	240.1 (+1.3)	CS	262.9 (−1.6)
	S	233.8 (+5.1)	H$_2$S $^2A_1$	294.0 (+0.7)		
Electron affinities	C	31.6 (−2.5)	CH$_3$	−1.8 (+3.6)	SH	52.6 (+1.8)
	O	32.6 (+1.1)	NH	7.4 (+1.4)	O$_2$	10.1 (+0.0)
	F	79.4 (−1.0)	NH$_2$	17.2 (+0.6)	NO	−1.3 (+1.8)
	Si	32.3 (−0.4)	OH	42.1 (+0.1)	CN	91.6 (−2.6)
	P	13.9 (+3.3)	SiH	27.8 (+1.6)	PO	24.1 (+1.0)
	S	45.7 (+2.2)	SiH$_2$	23.1 (+2.8)	S$_2$	36.6 (+1.7)
	Cl	83.0 (+0.4)	SiH$_3$	33.4 (−0.9)	Cl$_2$	52.9 (+2.2)
	CH	27.2 (+1.4)	PH	21.6 (+2.2)		
	CH$_2$	16.1 (−1.1)	PH$_2$	28.1 (+1.2)		
Proton affinities	NH$_3$	205.6 (−3.1)	SiH$_4$	153.4 (+0.6)	HCl	133.8 (−0.2)
	H$_2$O	161.0 (+4.1)	PH$_3$	186.3 (+0.8)		
	C$_2$H$_2$	153.9 (−1.6)	H$_2$S	168.4 (+0.4)		

[a]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

lents of the G2/QCI method[3(b),21] and its G3 analog[22] [Eqs. (8) and (9)],

$$E[\text{MR-G2/MRCI+Q}]$$
$$= E[\text{MRCI+Q/6-311+G}(3df,2p)] + \text{ZPVE} + \text{HLC}, \quad (8)$$

$$E[\text{MR-G3/MRCI+Q}]$$
$$= E[\text{MRCI+Q/G3MP2large}] + \Delta E(\text{SO}) + \text{ZPVE} + \text{HLC}. \quad (9)$$

In a third set of calculations, we have investigated the performance of pure MP2 and MR-MP2 analogs of G2- and G3-type procedures, denoting such methods as G2/MP2, G3/

MP2, MR-G2/MP2, and MR-G3/MP2.[22] For example, the multireference versions correspond to large-basis-set CASPT2 calculations,

$$E[\text{MR-G2/MP2}] = E[\text{CASPT2/6-311+G}(3df,2p)]$$
$$+ \text{ZPVE} + \text{HLC} \quad (10)$$

and

$$E[\text{MR-G3/MP2}] = E[\text{CASPT2/G3MP2large}] + \Delta E(\text{SO})$$
$$+ \text{ZPVE} + \text{HLC}. \quad (11)$$

The single-reference analogs are obtained as

TABLE V. MR-G3(MP2) heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G3(MP2) values.[a]

	Species		Species		Species	
Heats of formation	LiH	30.5 (+2.8)	PH_3	3.7 (−2.4)	F_2	−1.5 (+1.5)
	BeH	83.3 (−1.6)	H_2S	−4.9 (+0.0)	CO_2	−94.8 (+0.7)
	CH	141.2 (+1.3)	HCl	−23.1 (+1.0)	Na_2	29.5 (+4.5)
	$CH_2\ ^3B_1$	93.9 (−0.2)	Li_2	47.5 (+4.1)	Si_2	138.7 (+1.2)
	$CH_2\ ^1A_1$	101.3 (+1.5)	LiF	−80.3 (+0.2)	P_2	35.7 (−1.4)
	CH_3	34.3 (+0.7)	C_2H_2	54.7 (−0.5)	S_2	31.5 (−0.8)
	CH_4	−19.3 (+1.4)	C_2H_4	15.8 (−3.3)	Cl_2	0.0 (+0.0)
	NH	85.0 (+0.2)	CN	107.3 (−2.4)	NaCl	−46.6 (+3.0)
	NH_2	44.8 (+0.3)	HCN	32.4 (−0.9)	SiO	−23.7 (−0.9)
	NH_3	−8.4 (−2.6)	CO	−27.2 (+0.8)	CS	64.9 (+2.0)
	OH	8.2 (+1.2)	HCO	10.2 (−0.2)	SO	2.2 (−1.0)
	H_2O	−57.5 (−0.3)	HCHO	−25.3 (−0.7)	ClO	25.6 (−1.4)
	HF	−65.6 (+0.5)	CH_3OH	−47.3 (−0.7)	ClF	−12.5 (−0.7)
	$SiH_2\ ^1A_1$	63.0 (+2.2)	N_2	0.7 (−0.7)	CH_3Cl	−20.5 (+0.9)
	$SiH_2\ ^3B_1$	86.0 (+0.2)	N_2H_4	25.2 (−2.4)	CH_3SH	−6.7 (+1.2)
	SiH_3	47.5 (+0.4)	NO	21.3 (+0.3)	HOCl	−17.8 (+0.0)
	SiH_4	7.4 (+0.8)	O_2	0.2 (−0.2)	SO_2	−66.0 (−5.0)
	PH_2	33.2 (−0.1)	H_2O_2	−32.6 (+0.1)		
Ionization energies	Li	124.2 (+0.1)	Cl	296.7 (+2.4)	HCl	293.7 (+0.3)
	Be	219.6 (−4.7)	CH_4	293.2 (−2.2)	C_2H_2	264.3 (−1.4)
	B	189.9 (+1.5)	NH_3	232.7 (+2.1)	C_2H_4	241.0 (+1.3)
	C	258.5 (+1.2)	OH	299.6 (+0.4)	CO	324.5 (−1.4)
	N	334.5 (+0.8)	H_2O	291.0 (+0.0)	$N_2\ ^2\Sigma_g^+$	359.1 (+0.2)
	O	312.9 (+0.9)	HF	370.6 (−0.7)	$N_2\ ^2\Pi_u$	384.2 (+0.9)
	F	401.7 (+0.0)	SiH_4	254.1 (−0.4)	O_2	280.9 (−2.6)
	Na	115.1 (+3.4)	PH	234.8 (−0.7)	P_2	243.7 (−0.9)
	Mg	178.9 (−2.6)	PH_2	226.7 (−0.3)	S_2	215.1 (+0.7)
	Al	138.5 (−0.5)	PH_3	228.9 (−1.3)	Cl_2	265.9 (−0.7)
	Si	187.9 (+0.0)	SH	238.6 (+0.5)	ClF	292.0 (−0.1)
	P	241.8 (+0.1)	$H_2S\ ^2B_1$	241.2 (+0.2)	CS	263.2 (−1.9)
	S	235.9 (+3.0)	$H_2S\ ^2A_1$	294.6 (+0.1)		
Electron affinities	C	31.2 (−2.1)	CH_3	−2.5 (+4.3)	SH	54.2 (+0.2)
	O	31.8 (+1.9)	NH	6.6 (+2.2)	O_2	10.4 (−0.3)
	F	78.6 (−0.2)	NH_2	16.7 (+1.1)	NO	−0.3 (+0.8)
	Si	33.2 (−1.3)	OH	41.4 (+0.8)	CN	91.6 (−2.6)
	P	15.9 (+1.3)	SiH	29.7 (−0.3)	PO	26.2 (−1.1)
	S	47.5 (+0.4)	SiH_2	25.2 (+0.7)	S_2	38.7 (−0.4)
	Cl	83.7 (−0.3)	SiH_3	34.3 (−1.8)	Cl_2	57.4 (−2.3)
	CH	27.7 (+0.9)	PH	23.3 (+0.5)		
	CH_2	15.1 (−0.1)	PH_2	29.8 (−0.5)		
Proton affinities	NH_3	206.0 (−3.5)	SiH_4	153.3 (+0.7)	HCl	132.7 (+0.9)
	H_2O	161.1 (+4.0)	PH_3	184.9 (+2.2)		
	C_2H_2	153.1 (−0.8)	H_2S	167.0 (+1.8)		

[a]Values in kcal mol^{-1}. The heats of formation are 298 K values whereas the remaining quantities refer to 0 K.

$$E[\text{G2/MP2}] = E[\text{MP2/6-311}+\text{G}(3df,2p)]$$
$$+\text{ZPVE}+\text{HLC} \qquad (12)$$

and

$$E[\text{G3/MP2}] = E[\text{MP2/G3MP2large}] + \Delta E(\text{SO})$$
$$+\text{ZPVE}+\text{HLC}. \qquad (13)$$

Finally, we have examined for five of the methods, the effect of using MCQDPT2 in place of CASPT2. For example, MR(QD)-G2(MP2,SVP) is defined by

$$E[\text{MR(QD)-G2(MP2,SVP)}]$$
$$= E[\text{MRCI}+\text{Q/6-31G}(d)]$$
$$+ (E[\text{MCQDPT2/6-311}+\text{G}(3df,2p)]$$
$$- E[\text{MCQDPT2/6-31G}(d)]) + \text{ZPVE} + \text{HLC}. \qquad (5a)$$

Similar definitions apply to MCQDPT2 analogs of MR-G2(MP2), MR-G3(MP2), MR-G2/MP2, and MR-G3/MP2.

