Assessment for the mean value total dressing method: Comparison with coupled cluster including triples methods for BF, NO^+, CN^+, C_2, BeO, NH_3, CH_2, H_2O, BH, HF, SiH_2, Li_2, LiNa, $LiBe^+$, NeH^+, and O_3

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Limited previous experience with the mean value total dressing (MVTD) method had shown that MVTD energies for closed shell systems are generally better than CCSD(T) ones compared to FCI. The method, previously published as total dressing 2′(td-2′), is based on the single reference intermediate Hamiltonian theory. It is not a CC method but deals in a great part with the same physical effects that CC methods that incorporate amplitudes of triples such as CCSDT or its CCSDT-1n approaches. A number of test calculations comparing to diverse CC methods, as well as FCI and experiment when available, have been performed. The tests concern equilibrium energies in NH_3 and CH_2, equilibrium energies and distances in some diatomics (BF, NO^+, CN^+, C_2, BeO), different bond breaking situations (H_2O, BH, HF, SiH_2) and spectroscopic properties of different bonding conditions (Li_2, LiNa, $LiBe^+$, NeH^+, and O_3). The results are in general closer to the full CCSDT ones in the equilibrium regions and close to CCSDT-1 along most dissociation curves. A few exceptions to this rule are analyzed with the help of an approach to MVTD that does not take into account the effects of linked quadriexcitations. Such analysis suggests the interest of improving the treatment of effects of linked triples in the MVTD model. The separate contributions of linked and unlinked triples and quadruples are also analyzed for some of the above diatomics representing different behaviors of bond breaking. The interest of such analysis is illustrated in the NeH^+ molecule. The MVTD results show, in general, a high quality, provided that the nature of the correlation problem does not become largely multiconfigurational, as occurs in multiple bond dissociation or in the asymmetric stretching of ozone. © *1997 American Institute of Physics.* [S0021-9606(97)00739-3]

I. INTRODUCTION

Single-reference coupled cluster (CC) methods have been shown to be highly accurate for the calculation of electron correlation in chemical systems and processes which are well suited to a single-determinantal description.[1–12] Although they are not variational as the CI methods, they have the great advantage of being extensive and size consistent, properties that are characteristic of many body perturbation theory (MBPT) expansions truncated at a given order.[13–15] Besides this, the CC methods incorporate partial perturbative series summations to infinite order which make them very efficient. So, CC results are expected to represent an excellent approximation to FCI (i.e., to the exact results) for a given basis set of one-electron functions.[10,16–20]

Even in small closed shell systems in the equilibrium region, the fourth order in the perturbation must be taken into account to reach chemical accuracy (say to 1 or 2 mhartree) in the energy compared to FCI. Important parts of fifth order are also highly convenient.[21] To achieve this, CC methods that deal with the amplitudes of single, double, and triple excitations[6–9,22] must be considered. The full treatment of triples amplitudes in the CC equations, i.e., the CCSDT approach,[10,11,16] implies a significant increase of computational effort. So, a number of approximate methods have been proposed by different authors that incorporate more or less accurately the effects of fourth or higher order linked MBPT diagrams passing through triples, such as CCSD(T),[23,24] CCSDT-1a,[7–9,24,25] CCSDT-1b,[26] CCSDT-2,[27] and CCSDT-3[27] or the CC3 method recently proposed by Koch and co-workers.[28] In the following, we will refer collectively to the CC methods that include triples amplitudes as CC (with T) methods.

Another approach to the electron correlation problem is provided by the coupled electron pair approach (CEPA).[29–31] CEPA is not so complete as CC is in the treatment of nonlinear terms which are present in the CC equations, but it is still size extensive.

A general unified formulation of CEPA and CC methods has also been recently proposed by the Toulouse group on the basis of intermediate Hamiltonians theory by means of the so-called matrix dressing techniques.[32,33] Particular interest deserves a method known as the size-consistent self-consistent CI or $(SC)^2CI$[32] that is free of unlinked diagram contributions and easily generalizable to any truncated CI. The $(SC)^2$ procedure applied on a closed shell single-reference SDCI can be labeled as $(SC)^2$SDCI. It has been

shown that the converged $(SC)^2$SDCI procedure incorporates in the energy the cancellation to all perturbation orders of the MBPT-like unlinked diagrams which are responsible for the lack of size extensivity in SDCI. Other perturbational effects such as summations to infinite order of some series of exclusion violating principle (EPV) diagrams are also included. However, some important linked effects are still lacking, notably, the fourth order linked triple effects, as well as the usually less important linked quadruple ones.[34] The possibility of incorporating these effects by means of similar iterative matrix dressing methods as well as the equivalence of these procedures to some CC approaches has also been shown.[33,35]

