Hybrid correlation models based on active-space partitioning: Seeking accurate O(N5) ab initio methods for bond breaking

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Hybrid correlation models based on active-space partitioning: Seeking accurate $\mathcal{O}(N^5)$ *ab initio* methods for bond breaking

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Møller-Plesset second-order (MP2) perturbation theory remains the least expensive standard *ab initio* method that includes electron correlation, scaling as $\mathcal{O}(N^5)$ with the number of molecular orbitals N. Unfortunately, when restricted Hartree-Fock orbitals are employed, the potential energy curves calculated with this method are of little use at large interatomic separations because of the divergent behavior of MP2 in these regions. In our previous study [J. Chem. Phys. **122**, 234110 (2005)] we combined the MP2 method with the singles and doubles coupled cluster (CCSD) method to produce a hybrid method that retains the computational scaling of MP2 and improves dramatically the shape of the MP2 curves. In this work we expand the hybrid methodology to several other schemes. We investigate a new, improved MP2-CCSD method as well as a few other $\mathcal{O}(N^5)$ methods related to the Epstein-Nesbet pair correlation theory. Nonparallelity errors across the dissociation curve as well as several spectroscopic constants are computed for BH, HF, H_2O, CH^+, CH_4, and Li_2 molecules with the 6-31G* basis set and compared with the corresponding full configuration interaction results. We show that among the $\mathcal{O}(N^5)$ methods considered, our new hybrid MP2-CCSD method is the most accurate and significantly outperforms MP2 not only at large interatomic separations, but also near equilibrium geometries. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2222350]

I. INTRODUCTION

The accurate description of potential energy surfaces (PESs) has been and still remains one of the primary objectives of quantum chemistry.[1] Unfortunately, the standard hierarchy of single-reference electron correlation methods does not work reliably for bond-breaking reactions, particularly for reactions which make or break multiple bonds. The standard flavors of density functional theory (DFT) are usually unsuitable for the computation of PESs due to their poor qualitative and quantitative performance, especially at stretched geometries.[2,3] Although a variety of multireference methods can provide accurate results in virtually any bond-breaking reaction, in practice they tend to be difficult to derive, implement, and use, and moreover, they can be very expensive computationally. Thus it remains desirable to investigate more "black box" bond-breaking methods with favorable computational scaling. Recent work along these lines includes new methods by Head-Gordon and co-workers based on ideas from the generalized valence bond perfect-pairing approach,[4–6] the spin-flip approach of Krylov and co-workers,[7–11] and the method of moments and completely renormalized coupled-cluster methods of Piecuch and co-workers.[12–15] In this work, we explore hybrids of coupled-cluster and perturbation theories for reactions breaking single bonds.

Among the standard quantum chemical methods based on the restricted Hartree-Fock (RHF) reference, the cheapest qualitatively correct method for breaking single bonds in the ground state is the coupled-cluster theory with the inclusion of single and double excitations (CCSD).[16,17] Its formal scaling with the total number of occupied (o) and virtual (v) molecular orbitals and the number of iterations N_{it} required to converge the nonlinear CCSD equations is $N_{it}o^2v^4$. When we refer to the quality of the method in relation to bond breaking, we mean the correctness of the shape of the potential energy curve produced by this method rather than the absolute error in energy. The CCSD energy curves for reactions breaking single bonds usually overestimate the dissociation energy, but they are smooth and devoid of artifacts such as divergence at large interatomic distances. The latter defect is only too common among the methods which utilize perturbation theory: for example, both the second-order Møller-Plesset (MP2) theory and the CCSD(T) method[18] (often referred to as the "golden standard" of quantum chemistry) fail catastrophically at nonequilibrium geometries.[2,12,15,19–22] The failure of MP2 is especially regrettable since this method has a very low computational scaling, $\mathcal{O}(N^5)$, where N is the total number of orbitals, $N = o + v$. Another method that has a low formal scaling, $N_{it}N^5$, is the approximate second-order coupled cluster (CC2) method of Christiansen *et al.*[23] Unfortunately, its behavior at large interatomic distances remains largely unexplored (see, however, studies of CC2 energy curves around equilibrium geometries in Refs. 24 and 25). We touch on this topic in the current study.

Alternatively, when standard single-reference methods are used in conjunction with unrestricted Hartree-Fock (UHF) orbitals, the divergence at large interatomic distances

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is remedied. However, the UHF-based correlated wave functions often suffer from serious spin contamination.[26,27] Besides, the potential energy curves obtained by these methods can display an erroneous behavior in the intermediate bond-breaking region. In the case of unrestricted second order Møller-Plesset (UMP2) theory this erroneous behavior sometimes becomes so pronounced that it may be regarded as a grave defect of the method.[2]

Thus, it appears that one has to tolerate the computational scaling of $N_{it}N^6$ or higher in order to study the bond-breaking processes with at least qualitative correctness. Recently,[28] we proposed a very simple computational scheme, which scales as N^5 but approaches the CCSD method in accuracy. This method, which we originally denoted as MP2-CCSD [in this paper we refer to it as MP2-CCSD(I)], is a hybrid between the MP2 and the CCSD theories and benefits from the scaling of the former and the accuracy of the latter. This kind of hybrid was first studied by Nooijen,[29] although not in the context of bond-breaking reactions. It relies on the orbital partitioning into active and restricted spaces, which might seem unfortunate in that the user must choose which orbitals to make active. However, we verified that even in the case of the minimal active spaces (which can often be determined *a priori*) our method performs in a very satisfactory manner and is a vast improvement over MP2. With the modest increase of the size of the active space (which does not deteriorate the favorable N^5 scaling), the potential energy curves generated by MP2-CCSD(I) become essentially parallel to those generated by CCSD. In this work we describe and test a new $\mathcal{O}(N^5)$ hybrid method MP2-CCSD(II), which is similar to MP2-CCSD(I) in structure but is significantly more accurate, so that it rivals CCSD in accuracy even when the minimal active spaces are used. In Sec. II we present the methodology behind the MP2-CCSD(I) method. In Sec. III we give the description of the MP2-CCSD(II) method. Illustrative results are presented in Sec. IV.