Unless otherwise noted, all energy calculations were carried out using MOLPRO 96 [Ref. 23(a)] and MOLPRO 98.[23(b)] MOLPRO is currently the most efficient code available for such calculations. The MCQDPT2 calculations were per-

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TABLE VI. Comparison of the mean absolute deviations (kcal mol^{-1}) from experimental data for multi- and single-reference G2 and G3-type methods.[a]

Test set	ΔH_f	IE	EA	PA	Total
Number of comparisons	53	38	25	7	123
G2(MP2,SVP)	1.36	1.87	2.05	0.81	1.63
MR-G2(MP2,SVP)	1.38	1.38	1.40	1.76	1.41
MR(QD)-G2(MP2,SVP)	1.55	1.42	1.32	1.93	1.48
G2(MP2)	1.33	1.88	1.98	0.64	1.59
MR-G2(MP2)	1.56	1.49	1.55	1.54	1.54
MR(QD)-G2(MP2)	1.76	1.47	1.56	1.43	1.61
G3(MP2)	1.13	1.29	1.23	0.93	1.19
MR-G3(MP2)	1.23	1.13	1.12	1.98	1.22
MR(QD)-G3(MP2)	1.35	1.13	1.13	2.07	1.28
G2/QCI[b]	1.19	1.11	1.22	1.17	1.17
MR-G2/MRCI+Q	1.95	1.35	2.33	1.87	1.84
MR-G3/MRCI+Q	1.67	1.20	1.84	2.07	1.58
G2/MP2	5.61	3.45	2.94	1.81	4.19
MR-G2/MP2	1.69	2.29	2.32	1.70	2.01
MR(QD)-G2/MP2	2.26	2.25	2.53	2.00	2.29
G3/MP2	4.24	2.80	2.74	1.97	3.36
MR-G3/MP2	1.60	1.63	1.77	1.85	1.66
MR(QD)-G3/MP2	2.00	1.77	1.84	2.07	1.90

[a]Unless otherwise noted, all data refer to the 123 energy test set. In the case of the standard Gn methods, this involved reoptimization of the HLC parameters for the reduced set, leading to results that differ slightly from published values based on the full G2-1 test set (Refs. 3 and 4).
[b]Data obtained from Ref. 3(b) and refer to the full 125 energy G2-1 test set.

TABLE VII. Comparison of mean absolute deviations (MAD, kcal mol^{-1}) from experimental data for multi- and single-reference G2 and G3-type methods.[a]

Method	MAD	Method	MAD
G2(MP2.SVP)	1.60	MR-G2(MP2.SVP)	1.41
G2(MP2)	1.59	MR-G2(MP2)	1.54
G3(MP2)	1.19	MR-G3(MP2)	1.23
G2/QCI[b]	1.17	MR-G2/MRCI+Q	1.84
G3/QCI	$\cdots$	MR-G3/MRCI+Q	1.58
G2/MP2	4.19	Mr-G2/MP2	2.01
G3/MP2	3.36	MR-G3/MP2	1.66

[a]All data refer to the 123 molecule test set. In the case of the standard Gn methods, this involved reoptimization of the HLC parameters for the reduced set, leading to results that differ slightly from published values based on the full G2-1 test (Refs. 3, 4).
[b]Data obtained from Ref. 3(b) and refer to the full 125 energy G2-1 test set.

formed with GAMESS.[18] The total energies for all the systems investigated in the present study, as well as the MCQDPT2 tables of relative energies, are available as an EPAPS document (Tables S-I to S-XIX).[24]

B. The higher level correction

The G2 and G3 methods involve different forms of higher level corrections. The derivation of the parameters involved in the G2 and G3 methods are therefore discussed separately below. The justification and possible problems associated with the use of the higher level correction have previously been discussed by Pople et al.[2]

1. The test set

A slightly reduced version of the G2-1 test set[3(a)] was used to obtain the higher-level-correction parameters and to assess the performance of the various methods. The reduced set includes 123 of the 125 energy comparisons of the standard G2-1 set. The heats of formation of ethane and disilane were omitted because the [14, 14] full-valence active space in these two cases makes the MR-CI calculations computationally too demanding.

2. The G2 higher level correction

The G2 higher level correction has the form shown in Eq. (14), where n_α and n_β are the number of α and β valence electrons, respectively,

$$HLC = -An_\beta - Bn_\alpha. \tag{14}$$

We have used this form in all the G2-type methods examined in the present study. The B parameter is constrained to be 0.19 mHartrees in all cases so as to give the correct energy for the hydrogen atom, while the A parameter is chosen to

give the smallest mean absolute deviation from experiment for the 123 energy comparisons in our slightly reduced G2-1 test set. We have employed the same minimization procedure as Curtiss,[25] and we are able to reproduce the higher level correction and the mean absolute deviation reported by Curtiss et al. for the G2(MP2) method from the raw electronic energies.[3(c)] The optimized A parameters for the various G2-type methods are listed in Table I.

3. The G3 higher level correction

In the G3 method, there are separately optimized higher-level-correction terms for molecules and atoms. They have the form shown in Eq. (15) (molecules) and Eq. (16) (atoms),

$$HLC = -An_\beta - B(n_\alpha - n_\beta), \tag{15}$$

$$HLC = -Cn_\beta - D(n_\alpha - n_\beta). \tag{16}$$

We have used the same form of the HLC for all the G3-type methods examined here. The A, B, C, and D parameters are all obtained by minimization of the mean absolute deviation between experiment and theory for the 123 thermochemical quantities in the reduced G2-1 test set. Again, we have employed the same minimization procedure as Curtiss.[25] The optimized parameters for the six G3-type methods are listed in Table II. Starting from the raw electronic energies of the 299 energies in the entire G2/97 test set, our procedure reproduces [for both G3(MP2) and G3] the higher-level-correction parameters and the mean absolute deviations reported by Curtiss et al.[4(a),4(b)]

III. RESULTS AND DISCUSSION

Having optimized the higher-level-correction parameters for 12 different MR-Gn procedures (as well as two related single-reference Gn procedures), we are now in a position to assess their performance. Thermochemical properties that are examined include heats of formation (ΔH_f^0), ionization energies (IE), electron affinities (EA), and proton affinities (PA).

A. MR-G2(MP2,SVP), MR-G2(MP2), and MR-G3(MP2)

Relative energies calculated at the MR-G2(MP2,SVP), MR-G2(MP2), and MR-G3(MP2) levels are presented in

TABLE VIII. MR-G2/MRCI+Q[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G2/MRCI+Q values.[b]