The methods that incorporate both unlinked (their cancellation) and linked effects though dressing CI techniques are usually known as total dressing methods.[33,34] In general, the formulation of CC methods as total dressing methods requires a series of iteration cycles. Each cycle is made up of a matrix dressing step followed by a matrix root and eigenvector evaluation. Convergence in the energy and the wave function, starting from the SDCI ones, is usually achieved in 4 to 6 steps to the accuracy of 10^{-5} or 10^{-6} hartree[33,35] but better accuracy can be reached in a few additional steps, as required, e.g., for the numerical calculation of vibrational frequencies. In this way, both linked and unlinked effects are incorporated in the truncated CI matrix at each iteration.

An alternative approach has been proposed[34] which incorporate the effects of linked triples and quadruples in a single step after convergence of the $(SC)^2$SDCI iterative calculation. The last step proceeds through the calculation of the mean value of the $(SC)^2$SDCI wave function, $\tilde{\Psi}$, with respect to a dressed Hamiltonian. This approach is usually referred to as mean value total dressing (MVTD) approach. Different formulations can be conceived for the total dressing operator that corrects the Hamiltonian, so that different MVTD methods can be formulated.[34] One of them has been shown to be particularly efficient for approaching FCI in a few model systems[34] and for the calculation of spectroscopic properties in the single bond F_2 and HF diatomics.[36] We deal in this paper with this method and we will call it simply MVTD because no reference will be made in the following to other mean value methods. In a broad sense, MVTD accounts in a great part for physical effects that overlap with those included in CC (with T) methods, but it is not a CC method. Limited comparisons of results in previous papers[34,36] seem to indicate that MVTD can yield energies that lie between CCSD(T) and full CCSDT. In order to assess this preliminary but, up to now, insufficiently founded conclusion, we consider it worthwhile to perform a number of systematic tests, and this is the main goal of the present paper. If this preliminary conclusion holds this will mean that in a single noniterative step MVTD improves the near-to-CCSD level energies and spectroscopic properties given by $(SC)^2$SDCI to the largely more accurate near-to-CCSDT level ones. Therefore, highly accurate results could be reached without performing any direct coupling between triples or quadruples, provided that size-extensive quality singles and doubles coefficients (e.g., CEPA ones) are available.

The MVTD method and its physical contents are briefly summarized in Sec. II. In Sec. III seven model systems (BF, NO^+, CN^+, C_2, BeO, NH_3, and CH_2) are tested at equilibrium geometries with DZP basis sets. In Sec. IV four bond-breaking models are tested (BH, HF, H_2O, and SiH_2). In Sec. V large basis sets are used to test four systems (Li_2, $LiBe^+$, LiNa, and NeH^+) that correspond to different bonding situations attending to bond energies, correlation contributions or bond breaking. In Sec. VI a test calculation on the O_3 system helps to understand the limitations of the method. It is shown in Sec. VII how the behavior of linked and unlinked contributions of triples and quadruples change along the dissociation curves and how their profiles depend on the nature of the bond and the dissociating fragments. After a general discussion in Sec. VIII, some conclusions are summarized in Sec. IX.

II. METHOD

The mean value total dressing (MVTD) method used in the present paper was first published as the td-2′ method[34] in the context of research about intermediate effective Hamiltonians[37] introduced by the Toulouse group.[38,32] The MVTD method was conceived as an accurate and nondiverging (under degeneracy in the intermediate model space) alternative to the simple addition to the $(SC)^2$SDCI energy of perturbational fourth order linked contributions of triples and quadruples.[32] Such perturbational addition would show serious divergence problems, e.g., along single-bond breaking dissociation curves.