II. THE HYBRID METHODOLOGY

For RHF or UHF orbitals, the correlation energy of MP2 theory is written as the sum over all possible double excitations:

$$E_{corr}^{MP2} = \frac{1}{4} \sum_{ijab} \frac{|\langle ij||ab\rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \tag{1}$$

where ε_i is the energy of orbital i and $\langle ij||ab\rangle$ is the antisymmetrized two-electron integral in physicists' notation. The letters i, j label the occupied orbitals, whereas a, b refer to the virtual orbitals. It is always possible to formally divide the orbital space into four disjoint subsets: occupied active, occupied restricted, virtual active, and virtual restricted orbitals [see Fig. 1(a)]. Note that, so far, the denominations "restricted" (R) and "active" (A) do not indicate any constraint on the orbital excitations—these names are simply used for notational convenience. Although we consider only canonical RHF or UHF orbitals in our current discussion, the theory may be extended to non-Hartree-Fock orbitals. This would allow the use of, for example, multiconfigurational
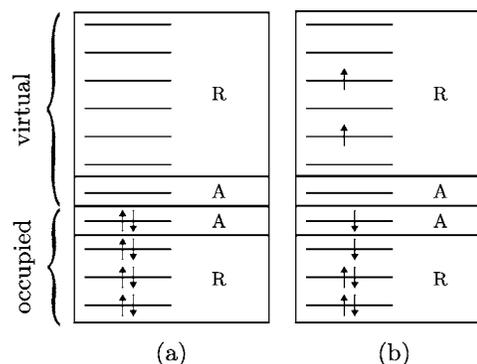
FIG. 1. (a) The separation of the orbital space into four subspaces. (b) An example of our notation: ARRR-type excitation.

self-consistent-field orbitals or natural orbitals, which might be more appropriate in some situations. Such extensions will be considered in future work.

Any double excitation from the closed-shell reference shown symbolically in Fig. 1(a) may then be labeled by the four-letter code $WXYZ$, where the first two letters (W and X) stand for the subspaces (A or R) from which the excitation was made and the last two letters (Y and Z) indicate the subspaces to which the electrons were excited. Obviously, $WXYZ$ is equivalent to $XWYZ$, etc. As an example, Fig. 1(b) shows an $ARRR$-type excitation. In a similar manner, any single excitation may be labeled by the two-letter code WX, where W shows from which subspace the electron was excited and X shows to which space it was excited.

Using this notation, we may rewrite the energy expression for the MP2 correlation energy as the sum of nine contributions:

$$E_{corr}^{MP2} = E_{AAAA}^{MP2} + E_{AAAR}^{MP2} + E_{AARR}^{MP2} + E_{ARAA}^{MP2} + E_{ARAR}^{MP2} + E_{ARRR}^{MP2}$$
$$+ E_{RRAA}^{MP2} + E_{RRAR}^{MP2} + E_{RRRR}^{MP2}. \tag{2}$$

We note that the CCSD spin-orbital energy expression,

$$E_{corr}^{CCSD} = \frac{1}{4} \sum_{ijab} \langle ij||ab\rangle (t_{ij}^{ab} + 2t_i^a t_j^b), \tag{3}$$

reduces to the MP2 spin-orbital expression (1) in the event that single excitations are neglected ($t_i^a = 0$) and the doubles' amplitudes are fixed in their first-order form, $t_{ij}^{ab(1)} = \langle ij||ab\rangle/(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$. Indeed, the MP2 energy is given as the first iteration of the CCSD procedure for RHF or UHF orbitals when the MP2 guesses are used for the amplitudes. This close connection between MP2 and CCSD is exploited in the current study.

In our previous work[28] we demonstrated for several small molecules that the $AAAA$ term, comprising no more than a handful of excitations for small active spaces, is primarily responsible for the divergence of the MP2 energy at large interatomic separations. The mechanistic substitution of the E_{AAAA}^{MP2} term with the E_{AAAA}^{CCSD} term (obtained from the CCSD calculation either in the full or active orbital space) in (2), which we called MP2+CCSD, does not lead to a very satisfactory potential energy curve, although even this simple operation redresses the sharp divergence of the MP2 energy curve. The MP2+CCSD energy curves show a small but,

nevertheless, noticeable "turning over" at large interatomic distances, which is clearly not a physical behavior. The recipe for the proper replacement of E_{AAAA}^{MP2} is to do so *self-consistently*, that is, adjust the *AAAA* contribution in the presence of other contributions. This idea lies at the foundation of hybrid methods previously developed by Nooijen[29] for the investigation of excited states. Kowalski and Piecuch integrated MP2 amplitudes into the state-universal multireference CCSD method to obtain an inexpensive hybrid version of the latter.[30,31] Our method that also employs this methodology includes the following simple steps:

(i)   Set up a CCSD calculation using the MP2 t_i^a and t_{ij}^{ab} amplitudes as guesses: $t_i^a = 0$ and $t_{ij}^{ab} = \langle ij||ab\rangle/(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)$.
(ii)   Procede with solving the CCSD equations, but update only those single and double t amplitudes that involve excitations within the active space only.
(iii)   Terminate the iterations when the active space amplitudes and energy no longer change.

This approach which we called MP2-CCSD in our previous paper[28] will be referred to as MP2-CCSD(I) in the present paper. The convergence of this procedure is usually no worse than the convergence of the conventional CCSD equations. If the typical dimension of the active space is on the order of just a few orbitals (σ and σ^* for the minimal active space), then step (ii) has the computational expense around $\mathcal{O}(N^4)$. The next section introduces an improved MP2-CCSD(II) method and gives details as to the scaling of the intermediates which are computed on each iteration step. In summary, the cost of the MP2-CCSD(I) method is dominated by the atomic orbital (AO) to molecular orbital (MO) transformation and is $\mathcal{O}(N^5)$. The potential energy curves generated by the MP2-CCSD(I) method normally level off at stretched geometries and show qualitative and quantatitative advantages over the MP2+CCSD curves and dramatic improvements over simple MP2.

III. AN IMPROVED $\mathcal{O}(N^5)$ HYBRID METHOD

The computational advantage gained in the MP2-CCSD(I) and MP2-CCSD(II) methods over the conventional CCSD method may be better understood from the analysis of the CCSD equations. We do not wish to complicate the present discussion and will therefore work with the CCSD equations written in a schematic form which stresses the most salient points. For greater detail, we refer the interested reader to the paper by by Stanton *et al.*[17] on the efficient implementation of CCSD.