	Species		Species		Species	
Heats of formation	LiH	31.3 (+2.0)	PH_3	−1.0 (+2.3)	F_2	2.0 (−2.0)
	BeH	83.1 (−1.4)	H_2S	−6.4 (+1.5)	CO_2	−94.2 (+0.1)
	CH	141.0 (+1.5)	HCl	−23.1 (+1.0)	Na_2	30.5 (+3.5)
	$CH_2\,^3B_1$	94.3 (−1.6)	Li_2	48.5 (+3.1)	Si_2	140.1 (−0.2)
	$CH_2\,^1A_1$	99.5 (+3.3)	LiF	−82.5 (+2.4)	P_2	34.0 (+0.3)
	CH_3	33.8 (+1.2)	C_2H_2	55.8 (−1.6)	S_2	36.3 (−5.6)
	CH_4	−20.6 (+2.7)	C_2H_4	11.6 (+0.9)	Cl_2	4.2 (−4.2)
	NH	85.2 (+0.0)	CN	107.4 (−2.5)	NaCl	−46.4 (+2.8)
	NH_2	43.7 (+1.4)	HCN	31.7 (−0.2)	SiO	−21.8 (−2.8)
	NH_3	−10.0 (−1.0)	CO	−27.8 (+1.4)	CS	65.7 (+1.2)
	OH	8.6 (+0.8)	HCO	10.3 (−0.3)	SO	6.7 (−5.5)
	H_2O	−57.9 (+0.1)	HCHO	−26.9 (+0.9)	ClO	28.6 (−4.4)
	HF	−65.0 (−0.1)	CH_3OH	−48.0 (+0.0)	ClF	−10.4 (+2.8)
	$SiH_2\,^1A_1$	60.7 (+4.5)	N_2	−0.2 (+0.2)	CH_3Cl	−19.9 (+0.3)
	$SiH_2\,^3B_1$	85.2 (+1.0)	N_2H_4	23.0 (−0.2)	CH_3SH	−6.2 (+0.7)
	SiH_3	45.3 (+2.6)	NO	21.2 (+0.4)	HOCl	−16.1 (−1.7)
	SiH_4	3.8 (+4.4)	O_2	3.0 (−3.0)	SO_2	−60.3 (−10.7)
	PH_2	30.5 (+2.6)	H_2O_2	−31.4 (−1.1)		
Ionization energies	Li	123.4 (+0.9)	Cl	296.6 (+2.5)	HCl	293.1 (+0.9)
	Be	218.3 (−3.4)	CH_4	293.1 (−2.1)	C_2H_2	261.4 (+1.5)
	B	189.9 (+1.5)	NH_3	232.5 (+2.3)	C_2H_4	243.9 (−1.6)
	C	258.2 (+1.5)	OH	299.4 (+0.6)	CO	323.4 (−0.3)
	N	333.5 (+1.8)	H_2O	290.6 (+0.4)	$N_2\,^2\Sigma_g^+$	358.6 (+0.7)
	O	312.7 (+1.1)	HF	369.5 (+0.4)	$N_2\,^2\Pi_u$	383.2 (+1.9)
	F	401.2 (+0.5)	SiH_4	255.0 (−1.3)	O_2	278.2 (+0.1)
	Na	114.1 (+4.4)	PH	232.7 (+1.4)	P_2	242.3 (+0.5)
	Mg	177.5 (−1.5)	PH_2	224.4 (+2.0)	S_2	211.8 (+4.0)
	Al	138.0 (+0.0)	PH_3	228.8 (−1.2)	Cl_2	265.1 (+0.1)
	Si	187.0 (+0.9)	SH	238.5 (+0.6)	ClF	291.3 (+0.6)
	P	240.2 (+1.7)	$H_2S\,^2B_1$	240.8 (+0.6)	CS	263.0 (−1.7)
	S	236.1 (+2.8)	$H_2S\,^2A_1$	294.0 (+0.7)		
Electron affinities	C	27.0 (+2.1)	CH_3	−2.3 (+4.1)	SH	52.6 (+1.8)
	O	30.6 (+3.1)	NH	5.9 (+2.9)	O_2	8.1 (+2.0)
	F	75.8 (+2.6)	NH_2	15.8 (+2.0)	NO	−4.3 (+4.8)
	Si	30.5 (+1.4)	OH	38.9 (+3.3)	CN	91.0 (−2.0)
	P	15.6 (+1.6)	SiH	27.1 (+2.3)	PO	20.8 (+4.3)
	S	46.3 (+1.6)	SiH_2	23.0 (+2.9)	S_2	36.9 (+1.4)
	Cl	82.7 (+0.7)	SiH_3	34.1 (−1.6)	Cl_2	50.8 (+4.3)
	CH	25.5 (+3.1)	PH	22.4 (+1.4)		
	CH_2	15.5 (−0.5)	PH_2	28.7 (+0.6)		
Proton affinities	NH_3	205.7 (−3.2)	SiH_4	152.7 (+1.3)	HCl	133.4 (+0.2)
	H_2O	161.1 (+4.0)	PH_3	185.5 (+1.6)		
	C_2H_2	154.2 (−1.9)	H_2S	167.9 (+0.9)		

[a]Corresponding to MRCI+Q/6-311+G($3df$,2p)+ZPVE+HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values whereas the remaining quantities refer to 0 K.

Tables III–V, while a statistical analysis, including a comparison with corresponding single-reference (SR) methods, is shown in Tables VI and VII.

Examination of Table VI shows that, in comparison with the corresponding single-reference methods, results for the three MR procedures are all slightly worse for heats of formation, significantly better for ionization energies and electron affinities, and significantly worse for proton affinities. The overall mean absolute deviations (MADs) are quite similar for MR-G2(MP2) compared with G2(MP2) and for MR-G3(MP2) compared with G3(MP2). However, MR-G2(MP2,SVP) produces better overall results than G2(MP2,SVP).

Of the 123 energy comparisons, there are 10 cases of deviations of $\geqslant 3$ kcal mol^{-1} for MR-G2(MP2,SVP), 15 cases for MR-G2(MP2), and 11 cases for MR-G3(MP2). Of these, eight are common to all three methods: the heats of formation of Li_2, Na_2, and SO_2, the ionization energies of Be, Na, and S, the electron affinity of CH_3 and the proton affinity of H_2O. In comparison, there are 21 cases of deviations of $\geqslant 3$ kcal mol^{-1} for G2(MP2,SVP), 12 cases for G2(MP2), and 10 cases for G3(MP2). Six of the eight deviant cases with the MR-Gn methods are also poor with G3(MP2): the heats of formation of Li_2, Na_2, and SO_2, and the ionization energies of Be, Na, and S. The poor results obtained for SO_2 in G2-type calculations have been shown previously by Martin[26] to be the result of inadequate basis sets.

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TABLE IX. MR-G3/MRCI+Q[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G3/MRCI+Q values.[b]

	Species		Species		Species	
Heats of formation	LiH	31.9 (+1.4)	PH_3	−0.1 (+1.4)	F_2	−2.7 (+2.7)
	BeH	81.7 (+0.0)	H_2S	−6.6 (+1.7)	CO_2	−93.9 (−0.2)
	CH	140.6 (+1.9)	HCl	−24.3 (+2.2)	Na_2	30.9 (+3.1)
	$CH_2\,^3B_1$	93.5 (+0.2)	Li_2	49.0 (+2.6)	Si_2	138.5 (+1.4)
	$CH_2\,^1A_1$	100.5 (+2.3)	LiF	−83.0 (+2.9)	P_2	34.2 (+0.1)
	CH_3	34.1 (+0.9)	C_2H_2	56.1 (−1.9)	S_2	33.6 (−2.9)
	CH_4	−19.2 (+1.3)	C_2H_4	12.8 (−0.3)	Cl_2	0.5 (−0.5)
	NH	84.4 (+0.8)	CN	107.8 (−2.9)	NaCl	−48.4 (+4.8)
	NH_2	44.1 (+1.0)	HCN	32.8 (−1.3)	SiO	−24.0 (−0.6)
	NH_3	−8.5 (−2.5)	CO	−27.2 (+0.8)	CS	65.3 (+1.6)
	OH	7.4 (+2.0)	HCO	10.4 (−0.4)	SO	3.7 (−2.5)
	H_2O	−57.9 (+0.1)	HCHO	−26.0 (+0.0)	ClO	25.8 (−1.6)
	HF	−66.2 (+1.1)	CH_3OH	−46.7 (−1.3)	ClF	−13.2 (+0.0)
	$SiH_2\,^1A_1$	60.7 (+4.5)	N_2	1.0 (−1.0)	CH_3Cl	−19.1 (−0.5)
	$SiH_2\,^3B_1$	83.7 (+2.5)	N_2H_4	25.6 (−2.8)	CH_3SH	−5.5 (+0.0)
	SiH_3	44.5 (+3.4)	NO	21.2 (+0.4)	HOCl	−17.9 (+0.1)
	SiH_4	3.9 (+4.3)	O_2	0.4 (−0.4)	SO_2	−62.7 (−8.3)
	PH_2	30.3 (+2.8)	H_2O_2	−32.4 (−0.1)		
Ionization energies	Li	124.9 (−0.6)	Cl	297.1 (+2.0)	HCl	294.0 (+0.0)
	Be	218.4 (−3.5)	CH_4	293.7 (−2.7)	C_2H_2	263.8 (−0.9)
	B	191.4 (+0.0)	NH_3	232.6 (+2.2)	C_2H_4	244.6 (−2.3)
	C	259.7 (+0.0)	OH	299.5 (+0.5)	CO	324.3 (−1.2)
	N	334.8 (+0.5)	H_2O	290.8 (+0.2)	$N_2\,^2\Sigma_g^+$	359.3 (+0.0)
	O	312.5 (+1.3)	HF	369.4 (+0.5)	$N_2\,^2\Pi_u$	383.9 (+1.2)
	F	400.4 (+1.3)	SiH_4	256.1 (−2.4)	O_2	280.2 (−1.9)
	Na	115.8 (+2.7)	PH	235.2 (−1.1)	P_2	243.4 (−0.6)
	Mg	177.6 (−1.3)	PH_2	227.0 (−0.6)	S_2	214.5 (+1.3)
	Al	139.9 (−1.9)	PH_3	229.8 (−2.2)	Cl_2	266.6 (−1.4)
	Si	188.6 (−0.7)	SH	239.9 (−0.8)	ClF	292.3 (−0.4)
	P	241.3 (+0.6)	$H_2S\,^2B_1$	242.1 (−0.7)	CS	263.7 (−2.4)
	S	237.5 (+1.4)	$H_2S\,^2A_1$	295.0 (−0.3)		
Electron affinities	C	27.7 (+1.4)	CH_3	−2.7 (+4.5)	SH	54.0 (+0.4)
	O	28.5 (+5.2)	NH	5.1 (+3.7)	O_2	7.8 (+2.3)
	F	73.1 (+5.3)	NH_2	15.4 (+2.4)	NO	−2.7 (+3.2)
	Si	32.1 (−0.2)	OH	37.9 (+4.3)	CN	91.5 (−2.5)
	P	17.2 (+0.0)	SiH	29.6 (−0.2)	PO	23.3 (+1.8)
	S	47.4 (+0.5)	SiH_2	25.7 (+0.2)	S_2	38.7 (−0.4)
	Cl	82.2 (+1.2)	SiH_3	35.2 (−2.7)	Cl_2	54.9 (+0.2)
	CH	26.7 (+1.9)	PH	24.2 (−0.4)		
	CH_2	15.0 (+0.0)	PH_2	30.3 (−1.0)		
Proton affinities	NH_3	206.3 (−3.8)	SiH_4	152.5 (+1.5)	HCl	132.9 (+0.7)
	H_2O	161.4 (+3.7)	PH_3	185.2 (+1.9)		
	C_2H_2	153.7 (−1.4)	H_2S	167.2 (+1.6)		