The $(SC)^2$CI method is a general iterative procedure to achieve the cancellation of unlinked diagrams to all perturbative orders for a given single or multireference CI. The resulting energy is size extensive and even separable (if localized MOs are used).[32] The method can be considered a full CEPA method so that the $(SC)^2$SDCI energy incorporates, besides the SDCI contributions and the canceled unlinked effects of triples and quadruples, infinite summations of some series of EPV diagrams. Such EPV diagrams are partly incorporated in the different CEPA-n approaches.[31]

The idea behind the MVTD method is to calculate the mean value of the $(SC)^2$SDCI wave function with respect to the so-called totally dressed Hamiltonian, i.e., a Hamiltonian operator to which some terms have been added by means of a ''dressing operator'' Δ which incorporate the effects of the external space (i.e., triples and quadruples on the closed shell reference ϕ_0.). Two diagonal dressing operators are used in the practical implementation of MVTD

(i) The $(SC)^2$ dressing operator

$$\Delta_{ii}^{(SC)^2} = \sum_{\substack{j \\ D_j^+ \phi_i \neq 0}} \tilde{c}_j H_{0j}, \tag{1}$$

where D_j^+ is the double excitation operator that creates ϕ_j from ϕ_0 and $\tilde{c}_j$ is the coefficient of the diexcitation ϕ_j obtained through diagonalization of the dressed SDCI matrix.

Once the iterative dress-then-solve-root procedure has converged, both the $(SC)^2$SDCI energy, $\tilde{E}$, and wave function

$$\tilde{\Psi}=\phi_0+\sum_{i\in S,D}\tilde{c}_i\phi_i \tag{2}$$

are available. Note that intermediate normalization is required in the definition of the dressing operators.

(ii) The total dressing operator

$$\Delta_{ii}^{\mathrm{TD}}=\frac{1}{\tilde{c}_i}\sum_{\alpha\in TQ}c_\alpha H_{i\alpha}, \tag{3}$$

where α runs over the external space of triples and quadruples.

In the present formulation of the MVTD method, the c_α coefficients appearing in Eq. (3) are estimated, for the triples, in a perturbative-like way

$$c_\alpha=\frac{\langle\phi_\alpha|H|\tilde{\Psi}\rangle}{\Delta_\alpha}, \tag{4}$$

where $\Delta_\alpha=H_{\alpha\alpha}-H_{00}$ is the so-called Epstein–Nesbet[39–41] or shifted[42–44] denominator for the triple ϕ_α.

For the quadruples, each c_α is estimated in a CCD-like way

$$c_\alpha=\sum_{\substack{(i,j)\\ D_i^+D_j^+\phi_0=\phi_\alpha}}\tilde{c}_i\tilde{c}_j, \tag{5}$$

where the symbol (i,j) stands for all the couples of disconnected diexcitations into which the quadruple ϕ_α can be decomposed. Of course, Eq. (5) does not means that we perform an actual CCD calculation because the $\tilde{c}_i$ coefficients are fixed at the $(SC)^2$ level. For the same reason, the coefficients obtained in Eq. (4) are not the second order coefficients of the EN perturbative expansion. This fact, along with the proper use of normalized coefficients in the definition of the mean value of the energy (see below), provides the damping of divergence behaviour at long bond distances.

The MVTD energy is obtained as

$$E^{\mathrm{MVTD}}=\langle\tilde{\boldsymbol{\Psi}}|H+\Delta^{\mathrm{TD}}|\tilde{\boldsymbol{\Psi}}\rangle, \tag{6}$$

where $\tilde{\boldsymbol{\Psi}}$ denotes the normalized $(SC)^2$SDCI wave function. One can take into account that the $(SC)^2$SDCI energy is $\tilde{E}=\langle\tilde{\boldsymbol{\Psi}}|H+\Delta^{(SC)^2}|\tilde{\boldsymbol{\Psi}}\rangle$ and that the $\Delta_{ii}^{\mathrm{TD}}$ operator includes as a particular term, the $\Delta_{ii}^{(SC)^2}$ operator. Hence the actual calculations are performed as

$$E^{\mathrm{MVTD}}=\tilde{E}+\langle\tilde{\boldsymbol{\Psi}}|\Delta^{\mathrm{TD}}-\Delta^{(SC)^2}|\tilde{\boldsymbol{\Psi}}\rangle. \tag{7}$$

Appropriate implementation of Eq. (7) allows for a separate estimation of the accumulated effects due to linked and unlinked diagrams containing only one triple or only one quadruple as its highest excitation so that we can write

$$\begin{aligned}E^{\mathrm{MVTD}}&=\tilde{E}+\Delta E_L^Q+\Delta E_L^T\\&\approx E^{\mathrm{SDCI}}+\Delta E_L^Q+\Delta E_L^T+\Delta E_{NL}^Q+\Delta E_{NL}^T.\end{aligned} \tag{8}$$

Note that the unlinked contributions are in fact the corrections to the SDCI energy required to have proper scaling with the number of electrons (size extensivity), while the linked contributions are additional contributions required to improve the accuracy of the method. Both linked and unlinked contributions correspond to fourth and higher order MBPT diagrams that do not imply direct coupling between triples and (or) quadruples, including some series of EPV ones.