The equation for each single-excitation t_1 amplitude may be written as a function f_1 as follows:

$$t_i^a = f_1\Bigg(\sum_e t_i^e \sum_{mnf} t_{mn}^{af}\langle mn||ef\rangle, \sum_m t_m^a \sum_{nef} t_{in}^{ef}\langle mn||ef\rangle,$$
$$\times \sum_{mef} t_{im}^{ef}\langle ma||ef\rangle, \sum_{men} t_{mn}^{ae}\langle nm||ei\rangle, \dots \Bigg)$$

in which we explicitly mention as arguments only the most computationally expensive terms. The cost of the terms in parentheses are o^2v^3, o^3v^2, o^2v^3, and o^3v^2, respectively. Here

o is the number of the occupied orbitals and v is the number of virtual orbitals. Similarly, the equation for each double-excitation t_2 amplitude is of the form

$$t_{ij}^{ab} = f_2\Bigg(\sum_{mn} t_{mn}^{ab} \sum_{ef} t_{ij}^{ef}\langle mn||ef\rangle, \sum_{ef} t_{ij}^{ef}\langle ab||ef\rangle,$$
$$\times \sum_{me} t_{im}^{ae} \sum_{nf} t_{jn}^{fb}\langle ma||ef\rangle, \dots \Bigg).$$

The terms in the parantheses scale as o^4v^2, o^2v^4, and o^3v^3, respectively. When we update only the AAt_1 amplitudes, the arguments of the function f_1 reduce to the scalings ov^2OV, o^2v^2O, ov^2OV, and o^2vOV, respectively, where O is the number of occupied orbitals in the active space and V is the number of virtual orbitals in the active space. Typically, and in the applications presented here, O and V are of the order of 1, so we may think of these scalings as ov^2, o^2v^2, ov^2, and o^2v, respectively. Even for "large" active spaces in multireference studies, there are usually only a handful of active orbitals, and their number will typically be much smaller than the number of inactive occupied or virtual orbitals. In addition, it is traditional to fix the size of the active space as independent of the size of the basis set (although for very high accuracy studies some exceptions exist[32]). In all the subsequent estimations here we make the assumption that O and V do not grow with the size of the basis set. Updating only the $AAAA$ terms when we solve the MP2-CCSD equations reduces the scaling of the arguments of the function f_2 to $o^2v^2O^2$, $o^2v^2V^2$, and o^2v^2OV, respectively. Or, removing the O and V dependences, we obtain the identical scaling o^2v^2 for each term. Taking into account the iterative nature of the method, we conclude that the computational cost of the MP2-CCSD(I) procedure is $(N_{it}o^2v^2)$. It is reasonable to assume that N_{it} does not depend on the size of the system, and so the total cost of the MP2-CCSD method is dominated by the orbital transformation procedure. Thus, the MP2-CCSD(I) has the formal scaling $\mathcal{O}(N^5)$.

It is easy to notice, however, that updating certain other types of amplitudes together with the AA and $AAAA$ amplitudes increases the cost of the resulting hybrid method only marginally and still keeps it much lower than the cost of the regular CCSD method. If we update the AR, RA, and RR single-excitation amplitudes, the cost of this operation will scale as o^2v^3. Furthermore, if we also update the $ARAA$ and $AAAR$ double-excitation amplitudes, the worst scaling that will result from this operation will be o^2v^3V, or simply o^2v^3 if V is on the order of 1. The method in which we update the AA, AR, RA, RR, $AAAA$, $ARAA$, and $AAAR$ amplitudes self-consistently in the presense of the rest of the amplitudes computed by the MP2 method we call the MP2-CCSD(II) method, scaling as $\mathcal{O}(N_{it}o^2v^3)$. With respect to the increase of the size of the system (if N_{it} is assumed constant), the scaling of MP2-CCSD(II) is still not worse than that of the MP2 method.

In constructing the MP2-CCSD(I) and MP2-CCSD(II) methods we relied on the MP2 theory as a source of inexpensive t amplitudes. One might ask whether there exists some other choice of the low-cost method. The Epstein-Nesbet (EN) pair-correlation theory or related constructs,
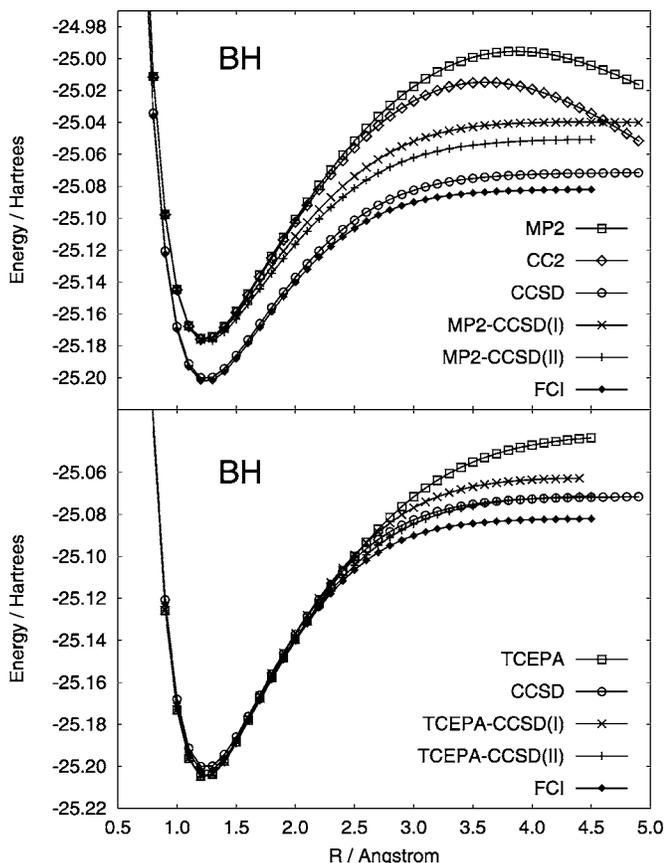
FIG. 2. Performance of the hybrid theories on the BH molecule in 6-31G* basis set.
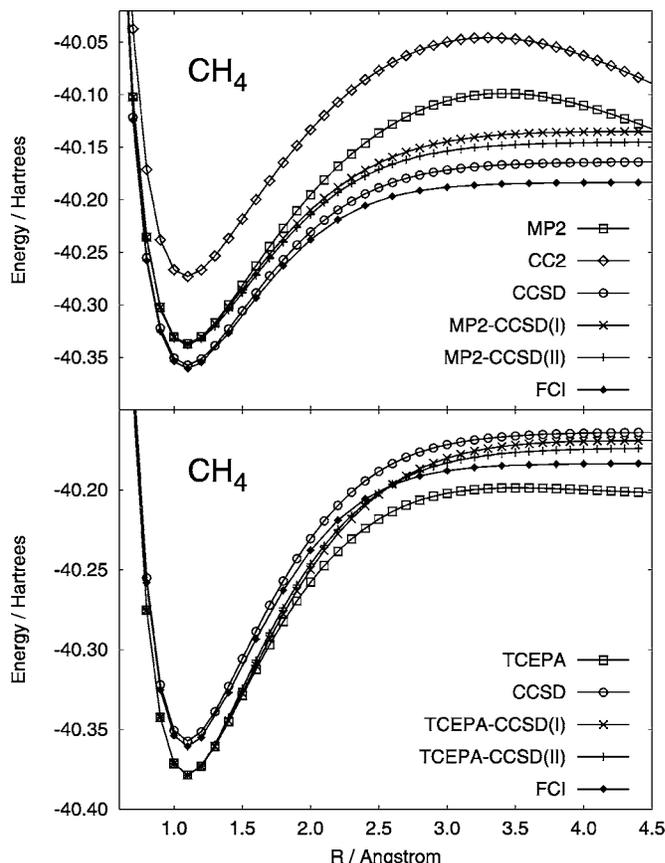
FIG. 3. Performance of the hybrid theories on the CH$_4$ molecule in 6-31G* basis set.