[a]Corresponding to MRCI+Q/G3MP2large+ZPVE+HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

Notably poorer performance by the MR procedures (compared with SR) is observed for the electron affinity of CH_3, and for the proton affinities of NH_3 and H_2O. The electron affinity of CH_3 is calculated to be negative by all the MR procedures, in contrast to the SR methods that all correctly predict a positive electron affinity. Likewise, the proton affinities of NH_3 and H_2O are consistently poorly predicted by the MR procedures. In fact, because the errors for NH_3 and H_2O are of opposite sign, the error in the proton-transfer reaction between H_3O^+ and NH_3 is a substantial 7.2–7.5 kcal mol^{-1}. In contrast, the corresponding SR procedures predict this proton-transfer energy with an accuracy of 1.9–2.2 kcal mol^{-1}.

MR-G3(MP2) performs best of the MR methods exam-

ined in this study. It gives results comparable to those of G3(MP2) for heats of formation, ionization energies, and electron affinities, but much poorer results for proton affinities. There are significant improvements for a small number of cases for which G3(MP2) gives larger errors: the heat of formation of CS, the ionization energy of O_2, and the electron affinities of C, O, and NH.

B. MR-G2/MRCI+Q and MR-G3/MRCI+Q

The MR-G2(MP2,SVP), MR-G2(MP2), and MR-G3(MP2) procedures aim to approximate the results of MRCI+Q/6-311+G($3df$,$2p$) or MRCI+Q/G3MP2large calculations (together with HLC and ZPVE corrections) by

TABLE X. G2/MP2[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and G2/MP2 values.[b]

	Species		Species		Species	
Heats of formation	LiH	38.4 (−5.1)	PH_3	12.1 (−10.8)	F_2	−3.4 (+3.4)
	BeH	79.1 (+2.6)	H_2S	−0.8 (−4.1)	CO_2	−120.3 (+26.2)
	CH	146.1 (−3.6)	HCl	−22.2 (+0.1)	Na_2	37.0 (−3.0)
	$CH_2\,^3B_1$	95.5 (−1.8)	Li_2	56.5 (−4.9)	Si_2	144.0 (−4.1)
	$CH_2\,^1A_1$	107.8 (−5.0)	LiF	−86.7 (+6.6)	P_2	34.0 (+0.3)
	CH_3	38.4 (−3.4)	C_2H_2	48.1 (+6.1)	S_2	29.4 (+1.3)
	CH_4	−13.9 (−4.0)	C_2H_4	12.5 (+0.0)	Cl_2	−1.7 (+1.7)
	NH	89.8 (−4.6)	CN	114.2 (−9.3)	NaCl	−46.8 (+3.2)
	NH_2	49.3 (−4.2)	HCN	21.6 (+9.9)	SiO	−34.7 (+10.1)
	NH_3	−7.8 (−3.2)	CO	−40.2 (+13.8)	CS	60.1 (+6.8)
	OH	9.6 (−0.2)	HCO	0.3 (+9.7)	SO	−4.4 (+5.6)
	H_2O	−60.4 (+2.6)	HCHO	−34.8 (+8.8)	ClO	27.9 (−3.7)
	HF	−69.5 (+4.4)	CH_3OH	−51.6 (+3.6)	ClF	−18.0 (+4.8)
	$SiH_2\,^1A_1$	70.3 (−5.1)	N_2	−9.9 (+9.9)	CH_2Cl	−21.2 (+1.6)
	$SiH_2\,^3B_1$	89.2 (−3.0)	N_2H_4	25.8 (−3.0)	CH_3SH	−2.9 (−2.6)
	SiH_3	53.7 (−5.8)	NO	14.3 (+7.3)	HOCl	−22.8 (+5.0)
	SiH_4	16.2 (−8.0)	O_2	−9.1 (+9.1)	SO_2	−89.2 (+18.2)
	PH_2	40.5 (−7.4)	H_2O_2	−37.6 (+5.1)		
Ionization energies	Li	123.2 (+1.1)	Cl	295.8 (+3.3)	HCl	294.7 (−0.7)
	Be	205.8 (+9.1)	CH_4	291.7 (−0.7)	C_2H_2	266.8 (−3.9)
	B	190.6 (+0.8)	NH_3	236.7 (−1.9)	C_2H_4	244.0 (−1.7)
	C	259.6 (+0.1)	OH	300.3 (−0.3)	CO	329.8 (−6.7)
	N	336.7 (−1.4)	H_2O	295.0 (−4.0)	$N_2\,^2\Sigma_g^+$	355.2 (+4.1)
	O	309.8 (+4.0)	HF	375.3 (−5.4)	$N_2\,^2\Pi_u$	394.1 (−9.0)
	F	401.7 (+0.0)	SiH_4	251.2 (+2.5)	O_2	270.3 (+8.0)
	Na	114.1 (+4.4)	PH	233.2 (+0.9)	P_2	247.2 (−4.4)
	Mg	169.6 (+6.7)	PH_2	225.1 (+1.3)	S_2	212.8 (+3.0)
	Al	134.3 (+3.7)	PH_3	224.5 (+3.1)	Cl_2	265.5 (−0.3)
	Si	185.3 (+2.6)	SH	236.6 (+2.5)	ClF	293.8 (−1.9)
	P	241.4 (+0.5)	$H_2S\,^2B_1$	240.5 (+0.9)	CS	279.9 (−18.6)
	S	232.0 (+6.9)	$H_2S\,^2A_1$	293.7 (+1.0)		
Electron affinities	C	28.7 (+0.4)	CH_3	0.8 (+1.0)	SH	54.4 (+0.0)
	O	32.9 (+0.8)	NH	6.9 (+1.9)	O_2	8.1 (+2.0)
	F	84.3 (−5.9)	NH_2	20.9 (−3.1)	NO	−3.4 (+3.9)
	Si	31.3 (+0.6)	OH	47.4 (−5.2)	CN	108.9 (−19.9)
	P	11.7 (+5.5)	SiH	26.8 (+2.6)	PO	22.5 (+2.6)
	S	45.7 (+2.2)	SiH_2	23.1 (+2.8)	S_2	37.3 (+1.0)
	Cl	85.5 (−2.1)	SiH_3	29.2 (+3.3)	Cl_2	55.3 (−0.2)
	CH	28.3 (+0.3)	PH	20.7 (+3.1)		
	CH_2	12.8 (+2.2)	PH_2	28.4 (+0.9)		
Proton affinities	NH_3	201.4 (+1.1)	SiH_4	152.6 (+1.4)	HCl	131.0 (+2.6)
	H_2O	162.1 (+3.0)	PH_3	186.5 (+0.6)		
	C_2H_2	151.1 (+1.2)	H_2S	166.1 (+2.7)		