A Δ^{TD} operator can be built for triples only if one limits the summation in Eq. (3) to triples. The resulting method differs from MVTD by the lack of the linked quadruples contribution ΔE_L^Q. As the linked effects of triples are taken into account in an essentially perturbative way, the method can be denoted as $(SC)^2$(T) following a notation convention similar to that of CCSD(T). Note, however, that the EN choice of the zeroth order Hamiltonian is used instead of the more common MP partition and that the normalized $(SC)^2$SDCI wave function is used in Eq. (6).

III. EQUILIBRIUM REGION CALCULATIONS

A number of model molecules have been chosen for which extensive CC calculations exist in the literature (BF, NO^+, CN^+, C_2, BeO).[45] Two additional molecules, NH_3 and CH_2, have been chosen for the availability of FCI benchmark calculations.[46,19] For the diatomics, the basis set was a standard Huzinaga[47]–Dunning[48] of DZ+P quality $(9s5p1d/4s2p1d)$ for B, C, N, O, and F with six component d functions. d orbital exponent and other details about the basis sets can be obtained from Ref. 45. For Be the $(9s4p1d/3s2p1d)$ set of Dunning and Hay[49] was used. For NH_3 the DZ+P basis set of ANO quality used in the benchmark calculation of Knowles and Handy[50] has been used. For CH_2 the Huzinaga–Dunning DZ+P[47,48] has been used as in the FCI calculation by Bauschlicher and Taylor[51] with six d functions for C. The two core MOs as well as the two highest virtuals have been frozen in all cases but for BeO where only one core and virtual were frozen. The N and C core MOs were frozen in NH_3 and CH_2. All these calculation conditions as well as others in this work have been chosen according to those of the reference calculations described in the literature.

The MVTD results concerning equilibrium bond distances and total energies are summarized in Tables I to VII. Tables I to V include also the harmonic frequencies. A number of CC results as well as the variational CISDTQ ones from other authors[45] for the same systems and basis sets have been included for comparison. Due to the relatively small linked quadruples contributions, $(SC)^2$SDCI results are in general similar to the CCSD ones. The dressing methods that include linked triples [$(SC)^2$(T) and MVTD] should be compared with CCSDT-1 and CCSDT methods.

BF and NO^+ are isoelectronic and have 14 electrons (only 10 of them were correlated). The correlation energy is larger for NO^+ and the difference between MVTD and CC results is slightly larger for this system. The MVTD energy of BF differs only by a few microhartrees from the CCSDT

TABLE I. Theoretical energies, distances, and harmonic frequencies for BF molecule using a DZ+P basis set.

	r_e (Å)	ω_e (cm^{-1})	E (hartree)
SCF[a]	1.268	1457	−124.133 657
SDCI[a]	1.286	1390	−124.364 791
$(SC)^2$SDCI	1.291	1371	−124.377 938
$(SC)^2$(T)	1.292	1370	−124.383 151
MVTD	1.295	1365	−124.386 584
CCSD[a]	1.292	1366	−124.380 120
CCSDT-1[a]	1.296	1347	−124.387 162
CCSDT[a]	1.295	1353	−124.386 589
CISDTQ[a]	1.294	1356	−124.385 797

[a]Reference 45.

TABLE III. Theoretical energies, distances, and harmonic frequencies for CN^+ molecule using a DZ+P basis set.

	r_e (Å)	ω_e (cm^{-1})	E (hartree)
SCF[a]	1.163	2176	−91.624 202
SDCI[a]	1.193	2102	−91.929 400
$(SC)^2$SDCI	1.176	1985	−91.962 851
$(SC)^2$(T)	1.220	2159	−91.981 544
MVTD	1.223	2125	−91.995 910
CCSD[a]	1.198	2027	−91.969 625
CCSDT-1[a]	1.176	1917	−92.008 487
CCSDT[a]	1.199	1987	−91.998 324
CISDTQ[a]	1.197	2001	−91.994 007

[a]Reference 45.

one. This is a fortuitous result, of course, but in all the examples included in this section, the MVTD results are closer to CCSDT than the CCSDT-1 ones. The same holds for the equilibrium distances r_e that, in most cases, are predicted by MVTD at the same value as full CCSDT within 0.001 Å. Of course, neither MVTD nor CC methods are variational and the relative position of their energies is not prefixed. So, in most cases, MVTD gives lower energy than CCSDT, but this is not always the case (e.g., in BeO).