whose computational cost is dominated by the AO-MO transformation, are worthy of investigation in this respect. We utilized the following formula for the computation of the double-excitation amplitudes:

$$t_{ij}^{ab} = \frac{\langle ij \| ab \rangle}{e_{ij} - \langle \Psi_{ij}^{ab} | H - E_0 | \Psi_{ij}^{ab} \rangle}, \tag{4}$$

where E_0 is the Hartree-Fock energy and e_{ij} are pair energies,

$$e_{ij} = \sum_{a<b} \langle ij \| ab \rangle t_{ij}^{ab}, \tag{5}$$

which constitute the correlation energy:

$$E_{\text{corr}} = \sum_{i<j} e_{ij}. \tag{6}$$

Equations (4) and (5) are solved iteratively until the values t_{ij}^{ab} and e_{ij} no longer change. We call this approach truncated coupled electron pair approximation (TCEPA) because its formulas naturally arise from the truncation of a summation in the well-known coupled electron pair approximation (CEPA) equations:[33,34]

$$\langle \Psi_{ij}^{ab} | H | \Psi_0 \rangle + \sum_{\substack{k<l \\ c<d}} \langle \Psi_{ij}^{ab} | H - E_0 | \Psi_{kl}^{cd} \rangle = e_{ij} c_{ij}^{ab} \tag{7}$$

and e_{ij} is

$$e_{ij} = \sum_{c<d} \langle \Psi_{ij}^{cd} | H | \Psi_0 \rangle t_{ij}^{cd}. \tag{8}$$

Observe that the neglect of e_{ij} in the denominator of (4) brings us to the second-order EN perturbation theory (which is equivalent to EN pair-correlation theory), and further approximation of $\langle \Psi_{ij}^{ab} | H - E_0 | \Psi_{ij}^{ab} \rangle$ through $\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$ yields the MP2 theory. Some denominators in the EN perturbation theory approach zero as the bond is being broken. This may be explained by the fact that certain orbitals i and a (as well as j and b) necessarily become degenerate along the dissociation coordinate and the expression $\langle \Psi_{ij}^{ab} | H | \Psi_{ij}^{ab} \rangle$ approaches E_0. A few computations convinced us that the EN perturbation theory diverges even faster than MP2. Murray and Davidson,[35] who compared the MP theory with one of the flavors of the EN theory for equilibrium geometries and up to the fifth order in the perturbation, also arrived at the conclusion that MP gives more predictable energies. TCEPA, however, promises a better dissociation behavior than the regular EN perturbation theory. If e_{ij} remains in the denominator (as in TCEPA), then the denominator is not likely to turn into zero since e_{ij} is the part of the correlation energy which actually becomes constant at the end of the dissociation. We also constructed the hybrid TCEPA-CCSD(I) and TCEPA-CCSD(II) models built exactly after the MP2-CCSD(I) and MP2-CCSD(II) models, respectively (the types of the amplitudes updated are the same). In TCEPA-CCSD(I) and TCEPA-CCSD(II) the t amplitudes which are not up-
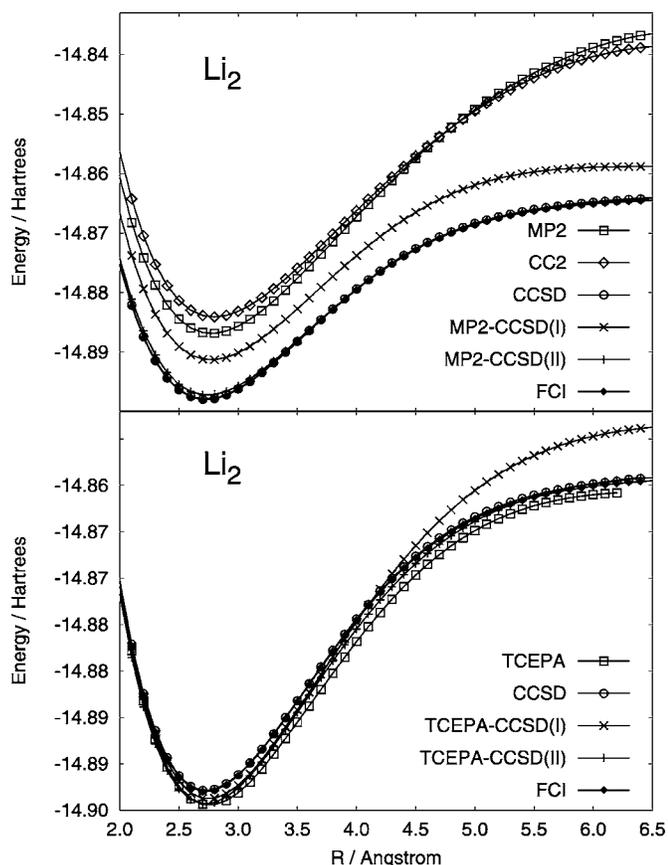
FIG. 4. Performance of the hybrid theories on the Li_2 molecule in 6-31G* basis set.

FIG. 5. The average nonparallelity errors (NPE) in the 6-31G* basis set relative to FCI. M-I, M-II, T-I, and T-II denote MP2–CCSD(I), MP2–CCSD(II), TCEPA-CCSD(I), and TCEPA-CCSD(II), respectively.

dated in the course of solving the CCSD equations come from Eqs. (4) and (5). Observe that by combining TCEPA with CCSD we do not attempt to correct or improve some particular feature of TCEPA (as we did with MP2 by substituting its AAAA amplitudes with the CCSD amplitudes). We merely wish to describe as many amplitudes as possible by a higher-quality method (CCSD) without disturbing the computational scaling of the lower-quality method (TCEPA).