[a]Corresponding to MP2/6-311+G($3df$,$2p$)+ZPVE+HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

assuming the additivity of correlation and basis set effects. It is of interest to examine the reliability of such additivity approximations by carrying out the large-basis-set MRCI+Q calculations explicitly. This gives rise to the MR-G2/MRCI+Q and MR-G3/MRCI+Q procedures, defined by Eqs. (8) and (9), which are analogous to the G2/QCI procedure examined previously.[3(b)] Relative energies at the MR-G2/MRCI+Q and MR-G3/MRCI+Q levels are presented in Tables VIII and IX, with statistical summaries included in Tables VI and VII.

Quite unexpectedly, MR-G2/MRCI+Q and MR-G3/MRCI+Q show larger overall deviations from experiment than MR-G2(MP2) and MR-G3(MP2), respectively. This means that the additivity approximations in Eqs.

(6) and (7) are actually helpful in improving the results (which become worse if the additivity is removed), which must surely be a fortuitous situation. There are now 23 (MR-G2/MRCI+Q) and 15 (MR-G3/MRCI+Q) cases for which the deviations from experiment exceed 3 kcal mol^{-1}. The MR-Gn/MRCI+Q procedures perform significantly worse than the corresponding standard MR-Gn methods for heats of formation and electron affinities, slightly worse for proton affinities and comparably for ionization energies.

Significantly larger errors (compared with standard MR-Gn) are observed for both MR-G2/MRCI+Q and MR-G3/MRCI+Q for the heats of formation of $SiH_2(^1A_1)$, SiH_4, and SO_2. In addition, MR-G2/MRCI+Q shows large errors for the heats of formation of S_2, Cl_2, SO, and ClO,

TABLE XI. G3/MP2[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and G3/MP2 values.[b]

	Species		Species		Species	
Heats of	LiH	36.9 (−3.6)	PH$_3$	9.3 (−8.0)	F$_2$	4.9 (−4.9)
Formation	BeH	78.4 (+3.3)	H$_2$S	−0.3 (−4.6)	CO$_2$	−113.6 (+19.5)
	CH	144.2 (−1.7)	HCl	−18.0 (−4.1)	Na$_2$	35.3 (−1.3)
	CH$_2$ $^3B_1$	91.2 (+2.5)	Li$_2$	54.9 (−3.3)	Si$_2$	141.4 (−1.5)
	CH$_2$ $^1A_1$	106.9 (−4.1)	LiF	−82.1 (+2.0)	P$_2$	33.0 (+1.3)
	CH$_3$	35.0 (+0.0)	C$_2$H$_2$	47.3 (+6.9)	S$_2$	30.7 (+0.0)
	CH$_4$	−16.4 (−1.5)	C$_2$H$_4$	10.2 (+2.3)	Cl$_2$	7.2 (−7.2)
	NH	85.6 (−0.4)	CN	113.5 (−8.7)	NaCl	−43.2 (−0.4)
	NH$_2$	46.2 (−1.1)	HCN	21.4 (+10.1)	SiO	−33.4 (+8.8)
	NH$_3$	−10.1 (−0.9)	CO	−36.2 (+9.8)	CS	62.7 (+4.2)
	OH	9.5 (−0.1)	HCO	1.9 (+8.1)	SO	−3.1 (+4.3)
	H$_2$O	−59.5 (+1.7)	HCHO	−32.6 (+6.6)	ClO	33.6 (−9.4)
	HF	−65.2 (+0.1)	CH$_3$OH	−51.1 (+3.1)	ClF	−8.0 (−5.2)
	SiH$_2$ $^1A_1$	68.7 (−3.5)	N$_2$	−10.0 (+10.0)	CH$_3$Cl	−17.6 (−2.0)
	SiH$_2$ $^3B_1$	84.6 (+1.6)	N$_2$H$_4$	22.8 (+0.0)	CH$_3$SH	−3.3 (−2.2)
	SiH$_3$	49.6 (−1.7)	NO	15.8 (+5.8)	HOCl	−16.4 (−1.4)
	SiH$_4$	12.7 (−4.5)	O$_2$	−7.6 (+7.6)	SO$_2$	−82.7 (+11.7)
	PH$_2$	36.9 (−3.8)	H$_2$O$_2$	−34.8 (+2.3)		
Ionization	Li	123.5 (+0.8)	Cl	299.3 (−0.2)	HCl	294.4 (−0.4)
energies	Be	208.9 (+6.0)	CH$_4$	291.1 (−0.1)	C$_2$H$_2$	266.2 (−3.3)
	B	190.6 (+0.8)	NH$_3$	235.6 (−0.8)	C$_2$H$_4$	243.4 (−1.1)
	C	259.7 (+0.0)	OH	299.1 (+0.9)	CO	329.5 (−6.4)
	N	336.5 (−1.2)	H$_2$O	294.0 (−3.0)	N$_2$ $^2\Sigma_g^+$	354.7 (+4.6)
	O	312.8 (+1.0)	HF	374.1 (−4.2)	N$_2$ $^2\Pi_u$	393.4 (−8.3)
	F	404.1 (−2.4)	SiH$_4$	251.1 (+2.6)	O$_2$	272.6 (+5.7)
	Na	114.4 (+4.1)	PH	236.0 (−1.9)	P$_2$	247.1 (−4.3)
	Mg	172.8 (+3.5)	PH$_2$	227.9 (−1.5)	S$_2$	215.8 (+0.0)
	Al	134.8 (+3.2)	PH$_3$	224.3 (+3.3)	Cl$_2$	265.8 (−0.6)
	Si	185.5 (+2.4)	SH	236.6 (+2.5)	ClF	293.5 (−1.6)
	P	241.1 (+0.8)	H$_2$S $^2B_1$	240.5 (+0.9)	CS	279.6 (−18.3)
	S	236.4 (+2.5)	H$_2$S $^2A_1$	293.6 (+1.1)		
Electron	C	28.1 (+1.0)	CH$_3$	−0.9 (+2.7)	SH	54.7 (−0.3)
affinities	O	34.1 (−0.4)	NH	5.0 (+3.8)	O$_2$	6.6 (+3.5)
	F	84.7 (−6.3)	NH$_2$	19.2 (−1.4)	NO	−1.5 (+2.0)
	Si	31.5 (+0.4)	OH	45.1 (−2.9)	CN	108.0 (−19.0)
	P	16.2 (+1.0)	SiH	30.2 (−0.8)	PO	25.2 (−0.1)
	S	49.9 (−2.0)	SiH$_2$	26.0 (−0.1)	S$_2$	37.8 (+0.5)
	Cl	88.4 (−5.0)	SiH$_3$	29.1 (+3.4)	Cl$_2$	58.6 (−3.5)
	CH	30.0 (−1.4)	PH	21.2 (+2.6)		
	CH$_2$	11.1 (+3.9)	PH$_2$	28.8 (+0.5)		
Proton	NH$_3$	201.9 (+0.6)	SiH$_4$	152.4 (+1.6)	HCl	130.6 (+3.0)
affinities	H$_2$O	162.4 (+2.7)	PH$_3$	186.2 (+0.9)		
	C$_2$H$_2$	150.6 (+1.7)	H$_2$S	165.5 (+3.3)		

[a]Corresponding to MP2/G3MP2large + ΔE(SO) + ZPVE + HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

while MR-G3/MRCI+Q performs poorly for NaCl. Both MR-G2/MRCI+Q and MR-G3/MRCI+Q significantly underestimate electron affinities, with a noticeable deterioration in the predictions for O, F, OH, O$_2$, NO, and PO. The proton affinities of NH$_3$ and H$_2$O continue to be poorly predicted.