CN^+, C_2, and BeO are isoelectronic, with 12 electrons each. In this study, eight electrons have been correlated for CN^+ and C_2, and ten electrons have been correlated for BeO. These molecules are discussed together because they are particularly badly described at the single-determinantal level. So, these are systems for which methods including effects of triples are of special interest[45] and represent difficult tests for single reference methods.

The energy differences in these three molecules between MVTD and CCSDT are of the order of a few mhartree (−1.0 to 2.65). The same differences in the case of CCSDT-1 approaches are significantly larger, ranging from −2.5 for C_2 to −10.16 for CN^+. The case of BeO deserves a special comment. It is known that for this system and basis set, CCSDT-1 predicts particularly overestimated energy and equilibrium distance if compared to full CCSDT (and experiment). This has been attributed to a bad treatment of the triples in the CCSDT-1 approach.[45] At the same time, CCSD performs better than expected for this system. We can note two points from our results on BeO. First, MVTD gives results close to CCSDT, as in the other systems here considered, both for energies and equilibrium distances. Second, CCSD for this systems predicts an energy which is very close to the $(SC)^2$SDCI one (less than 0.1 mhartree apart). This could suggest that the linked effects of quadruples is negligible in this system. However, the difference between $(SC)^2$(T) and MVTD energies, which also accounts for the linked effects of quadruples, is about 7.3 mhartree (for a very similar change in the geometry), a quantity that is far from being negligible. The good quality of the results of the MVTD approach does not differ from that of the other systems considered in this work. This would suggest that for this particular system and calculation conditions (basis set, frozen core, etc.) both CCSD and CCSDT-1 approaches are facing to particular difficulties that requires going up to CCSDT for a proper treatment.

In the case of CN^+, a bad treatment of triples has been still attributed to the CCSDT-1 approach,[45] and again MVTD performs better for the energy. However, the MVTD equilibrium distance is overestimated for this triple bond system, far away from the experimental value of 1.173 Å.[52] As well as for BeO, CCSD predicts the equilibrium bond length very close to CCSDT, while the linked quadruples effects seem to have an important role in the differences of r_e. Note, e.g., a difference of 6.8 mhartree between CCSD and $(SC)^2$SDCI energies for a difference in r_e of 0.026 Å and compare it to a difference of 14.4 mhartree between MVTD and $(SC)^2$(T) both at $r_e = 1.22$ Å. The triple bond nature of this system is an important factor to consider. Although the MVTD energy

TABLE II. Theoretical energies, distances, and harmonic frequencies for NO^+ molecule using a DZ+P basis set.

	r_e (Å)	ω_e (cm^{-1})	E (hartree)
SCF[a]	1.045	2824	−128.936 257
SDCI[a]	1.078	2500	−129.237 503
$(SC)^2$SDCI	1.085	2379	−129.253 648
$(SC)^2$(T)	1.090	2377	−129.266 133
MVTD	1.094	2319	−129.274 054
CCSD[a]	1.087	2400	−129.260 278
CCSDT-1[a]	1.097	2258	−129.274 616
CCSDT[a]	1.094	2308	−129.273 290
CISDTQ[a]	1.094	2319	−129.273 041

[a]Reference 45.

TABLE IV. Theoretical energies, distances, and harmonic frequencies for C_2 molecule using a DZ+P basis set.

	r_e (Å)	ω_e (cm^{-1})	E (hartree)
SCF[a]	1.250	1917	−75.389 676
SDCI[a]	1.257	1902	−75.666 991
$(SC)^2$SDCI	1.260	1880	−75.693 531
$(SC)^2$(T)	1.261	1876	−75.718 127
MVTD	1.267	1848	−75.729 180
CCSD[a]	1.263	1862	−75.702 742
CCSDT-1[a]	1.270	1818	−75.730 637
CCSDT[a]	1.267	1829	−75.728 136
CISDTQ[a]	1.265	1843	−75.724 770

[a]Reference 45.