The MP2-CCSD(I) and MP2-CCSD(II) energy expressions are invariant to rotations of orbitals within the four distinct subspaces: restricted occupied, active occupied, active virtual, and restricted virtual. (The only caveat being that if one actually employed orbitals other than canonical Hartree-Fock orbitals, the equation for the fixed MP2 amplitudes would have to be generalized.) Because restricted and active orbitals are treated differently when solving for the

cluster amplitudes, of course, the energy will change if there is any mixing between orbital subspaces. A drawback to the TCEPA-based methods is that they do not share the invariance of the energy with respect to rotations within each of the orbital subspaces.

One more $\mathcal{O}(N^5)$ candidate for a possible hybridization with coupled-cluster method is CC2. As demonstrated below, the divergence of CC2 at large interatomic separations may be even worse than that of MP2, and therefore we ruled out the idea of constructing a hybrid method built on CC2.

IV. RESULTS AND DISCUSSION

The hybrid methods introduced in the previous sections were implemented in a prototype code built on the PSI3.2 (Ref. 36) suite of quantum chemical programs and libraries. Here we test the performance of the theoretical constructs discussed above against results from full configuration interaction (FCI), which exactly solves the nonrelativistic electronic Schrödinger equation within the given one-particle basis set. Because of the high cost of these FCI computations, we restrict our attention in this work to the small molecules H_2, BeH^+, BH, HF, H_2O, CH^+, CH_4, and Li_2, all in the 6-31G* basis set. The largest FCI computations performed here, using the DETCI module[37] of PSI3, were for CH_4, which required 566 193 485 determinants (all electrons were correlated in the computations reported here). We note that the CCSD method, which the MP2-CCSD hybrids attempt to

TABLE I. Nonparallelity errors in hartree computed in the 6-31G* basis set.

Molecule	Interval (Å)	Step (Å)	CCSD	MP2	CC2	MP2-CCSD(I)	MP2-CCSD(II)	TCEPA	TCEPA-CCSD(I)	TCEPA-CCSD(II)
H_2	0.5–3.9	0.1	0.0000	0.0728	0.0670	0.0049	0.0035	0.0060	0.0085	0.0012
BeH^+	0.6–4.1	0.1	0.0005	0.0456	0.0359	0.0070	0.0077	0.0290	0.0065	0.0054
BH	0.8–4.4	0.1	0.0083	0.0626	0.0447	0.0177	0.0075	0.0414	0.0224	0.0138
CH^+	0.6–4.0	0.1	0.0105	0.0616	0.0330	0.0338	0.0249	0.0778	0.0274	0.0125
Li_2	2.0–6.0	0.1	0.0002	0.0157	0.0123	0.0032	0.0011	0.0019	0.0041	0.0016
HF	0.8–3.8	0.2	0.0209	0.0624	0.0990	0.0265	0.0210	0.0302	0.0397	0.0338
CH_4	0.7–4.4	0.1–0.2	0.0166	0.0639	0.0532	0.0264	0.0178	0.0061	0.0324	0.0275
H_2O	0.7–4.0	0.1	0.0219	0.0837	0.0980	0.0263	0.0085	0.0464	0.0405	0.0343

TABLE II. Spectroscopic constants of H_2, BeH^+, and BH computed using different methods in the 6-31G* basis set.

Molecule	Method	E_{min}	r_e	ω_e	$\omega_e x_e$	B_e	α_e	$\bar{D}_e$ ($\times 10^{-4}$)
H_2	MP2	$-1.144\,141$	0.7375	4533.58	126.1	61.502	3.0529	452.75
	CC2	$-1.144\,174$	0.7377	4527.85	126.7	61.466	3.0647	453.08
	MP2-CCSD(I)	$-1.146\,218$	0.7448	4367.81	143.2	60.305	3.4182	459.83
	MP2-CCSD(II)	$-1.149\,402$	0.7499	4297.58	140.1	59.483	3.3815	455.82
	CCSD	$-1.151\,698$	0.7462	4367.09	141.7	60.080	3.3615	445.49
	TCEPA	$-1.151\,003$	0.7442	4403.38	141.8	60.404	3.3403	454.66
	TCEPA-CCSD(I)	$-1.151\,508$	0.7455	4384.19	140.1	60.199	3.3257	454.00
	TCEPA-CCSD(II)	$-1.152\,484$	0.7473	4354.30	141.1	59.910	3.3506	453.66
	FCI	$-1.151\,698$	0.7462	4367.09	141.7	60.080	3.3615	454.85
BeH^+	MP2	$-14.873\,13$	1.3208	2280.90	34.3	10.660	0.2631	9.315
	CC2	$-14.873\,38$	1.3215	2275.49	34.5	10.649	0.2651	9.330
	MP2-CCSD(I)	$-14.873\,68$	1.3240	2251.12	37.8	10.609	0.2799	9.426
	MP2-CCSD(II)	$-14.876\,56$	1.3338	2176.70	42.6	10.454	0.3086	9.644
	CCSD	$-14.881\,54$	1.3311	2193.06	40.4	10.496	0.2985	9.618
	TCEPA	$-14.879\,41$	1.3264	2269.61	39.1	10.571	0.2322	9.172
	TCEPA-CCSD(I)	$-14.879\,80$	1.3283	2252.92	43.2	10.541	0.2437	9.230
	TCEPA-CCSD(II)	$-14.881\,46$	1.3339	2214.01	44.3	10.451	0.2492	9.316
	FCI	$-14.881\,59$	1.3312	2192.20	40.4	10.495	0.2988	9.621
BH	MP2	$-25.175\,87$	1.2331	2451.40	47.6	12.007	0.3946	11.522
	CC2	$-25.176\,34$	1.2339	2443.36	48.3	11.993	0.3986	11.556
	MP2-CCSD(I)	$-25.176\,60$	1.2373	2399.63	55.1	11.926	0.4306	11.783
	MP2-CCSD(II)	$-25.177\,80$	1.2436	2336.48	57.7	11.805	0.4556	12.054
	CCSD	$-25.200\,77$	1.2443	2355.06	53.1	11.793	0.4281	11.183
	TCEPA	$-25.205\,11$	1.2371	2441.54	48.7	11.930	0.3828	11.393
	TCEPA-CCSD(I)	$-25.205\,05$	1.2370	2449.62	45.7	11.933	0.3723	11.327
	TCEPA-CCSD(II)	$-25.205\,41$	1.2393	2427.72	47.0	11.887	0.3797	11.400
	FCI	$-25.202\,65$	1.2448	2347.73	54.1	11.784	0.4333	11.874

mimic at lower computational cost, performs reasonably well for bond breaking in these molecules.[2] The active spaces of the first five molecules consist of just σ and σ^*, whereas those of CH^+, CH_4, and Li_2 are slightly larger (because of the energetic proximity of other orbitals to σ and σ^* or the intersection of σ and σ^* with other orbitals along the dissociation curve). The active spaces of CH^+, CH_4, and Li_2 are $(2a_1b_1b_2)$, $(3a'a'')$, and $(2a_gb_{1u}b_{2u}b_{3u})$, respectively. We considered the reactions in which a single bond to hydrogen is broken, or in the case of Li_2, the unimolecular dissociation $Li_2 \rightarrow 2Li$. In the case of CH_4, for simplicity we fixed the nondissociating bonds at 1.086 Å, and the HCH angles were 109.471 22°. Likewise in H_2O, one bond length was fixed at 0.967 Å, and the HOH angle was 107.6°.