C. G2/MP2 and G3/MP2

The G2/QCI procedure[3(b)] obtains relative energies on the basis of QCISD(T)/6-311+G($3df$,$2p$) calculations together with ZPVE and HLC corrections. It is of interest to see how the corresponding MP2 calculations fare. With this in mind, we have analyzed results corresponding to

MP2/6-311+G($3df$,$2p$) + ZPVE + HLC and MP2/G3MP2 large + ZPVE + HLC. These procedures are designated G2/MP2 and G3/MP2, respectively, and are defined by Eqs. (12) and (13). Calculated relative energies are presented in Tables X and XI, with statistical summaries again included in Tables VI and VII.

It is immediately clear from Tables VI and VII that G2/MP2 and G3/MP2 are not particularly useful levels of theory from the viewpoint of thermochemical reliability. The mean absolute deviations are 4.19 and 3.36 kcal mol^{-1}, with 69 and 53, respectively, out of the 123 energy comparisons showing deviations exceeding 3 kcal mol^{-1}. The only area where the errors are modest is for proton affinities. The G2/

TABLE XII. MR-G2/MP2[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G2/MP2 values.[b]

	Species		Species		Species	
Heats of formation	LiH	30.0 (+3.3)	PH$_3$	4.9 (−3.6)	F$_2$	−1.4 (+1.4)
	BeH	85.6 (−3.9)	H$_2$S	−3.7 (−1.2)	CO$_2$	−101.6 (+7.5)
	CH	142.2 (+0.3)	HCl	−22.7 (+0.6)	Na$_2$	29.0 (+5.0)
	CH$_2$ $^3B_1$	94.3 (−0.6)	Li$_2$	47.1 (+4.5)	Si$_2$	139.1 (+0.8)
	CH$_2$ $^1A_1$	102.4 (+0.4)	LiF	−82.5 (+2.4)	P$_2$	35.3 (−1.0)
	CH$_3$	35.2 (−0.2)	C$_2$H$_2$	52.4 (+1.8)	S$_2$	28.9 (+1.8)
	CH$_4$	−18.3 (+0.4)	C$_2$H$_4$	11.0 (+1.5)	Cl$_2$	0.5 (−0.5)
	NH	86.1 (−0.9)	CN	104.9 (+0.0)	NaCl	−48.5 (+4.9)
	NH$_2$	45.6 (−0.5)	HCN	30.8 (+0.7)	SiO	−19.9 (−4.7)
	NH$_3$	−7.2 (−3.8)	CO	−27.3 (+0.9)	CS	64.7 (+2.2)
	OH	8.3 (+1.1)	HCO	9.6 (+0.4)	SO	−1.4 (+2.6)
	H$_2$O	−57.1 (−0.7)	HCHO	−26.1 (+0.1)	ClO	23.9 (+0.3)
	HF	−66.7 (+1.6)	CH$_3$OH	−47.2 (−0.8)	ClF	−13.3 (+0.1)
	SiH$_2$ $^1A_1$	63.5 (+1.7)	N$_2$	0.4 (−0.4)	CH$_3$Cl	−21.5 (+1.9)
	SiH$_2$ $^3B_1$	86.2 (+0.0)	N$_2$H$_4$	25.4 (−2.6)	CH$_3$SH	−4.2 (−1.3)
	SiH$_3$	48.1 (−0.2)	NO	19.5 (+2.1)	HOCl	−17.9 (+0.1)
	SiH$_4$	8.0 (+0.2)	O$_2$	−4.5 (+4.5)	SO$_2$	−74.1 (+3.1)
	PH$_2$	34.4 (−1.3)	H$_2$O$_2$	−33.6 (+1.1)		
Ionization energies	Li	123.4 (+0.9)	Cl	295.6 (+3.5)	HCl	292.9 (+1.1)
	Be	219.5 (−4.6)	CH$_4$	291.4 (−0.4)	C$_2$H$_2$	261.7 (+1.2)
	B	186.5 (+4.9)	NH$_3$	230.6 (+4.2)	C$_2$H$_4$	244.0 (−1.7)
	C	256.1 (+3.6)	OH	299.4 (+0.6)	CO	319.7 (+3.4)
	N	334.0 (+1.3)	H$_2$O	290.1 (+0.9)	N$_2$ $^2\Sigma_g^+$	355.6 (+3.7)
	O	312.0 (+1.8)	HF	372.2 (−2.3)	N$_2$ $^2\Pi_u$	383.7 (+1.4)
	F	402.7 (−1.0)	SiH$_4$	252.1 (+1.6)	O$_2$	283.1 (−4.8)
	Na	114.1 (+4.4)	PH	232.5 (+1.6)	P$_2$	243.2 (−0.4)
	Mg	178.7 (−2.4)	PH$_2$	224.0 (+2.4)	S$_2$	215.2 (+0.6)
	Al	134.1 (+3.9)	PH$_3$	225.9 (+1.7)	Cl$_2$	263.3 (+1.9)
	Si	185.2 (+2.7)	SH	236.5 (+2.6)	ClF	290.0 (+1.9)
	P	241.4 (+0.5)	H$_2$S $^2B_1$	238.9 (+2.5)	CS	259.7 (+1.6)
	S	233.6 (+5.3)	H$_2$S $^2A_1$	293.1 (+1.6)		
Electron affinities	C	31.4 (−2.3)	CH$_3$	−4.6 (+6.4)	SH	52.7 (+1.7)
	O	34.3 (−0.6)	NH	6.9 (+1.9)	O$_2$	10.6 (−0.5)
	F	83.5 (−5.1)	NH$_2$	16.0 (+1.8)	NO	3.0 (−2.5)
	Si	31.7 (+0.2)	OH	43.9 (−1.7)	CN	88.6 (+0.4)
	P	13.4 (+3.8)	SiH	26.8 (+2.6)	PO	28.8 (−3.7)
	S	45.7 (+2.2)	SiH$_2$	22.0 (+3.9)	S$_2$	35.6 (+2.7)
	Cl	84.2 (−0.8)	SiH$_3$	30.8 (+1.7)	Cl$_2$	58.2 (−3.1)
	CH	27.0 (+1.6)	PH	20.7 (+3.1)		
	CH$_2$	13.4 (+1.6)	PH$_2$	27.0 (+2.3)		
Proton affinities	NH$_3$	207.6 (−5.1)	SiH$_4$	154.6 (−0.6)	HCl	133.1 (+0.5)
	H$_2$O	161.2 (+3.9)	PH$_3$	186.9 (+0.2)		
	C$_2$H$_2$	153.6 (−1.3)	H$_2$S	168.5 (+0.3)		

[a]Corresponding to CASPT2/6-311+G($3df$,$2p$)+ZPVE+HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values whereas the remaining quantities refer to 0 K.

MP2 and G3/MP2 methods are not recommended for general use.

D. MR-G2/MP2 and MR-G3/MP2

The multireference analogs of G2/MP2 and G3/MP2 use large-basis-set MR-MP2 (specifically CASPT2) calculations together with ZPVE and HLC corrections. They are designated MR-G2/MP2 and MR-G3/MP2 and are defined by Eqs. (10) and (11), respectively. Results are presented in Tables XII and XIII.

Examination of the statistical summaries in Tables VI and VII shows a number of interesting points. In the first place, MR-G2/MP2 and MR-G3/MP2 perform significantly better than G2/MP2 and G3/MP2, with MADs of 2.01 and 1.66 kcal mol^{-1} compared with 4.19 and 3.36 kcal mol^{-1}. They are only slightly worse than MR-G2/MRCI+Q and MR-G3/MRCI+Q (MADs of 1.84 and 1.58 kcal mol^{-1}, respectively). However, they do not perform as well as the standard MR-Gn procedures. For example, the MADs are larger than with MR-Gn(MP2) for virtually all the thermochemical properties in Table VI.

There are 31 (MR-G2/MP2) and 23 (MR-G3/MP2) out of 123 energy comparisons for which the error exceeds 3 kcal mol^{-1}. Large errors occur for most of the systems that were noted in connection with the standard MR-Gn procedures. However, there are additional cases for which there

TABLE XIII. MR-G3/MP2[a] heats of formation, ionization energies, electron affinities, and proton affinities. Values in parentheses are the differences between experimental and MR-G3(MP2)/MP2 values.[b]

	Species		Species		Species	
Heats of formation	LiH	29.7 (+3.6)	PH_3	4.4 (−3.1)	F_2	−0.4 (+0.4)
	BeH	85.9 (−4.2)	H_2S	−3.4 (−1.5)	CO_2	−98.5 (+4.4)
	CH	142.4 (+0.1)	HCl	−21.5 (−0.6)	Na_2	28.6 (+5.4)
	$CH_2\ ^3B_1$	94.5 (−0.8)	Li_2	46.7 (+4.9)	Si_2	139.8 (+0.1)
	$CH_2\ ^1A_1$	102.4 (+0.4)	LiF	−81.1 (+1.0)	P_2	35.2 (−0.9)
	CH_3	35.1 (−0.1)	C_2H_2	52.1 (+2.1)	S_2	30.7 (+0.0)
	CH_4	−18.7 (+0.8)	C_2H_4	10.6 (+1.9)	Cl_2	2.4 (−2.4)
	NH	86.3 (−1.1)	CN	106.0 (−1.1)	NaCl	−47.9 (+4.3)
	NH_2	45.7 (−0.6)	HCN	31.1 (+0.4)	SiO	−20.6 (−4.0)
	NH_3	−7.5 (−3.5)	CO	−25.3 (−1.18)	CS	65.7 (+1.2)
	OH	8.9 (+0.5)	HCO	11.5 (−1.5)	SO	0.1 (+1.1)
	H_2O	−56.8 (−1.0)	HCHO	−24.8 (−1.2)	ClO	26.2 (−2.0)
	HF	−65.6 (+0.5)	CH_3OH	−46.5 (−1.5)	ClF	−10.4 (−2.8)
	$SiH_2\ ^1A_1$	63.1 (+2.1)	N_2	0.9 (−0.9)	CH_3Cl	−20.0 (+0.4)
	$SiH_2\ ^3B_1$	86.1 (+0.1)	N_2H_4	25.3 (−2.5)	CH_3SH	−3.9 (−1.6)
	SiH_3	47.5 (+0.4)	NO	21.3 (+0.3)	HOCl	−16.1 (−1.7)
	SiH_4	6.9 (+1.3)	O_2	−2.6 (+2.6)	SO_2	−72.4 (+1.4)
	PH_2	34.2 (−1.1)	H_2O_2	−33.0 (+0.5)		
Ionization energies	Li	124.3 (+0.0)	Cl	297.3 (+1.8)	HCl	294.6 (−0.6)
	Be	221.0 (−6.1)	CH_4	292.9 (−1.9)	C_2H_2	265.0 (−2.1)
	B	187.4 (+4.0)	NH_3	231.5 (+3.3)	C_2H_4	245.4 (−3.1)
	C	256.8 (+2.9)	OH	300.2 (−0.2)	CO	321.4 (+1.7)
	N	334.4 (+0.9)	H_2O	291.1 (−0.1)	$N_2\ ^2\Sigma_g^+$	357.0 (+2.3)
	O	313.1 (+0.7)	HF	373.0 (−3.1)	$N_2\ ^2\Pi_u$	385.1 (+0.0)
	F	403.3 (−1.6)	SiH_4	253.9 (−0.2)	O_2	283.8 (−5.5)
	Na	115.2 (+3.3)	PH	233.9 (+0.2)	P_2	244.9 (−2.1)
	Mg	180.2 (−3.9)	PH_2	225.5 (+0.9)	S_2	216.7 (−0.9)
	Al	135.5 (+2.5)	PH_3	227.6 (+0.0)	Cl_2	265.5 (−0.3)
	Si	186.3 (+1.6)	SH	238.6 (+0.5)	ClF	291.7 (+0.2)
	P	242.0 (−0.1)	$H_2S\ ^2B_1$	240.9 (+0.5)	CS	261.1 (+0.2)
	S	236.3 (+2.6)	$H_2S\ ^2A_1$	294.9 (−0.2)		
Electron affinities	C	31.1 (−2.0)	CH_3	−4.1 (+5.9)	SH	54.9 (−0.5)
	O	33.7 (+0.0)	NH	6.8 (+2.0)	O_2	11.1 (−1.0)
	F	82.4 (−4.0)	NH_2	16.3 (+1.5)	NO	3.2 (−2.7)
	Si	32.8 (−0.9)	OH	43.7 (−1.5)	CN	89.7 (−0.7)
	P	16.3 (+0.9)	SiH	28.4 (+1.0)	PO	30.1 (−5.0)
	S	48.2 (−0.3)	SiH_2	23.6 (+2.3)	S_2	38.1 (+0.2)
	Cl	85.2 (−1.8)	SiH_3	32.7 (−0.2)	Cl_2	61.3 (−6.2)
	CH	27.0 (+1.6)	PH	23.1 (+0.7)		
	CH_2	13.7 (+1.3)	PH_2	29.3 (+0.0)		
Proton affinities	NH_3	208.1 (−5.6)	SiH_4	154.3 (−0.3)	HCl	132.6 (+1.0)
	H_2O	161.5 (+3.6)	PH_3	186.5 (+0.6)		
	C_2H_2	153.1 (−0.8)	H_2S	167.8 (+1.0)		

[a]Corresponding to CASPT2/G3MP2large$+\Delta E$(SO)$+$ZPVE$+$HLC.
[b]Values in kcal mol^{-1}. The heats of formation are 298 K values, whereas the remaining quantities refer to 0 K.

are noticeable errors. In the case of heats of formation, CO_2, SiO, NH_3, and O_2 now show significant errors, and the error for SO_2 has moved from large negative to small positive. The MR-Gn/MP2 ionization energies are significantly worse than corresponding MR-Gn(MP2) values, and significant errors now occur at both MR-Gn/MP2 levels for the additional systems B, NH_3, and O_2. In the case of electron affinities, there are very large deviations for CH_3 (+6.4 and +5.9 kcal mol^{-1}, respectively), and F, PO, and Cl_2 also have large errors. The errors in the H_3O^+/NH_3 proton-transfer energy are now 9.0–9.2 kcal mol^{-1}. Despite these shortcomings, the MR-G3/MP2 procedure may prove useful in situations for which single-reference methods are inadequate, especially

since the use of large active spaces is more limiting for MR-CI than for MR-MP2 methods.

E. MCQDPT2 vs CASPT2

Our default MR-MP2 method is the CASPT2 procedure of the MOLPRO suite of programs.[15,23] However, it is of interest to see how the alternative MCQDPT2 procedure that is available in the GAMESS program[18] compares. Results analogous to those of Tables III, IV, V, XII, and XIII are available as an EPAPS document.[24] Statistical summaries are included in Table VI.

The general observation is that the CASPT2-based re-

TABLE XIV. MR-Gn and Gn timings.[a]

Method	NH$_3$	C$_2$H$_2$	HCHO
MR-G3/MP2	11.9	235.4	382.3
MR-G2/MP2	12.0	235.8	385.1
MR-G3(MP2)	68.5	3047.0	4160.4
MR-G2(MP2,SVP)	68.6	3047.4	4163.2
MR-G2(MP2)	84.4	3197.8	4958.3
MR-G3/MRCI+Q	90.9	3440.0	4500.9
MR-G2/MRCI+Q	93.5	3487.7	4606.4
G3/MP2	3.9	4.0	4.1
G2/MP2	3.9	4.0	4.3
G3(MP2)	27.6	29.6	32.8
G2(MP2,SVP)	27.6	29.6	33.0
G2(MP2)	40.0	32.9	41.0
G3/QCI	34.1	51.0	70.6
G2/QCI	37.6	49.6	87.7

[a]In seconds using MOLPRO 98 on a single processor of a VPP300 with 1700 Mb memory. The active-space sizes for NH$_3$, C$_2$H$_2$, and HCHO are (8,7), (10,10), and (12,10) for NH$_3$, C$_2$H$_2$, and HCHO, respectively. The Gn timings refer to Gn(CCSD) calculations, i.e., in which CCSD(T) is used in place of QCISD(T).