Figures 2–4 demonstrate the potential energy curves obtained with the hybrid models, which are plotted together with those obtained with the traditional models MP2 and CCSD, as well as with the CC2 method and with FCI. Potential energy curves for the other test cases are qualitatively similar. Let us initially consider the more standard methods, plus the MP2-CCSD hybrid methods, shown in the top half of the figures. The standard methods MP2 and CCSD feature their typical behavior in Figs. 2 (BH) and 3 (CH_4). The MP2 curve becomes unphysical at intermediate internuclear distances, and then the energy diverges at large internuclear distances. Note that the CC2 curves are qualitatively similar to MP2 and also show divergence at large distances. CCSD,

in contrast, performs reasonably well, yielding an energy which is somewhat too high at the dissociation limit. Our initial MP2-CCSD hybrid method, MP2-CCSD(I), behaves like MP2 near equilibrium, but avoids the unphysical behavior of MP2 at larger internuclear distances. Moreover, the MP2-CCSD(I) curves are roughly parallel to those of CCSD, which the method approximates. The same can be said for the MP2-CCSD(II) method, which is quite similar to MP2-CCSD(I), but yields somewhat lower energies at large distances. A more quantitative comparison of these methods is presented below.

The performance of the methods is somewhat different for the dissociation of Li_2, shown in Fig. 4. The behavior of MP2 is again unphysical (and the curve turns over again at larger distances than those shown in the figure). Again, CC2 behaves similarly to MP2. However, in this case the CCSD curve is nearly coincident with FCI. MP2-CCSD(I) again produces a resonable curve, although it yields a significantly lower energy than MP2 near equilibrium in this case. In contrast to its behavior for BH and CH_4, MP2-CCSD(II) now gives a much lower energy than MP2-CCSD(I) at all distances and, indeed, is nearly identical to CCSD and FCI.

Let us now turn to the lower parts of Figs. 2–4, which display results from the TCEPA method introduced above. We noted that the energy denominators in (4) are nonvanishing, and so one might expect better behavior at large internuclear separations than that seen for standard MP2. Indeed,

TABLE III. Spectroscopic constants of CH$^+$, Li$_2$, and HF computed using different methods in the 6-31G* basis set.

Molecule	Method	E_{min}	r_e	ω_e	$\omega_e x_e$	B_e	α_e	$\bar{D}_e$ ($\times 10^{-4}$)
CH$^+$	MP2	−37.965 26	1.1195	3039.74	62.3	14.468	0.4876	13.111
	CC2	−37.965 65	1.1199	3033.28	63.0	14.457	0.4911	13.136
	MP2-CCSD(I)	−37.971 42	1.1143	3054.53	74.1	14.601	0.5326	13.346
	MP2-CCSD(II)	−37.979 90	1.1160	3024.52	72.3	14.558	0.5385	13.492
	CCSD	−37.994 27	1.1284	2930.87	68.5	14.240	0.5245	13.446
	TCEPA	−37.998 84	1.1236	2955.43	43.5	14.362	0.5709	13.566
	TCEPA-CCSD(I)	−37.995 92	1.1267	2915.13	37.2	14.282	0.5701	13.713
	TCEPA-CCSD(II)	−37.997 12	1.1297	2882.33	21.0	14.208	0.5186	13.809
	FCI	−37.996 28	1.1293	2919.43	69.5	14.218	0.5297	13.489
Li$_2$	MP2	−14.886 85	2.7731	339.34	2.2	0.625	0.0050	0.085
	CC2	−14.886 94	2.7753	337.67	2.2	0.624	0.0051	0.085
	MP2-CCSD(I)	−14.891 29	2.7701	330.79	2.4	0.626	0.0055	0.090
	MP2-CCSD(II)	−14.897 19	2.7387	334.71	2.8	0.641	0.0058	0.094
	CCSD	−14.897 90	2.7254	340.09	2.8	0.647	0.0054	0.094
	TCEPA	−14.899 43	2.7566	329.53	2.4	0.632	0.0054	0.094
	TCEPA-CCSD(I)	−14.897 93	2.7381	339.06	2.3	0.641	0.0050	0.092
	TCEPA-CCSD(II)	−14.899 32	2.7259	340.08	2.6	0.647	0.0054	0.094
	FCI	−14.897 99	2.7249	339.96	2.7	0.647	0.0057	0.094
HF	MP2	−100.184 2	0.9339	4040.83	83.5	20.196	0.7379	20.180
	CC2	−100.185 1	0.9349	4019.61	84.8	20.153	0.7458	20.265
	MP2-CCSD(I)	−100.184 5	0.9355	3989.97	91.4	20.125	0.7780	20.480
	MP2-CCSD(II)	−100.185 6	0.9391	3922.40	90.0	19.974	0.7874	20.719
	CCSD	−100.188 4	0.9342	4024.03	86.9	20.183	0.7543	20.309
	TCEPA	−100.233 9	0.9446	3857.97	97.7	19.742	0.8143	20.678
	TCEPA-CCSD(I)	−100.233 7	0.9433	3901.95	87.2	19.793	0.7672	20.373
	TCEPA-CCSD(II)	−100.232 8	0.9420	3914.49	90.2	19.849	0.7798	20.413
	FCI	−100.190 6	0.9355	3997.62	88.4	20.125	0.7634	20.401

the behavior of TCEPA is perhaps not as catastrophic as MP2, but the curves are seriously flawed. For BH, the energy is far too high compared to FCI or other methods, and for CH$_4$, the TCEPA curve lies significantly below FCI at intermediate and large internuclear distances. For Li$_2$, the TCEPA curve is somewhat close to the FCI curve, but again the energy is lower. The erratic behavior of the TCEPA results are not encouraging for this method by itself. Examining the curves from the TCEPA-CCSD hybrids discussed above, we see that they are generally improved over straight TCEPA. For BH and CH$_4$, TCEPA-CCSD(I) mimics TCEPA at short distances and significantly improves upon it at large distances. For Li$_2$, however, at large distances TCEPA-CCSD(I) ruins the fairly good TCEPA results. The more complete hybrid method TCEPA-CCSD(II) performs much better, yielding results quite close to CCSD (and to FCI) for BH and Li$_2$. For CH$_4$, the TCEPA-CCSD(II) curve is quite similar to that of CCSD or FCI, but it is shifted down to significantly lower energies, approximately matching the surprisingly low TCEPA energies at equilibrium.

Having discussed the qualitative features of the results, let us turn to a more quantitative assessment. The most important consideration is how parallel the approximate potential curves are to the exact FCI curves. This can be judged using the so-called nonparallelity error (NPE), which is defined as the difference between the largest error and the smallest error across a certain representative interval of in-

teratomic separations. All the NPEs in this work were computed with respect to the FCI data. Table I presents the NPEs for eight molecules: H$_2$, BeH$^+$, BH, CH$^+$, Li$_2$, HF, CH$_4$, and H$_2$O. Based on the qualitative assessment above, it is no surprise that MP2 and CC2 exhibit very large NPEs over the intervals considered. Consistent with our previous work,[2] NPEs for CCSD are modest for these reactions, ranging from less than 1 mhartree for Li$_2$ up to about 22 mhartree (13 kcal mol^{-1}) for HF and H$_2$O. While these errors are not acceptable for high-accuracy work, they may be acceptable in some applications, and they will be much smaller for reactions in which bonds are made and broken simultaneously in the transition state.[38]

Our first hybrid method based on MP2 amplitudes, MP2-CCSD(I), produces NPEs which are typically several times lower than those of MP2, but still somewhat larger than those of CCSD. MP2-CCSD(II) systematically improves the NPEs even further—it almost always works better than MP2-CCSD(I) and it frequently rivals CCSD. Consistent with the erratic behavior of the TCEPA curves in Figs. 2–4 the NPEs of the TCEPA method are irregular. Except for the CH$^+$ molecule, they are lower than those of MP2, but this improvement is not predictable: sometimes TCEPA outperforms even MP2-CCSD(II) and CCSD, but in other cases it is much worse. The TCEPA-CCSD(I) and TCEPA-CCSD(II) methods are more systematic in this regard: the NPEs of
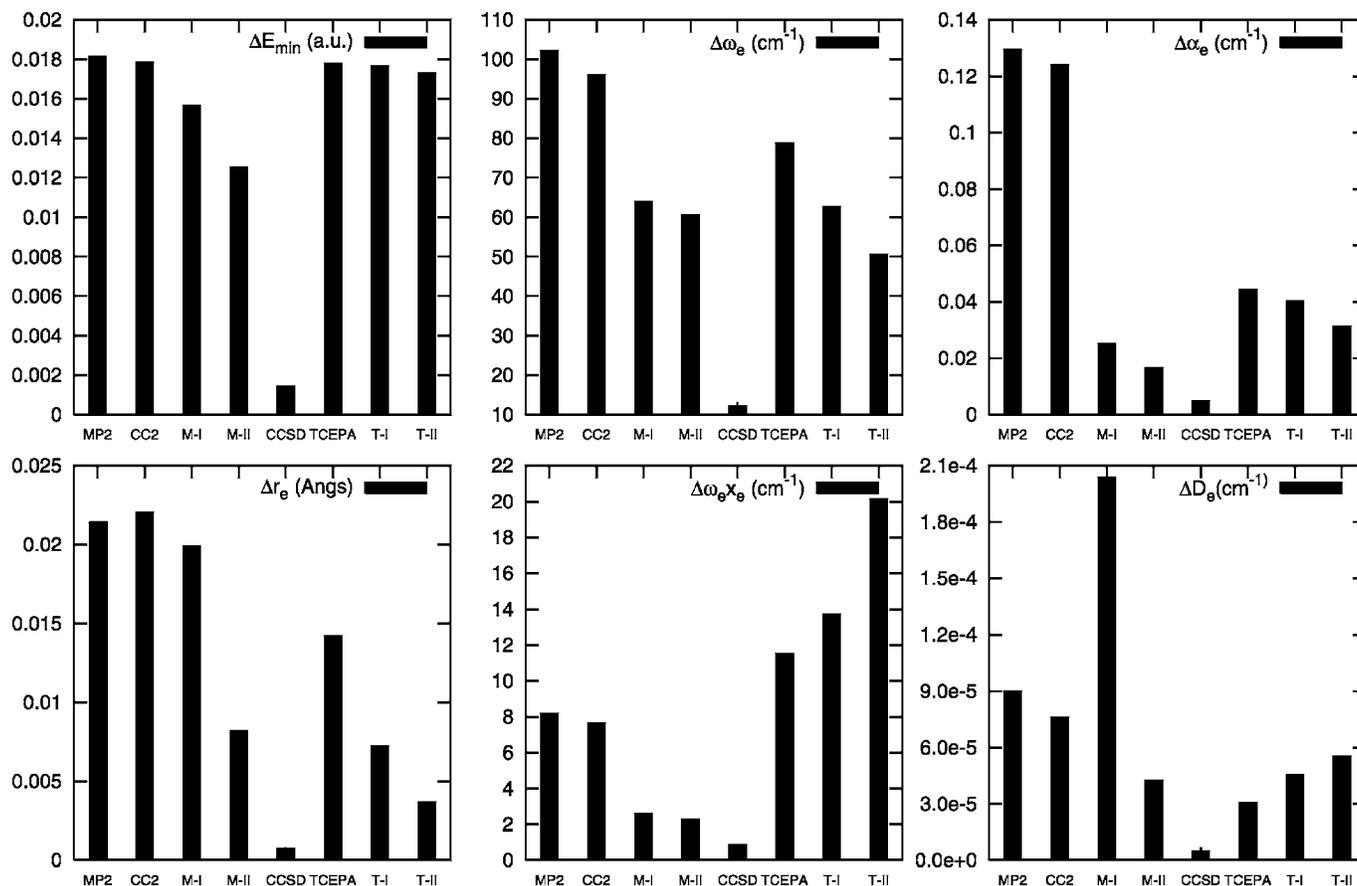
FIG. 6. The root mean square (rms) errors of various spectroscopic constants in 6-31G* basis set relative to FCI. M-I, M-II, T-I, and T-II denote MP2-CCSD(I), MP2-CCSD(II), TCEPA-CCSD(I), and TCEPA-CCSD(II), respectively.

TCEPA-CCSD(II) are always lower than those of TCEPA-CCSD(I), although on average they are not quite as good as those of MP2-CCSD(II). Figure 5 displays the NPEs averaged over the test cases considered here. Among the $\mathcal{O}(N^5)$ methods considered here, MP2-CCSD(II) performs best. It is remarkable that the average NPE of MP2-CCSD(II) is just as low as that of CCSD. The second best method is TCEPA-CCSD(II), which confirms our assumption that the inclusion of some additional amplitudes at the CCSD level should result in higher accuracy.