TABLE XV. Comparison of the ten largest deviations between experiment and the values calculated by MR-G3(MP2) and G3(MP2).[a]

Quantity	MR-G3(MP2)[b]	Quantity	G3(MP2)[c]
ΔH_f^0(SO$_2$)	−5.0 (−3.9)	IE(Be)	−5.4 (−4.7)
IE(Be)	−4.7 (−5.4)	EA(NH)	+4.5 (+2.2)
ΔH_f^0(Na$_2$)	+4.5 (+3.3)	IE(O$_2$)	−4.0 (−2.6)
EA(CH$_3$)	+4.3 (+1.7)	ΔH_f^0(SO$_2$)	−3.9 (−5.0)
PA(H$_2$O)	+4.0 (+1.8)	IE(S)	+3.6 (+3.0)
PA(NH$_3$)	−3.5 (−0.4)	EA(C)	+3.6 (−2.1)
IE(Na)	+3.4 (+3.2)	EA(O)	+3.3 (+1.9)
ΔH_f^0(C$_2$H$_4$)	−3.3 (+0.7)	ΔH_f^0(Na$_2$)	+3.3 (+4.5)
ΔH_f^0(NaCl)	+3.0 (+1.5)	ΔH_f^0(CS)	+3.2 (+2.0)
IE(S)	+3.0 (+3.6)	IE(Na)	+3.2 (+3.4)

[a]In kcal mol^{-1}.
[b]Values in parentheses are the corresponding G3(MP2) deviations from Ref. 4(b).
[c]Taken from Ref. 4(b); values in parentheses are the corresponding MR-G3(MP2) deviations from the present work.

sults and MCQDPT2-based results are normally very similar. With MR-G2(MP2,SVP), there are nine cases where the difference lies between 1 and 3 kcal mol^{-1} and just one case (NaCl) where the difference is greater than 3 kcal mol^{-1}. With MR-G2(MP2), there are eight cases where the difference lies between 1 and 3 kcal mol^{-1}, two cases (NaCl and CH$_3$SH) where the difference lies between 3 and 5 kcal mol^{-1}, and one case (Cl$_2$) where the difference exceeds 5 kcal mol^{-1}. For MR-G3(MP2), there are five cases where the difference lies between 1 and 3 kcal mol^{-1} and one case (NaCl) where the difference exceeds 3 kcal mol^{-1}. The differences are larger with MR-G2/MP2 and MR-G3/MP2, with 33 and 30 cases, respectively, of differences lying between 1 and 3 kcal mol^{-1}, and two and three cases, respectively, of differences exceeding 3 kcal mol^{-1}.

Although the differences between the results of the CASPT2-based methods and MCQDPT2-based methods are relatively small, it may be seen from Table VI that the CASPT2-based methods virtually always perform slightly better statistically.

F. Timing comparisons and additional comments

Because the choice of method in quantum chemistry studies often involves a compromise between accuracy and computational expense, it is important to examine the relative timings of the various MR-Gn procedures introduced in the present article and to make comparisons with corresponding standard single-reference Gn methods. It should be emphasized that the timings depend on many factors and so the present data are intended largely to enable qualitative conclusions to be drawn.

We can see from Table XIV that for active spaces of up to about 8 orbitals, all methods are very cheap. For 10 and 12 active orbitals, the times increase rapidly for the MR-Gn procedures that involve MR-CI calculations, while for 14 and 16 active orbitals, such procedures are starting to become intractable. Elimination of the MR-CI component, as

in the MR-G2/MP2 and MR-G3/MP2 methods, leads to a substantial reduction in CPU time. The cost of the standard (SR) Gn methods goes up much more slowly than the MR methods. We should emphasize that in this initial implementation of MR-Gn procedures, we uniformly use a full-valence active space and this leads to the very rapid increase in computational cost with size of molecule. Clearly this will be modified in implementations that use smaller active spaces.

The relative costs of the MR methods for the larger active spaces follow the pattern,[27]

$$\text{MR-G2/MP2} \sim \text{MR-G3/MP2} \ll \text{MR-G2(MP2,SVP)}$$
$$\sim \text{MR-G3(MP2)} < \text{MR-G2/MRCI+Q}$$
$$\sim \text{MR-G3/MCRCI+Q}. \qquad (17)$$

There is a large increase in CPU time in going from MR-G3/MP2 to MR-G3(MP2) but a much smaller further increase in going to MR-G3/MRCI+Q.

The single-reference methods show the same pattern,

$$\text{G2/MP2} \sim \text{G3/MP2} \ll \text{G2(MP2,SVP)}$$
$$\sim \text{G3(MP2)} < \text{G2/QCI} \sim \text{G3/QCI}. \qquad (18)$$

The MR-G2/MRCI+Q and MR-G3/MRCI+Q procedures are the most demanding of the methods investigated in the present work in terms of both memory and CPU usage. However, our results show that these two methods are by no means the most accurate. This is not an overly comforting situation, since the aim of the other methods that we have examined is to approximate their large-basis-set MRCI+Q counterparts by means of additivity. It turns out that the MR-G2 and MR-G3 schemes that we have devised do not succeed very well in mimicking the MR-Gn/MRCI+Q results. This state of affairs fortuitously results in cheaper methods [MR-G2(MP2,SVP) and MR-G3(MP2)] that are more accurate than their more expensive counterparts (MR-G2/MRCI+Q and MR-G3/MRCI+Q).

The two MR methods for which the correlation correction is based on the 6-31G(d) split-valence basis set [MR-G2(MP2,SVP) and MR-G3(MP2)] give the most accurate

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results. Table XV lists the ten worst predictions of the G3(MP2) method together with the corresponding MR-G3(MP2) values and vice versa. It can be seen that five out of the ten cases are common to the two lists, and that both methods give poor predictions in most of the remaining ten cases as well. Individual results have been discussed in previous sections.

Overall, the agreement between theory and experiment is best in the case of the MR-G3(MP2) method, and since this is also one of the more efficient methods in terms of resources, we recommend the use of MR-G3(MP2) for future studies of systems with significant multireference character. MR-G3/MP2 does not perform as well as MR-G3(MP2) but is significantly less expensive. It may be useful in situations that would benefit from an MR treatment but for which the MR-CI calculations are not tractable.

IV. CONCLUSIONS

We have introduced twelve multireference equivalents of the G2 and G3 methods using reduced Møller–Plesset orders and assessed their performance on a slightly reduced G2-1 test set. Whereas single-reference Gn-type procedures aim to approximate large-basis-set QCISD(T) calculations through additivity approximations, the MR-Gn methods aim to approximate large-basis-set MRCI+Q results.

We find that models based on explicit large-basis-set MRCI+Q calculations (together with ZPVE and higher level corrections) do not perform particularly well. In addition, our results indicate that the Gn-type additivity approximations hold less well for the MR-Gn methods than they do for the parent single-reference Gn methods. This leads to the somewhat fortuitous situation in which incorporation of additivity approximations in the MR-Gn procedures results in an accuracy which is better than that of MR-Gn/MRCI+Q and is generally comparable to that of the corresponding single-reference methods.

MR-G3(MP2) is the most accurate of the MR-Gn methods that we have examined and it is also one of the least computationally demanding. The mean absolute deviation between calculated and experimental values for the test set of (123) energies is 1.22 kcal mol^{-1}, compared with 1.19 kcal mol^{-1} for standard G3(MP2). MR-G3(MP2) performs comparably to G3(MP2) for heats of formation, ionization energies, and electron affinities but significantly worse for proton affinities.

The present test set involves systems for which a single-reference treatment is reasonably adequate. It is encouraging that MR-G3(MP2) performs comparably to G3(MP2) for such systems. However, the main purpose of the present study was to develop procedures that could handle systems for which a single-reference treatment is *not* adequate. It is likely that the performance of MR-G3(MP2) will improve relative to G3(MP2) for situations of this type. Studies of such systems are in progress.

The MR-G3/MP2 procedure (MAD=1.66 kcal mol^{-1}), which corresponds to a large-basis set CASPT2 +ZPVE+HLC treatment, does not perform as well as MR-G3(MP2) but it is computationally much less expensive because it does not require an MR-CI calculation. It may prove useful in circumstances where a multireference treatment is desirable but the MR-CI calculation is not affordable.

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[22] Note that the G3-type procedures defined by Eqs. (9), (11), and (13) should strictly include the designation G3(MP2) rather than G3 because they use the G3MP2large basis set rather than the G3large set. However, the G3 labels are used here for simplicity.

[23] (a) MOLPRO 96 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlof, R. D. Amos, M. J. O. Deegan *et al.*; (b) MOLPRO 98.1 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning *et al.*.

[24] See EPAPS Document No. E-JCPSA6-115-303143 for BINHEX WORD 98 text files containing the thermochemical results obtained with the MCQDPT2-based procedures (Tables S-I to S-V) and the total energies calculated with all the methods (Tables S-VI to S-XIX). This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

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