Although MP2 fails at large interatomic distances, it works well near the bottom of the potential energy well. Therefore it is interesting to explore whether the new MP2-CCSD(II) method improves not only the behavior at large internuclear separations, but also the quality of results near equilibrium. If so, MP2-CCSD(II) might be preferable to MP2 not only for bond-breaking applications or cases where electronic near degeneracies can become important, but also for routine computations of equilibrium molecular properties. Tables II and III present results for a number of spectroscopic properties, computed by fitting nine energy points evenly spaced by 0.005 Å about the equilibrium bond distance r_e to an eighth-order polynomial, $U(r)$. Each energy calculation was converged to at least 10^{-12} hartree and fitting errors are monitored to avoid numerical instabilities.

The familiar spectroscopic constants are computed by evaluating the zeroth- to fourth-order derivatives of $U(r)$ at r_e and utilizing the following relations:[39,40]

$$B_e \equiv \frac{h}{8\pi^2 \mu r_e^2}, \quad \omega_e \equiv \frac{1}{2\pi}\left(\frac{U''|_{r_e}}{\mu}\right)^{1/2}, \tag{9}$$

$$\omega_e x_e \equiv \frac{B_e^2 r_e^4}{4h\omega_e^2}\left(\frac{10 B_e r_e^2 (U'''|_{r_e})^2}{3h\omega_e^2} - U^{iv}|_{r_e}\right), \tag{10}$$

$$\alpha_e \equiv -\frac{2B_e^2}{\omega_e}\left(\frac{2B_e r_e^3 U'''|_{r_e}}{h\omega_e^2} + 3\right), \quad \bar{D}_e \equiv \frac{4B_e^3}{\omega_e^2}. \tag{11}$$

Here, μ is the reduced mass, B_e is the rotational constant, ω_e is the harmonic vibrational frequency, $\omega_e x_e$ is the anharmonicity constant, α_e is the vibration-rotation coupling constant, and $\bar{D}_e$ is the centrifugal distortion constant.

Regarding the total energies at equilibrium, $E_{\min}$, note that those of the TCEPA-based methods are often significantly lower than those of FCI (as mentioned above). The MP2-based hybrid methods as well as CC2 tend to act like MP2 itself in their prediction of $E_{\min}$. Considering the equilibrium bond length r_e, MP2 systematically underestimates this parameter (except for Li_2), while TCEPA behaves irregularly. Figure 6 shows the root mean square (rms) errors for the spectroscopic constants. After CCSD, the lowest rms values of r_e belong to TCEPA-CCSD(II), TCEPA-CCSD(I), and MP2-CCSD(II). The individual equilibrium distances produced by the MP2-CCSD methods are typically shorter than those produced by the TCEPA-CCSD methods. The con-

stants α_e and $\omega_e x_e$ depend on the third and fourth derivatives, respectively, of the potential and so are sensitive to the shape of the potential. MP2-CCSD(II) is the best performer among the hybrid methods for these constants, while the TCEPA-based hybrid methods are inferior to the MP2-based hybrids for these characteristics. Somewhat unexpectedly, the errors of MP2-CCSD(II) for the α_e, ω_e, and $\bar{D}_e$ constants frequently have the sign different from those of all other methods. The centrifugal distortion constant $\bar{D}_e$ is estimated with similar quality by MP2-CCSD(II) and the TCEPA-based methods, all of which perform better than MP2 or CC2. The larger rms error observed for MP2-CCSD(I) is due almost entirely to a single poor result for the H_2 molecule. The rms errors for B_e are omitted from Fig. 6 because this characteristic is proportional to r_e^{-2} and its errors are tied to r_e errors. Judging from the magnitude of the rms errors of the spectroscopic constants, we conclude that MP2-CCSD(II) is the most consistent among the $\mathcal{O}(N^5)$ methods near equilibrium. The CC2 method shows only a slight improvement over MP2, while the TCEPA-based methods apparently have difficulty for the quantities depending on third and fourth derivatives.

V. CONCLUSIONS

In this work we have employed hybrid methodology to construct several new methods referred to as MP2-CCSD(II), TCEPA-CCSD(I), and TCEPA-CCSD(II), seeking to find an $\mathcal{O}(N^5)$ scheme that improves upon the performance of the previous, MP2-CCSD(I), method. The computation of the NPEs and several spectroscopic constants for a number of simple molecules has shown that MP2-CCSD(II) works noticeably better than MP2 and sometimes rivals even CCSD, which scales as $\mathcal{O}(N^6)$. The average NPE of MP2-CCSD(II) is not noticeably worse than that of CCSD. The simplicity of formulation, the inexpensiveness, and the accuracy of the MP2-CCSD(II) method express the hope that it might be used instead of MP2 in many situations where the latter is currently applied.

A few limitations of MP2-CCSD(II) (equally applicable to our other hybrid methods) must be mentioned, however. First, we do not expect it to exhibit an impressive performance in cases where CCSD itself should fail. Such cases may include breaking multiple bonds or other cases of strong electronic near degeneracies. A more sophisticated hybrid scheme may be desirable to deal with these issues. For example, the inclusion of higher than double excitations or accounting for the multireference character of the ground state may be needed. Indeed, work is in progress on such schemes as MP2-CCSDTQ and MP2-MCSCF, which will be more suitable to conform to these requirements. Second, as all the methods are based on the active space partitionings, MP2-CCSD(II) obliges the researcher to select a proper active space. We believe that in many cases the minimal dimension of the active space (i.e., only σ and σ^* for single bonds) should be satisfactory, but sometimes slightly larger active spaces may be required. Such complications arise when there are orbitals whose energies are very close to those of σ and σ^*, or when the character of the σ and σ^* orbitals may change along the reaction coordinate.

An attractive application for the new MP2-CCSD(II) method would be to systems for which CCSD performs well but MP2 misbehaves. In a separate study,[38] where we investigate radical hydrogen abstraction reactions, the enthalpies produced by CCSD with noniterative triples, CCSD(T), are relatively insensitive to the choice of the reference function, whether UHF or restricted open-shell Hartree-Fock (ROHF). However, the enthalpies computed with MP2 depend crucially on the choice of the reference. In addition, the ROHF-based MP2 method produces some unacceptable artifacts, whereas the UHF-based MP2 method suffers from serious spin contamination. We believe that the MP2-CCSD(II) method would alleviate such problems of MP2 if applied to these systems and we plan to explore this in future work.

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