TABLE V. Theoretical energies, distances, and harmonic frequencies for BeO molecule using a DZ+P basis set.

	r_e (Å)	ω_e (cm^{-1})	E (hartree)
SCF[a]	1.312	1690	−89.423 222
SDCI[a]	1.346	1530	−89.633 083
$(SC)^2$SDCI	1.360	1457	−89.655 271
$(SC)^2$(T)	1.355	1444	−89.656 294
MVTD	1.363	1417	−89.663 642
CCSD[a]	1.351	1511	−89.655 281
CCSDT-1[a]	1.400	1164	−89.672 091
CCSDT[a]	1.368	1413	−89.666 290
CISDTQ[a]	1.367	1419	−89.665 616

[a]Reference 45.

continues to be nearer to CCSDT and CCSDT-1, the bond distance is poor. The question is left open if this is a behavior related to this particular basis set. See below for a discussion about a more general limitation related to the triple nature of the bond.

The ω_e results reported in Tables I to V show that, with the exception of CN^+, the mean deviation from the CCSDT values is 12 cm^{-1}. They are always overestimated and, consequently, MVTD values deviate less from the experimental values than CCSDT ones with the present basis sets. Contrarily, for the same systems, CCSDT-1 shows underestimated values and in the particular case of BeO it deviates about -250 cm^{-1} from the CCSDT value.

The energy results for NH_3 at a unique geometry are shown in Table VI. This calculation is of great interest due to the relatively large dimension and good quality of the basis set which has been frequently used[50,46,53] in the achievement of a 4-atoms, 28-active orbitals, 8-electron FCI benchmark calculation. The FCI energy has been recently revisited and established very accurately as being $-56.424\,006\,98$ hartree.[46] Another recent FCI estimation accurate to 1×10^{-4} hartree[53] agrees with this result. As reported in Table VI, CCSDT is still 0.3 mhartree over FCI, while MVTD is in error by only 0.2 mhartree, CCSDT-1b by 0.5 mhartree, and CCSD(T) by 0.6 mhartree. So, for this system and compared to CCSDT the errors are -0.14 mhartree for MVTD and $+0.16$ for CCSDT-1b. Note that the estimate of the quadruples linked effects from the energy differences between CCSD and $(SC)^2$SDCI and between MVTD and $(SC)^2$(T) are largely more coincident (2.65 vs 2.59 mhartree) in this case than in the previous systems, because the same molecular geometry of NH_3 was used with all methods.

TABLE VI. Theoretical energies for NH_3[a] molecule using a DZ+P basis set.

	E (hartree)	ΔE to FCI (mhartree)
SCF	−56.213 741	-
SDCI	−56.411 050	-
$(SC)^2$SDCI	−56.417 029	-
$(SC)^2$(T)	−56.421 226	2.8
MVTD	−56.423 815	0.2
CCSD	−56.419 681	-
CCSD(T)	−56.423 429	0.6
CCSDT-1b	−56.423 510	0.5
CCSDT	−56.423 675	0.3
FCI[b]	−56.424 007	-

[a]Geometry in atomic units: N(0,0,0); H (1.772, 0, 0.7213); and (−0.886, ±1.5346, 0.7213).
[b]Reference 46.

TABLE VII. Theoretical energies for CH_2[a] molecule using a DZ+P basis set.

	E (hartree)	ΔE (mhartree)
SCF	−38.886 297	-
SDCI	−39.018 284	-
$(SC)^2$SDCI	−39.022 156	5.0
$(SC)^2$(T)	−39.025 454	1.7
MVTD	−39.027 183	0.0
FCI[b]	−39.027 183	-

[a]Geometry in atomic units: C(0,0,0); H (±1.644 40, 0, 1.322 13).
[b]Reference 51.

The results for closed shell CH_2 in Table VII show also the excellent value of MVTD energy if compared to FCI. Of course, this result, as well as that for BF, must be considered as fortuitous. However, the methods under consideration are essentially size extensive, so that good performance compared to FCI can be reasonably expected for larger systems and greater number of correlated electrons at equilibrium geometries.

As a general conclusion from this section, we can say that MVTD calculated energies and bond distances are, in general, closer to the CCSDT ones than those from CCSDT-1 or CCSD(T) and represent a good approach to FCI. In fact, the errors of MVTD to FCI, at equilibrium geometries, are similar to the errors of some methods that ensure the fifth order of perturbation such as QCISD(TQ) or BD(TQ)[25] having comparable computational cost ($n_{\text{iter}}N^6+N^8$). Good MVTD energies and bond distances usually have associated good ω_e values.

IV. BOND STRETCHING CALCULATIONS

The stretching of one single bond or the simultaneous stretching of two single bonds represent two levels of difficulty for the single-reference (i.e., essentially dynamic-correlation oriented) methods that we are considering in this work. The performance of MVTD against CC methods has been tested here for BH, HF, and H_2O in the same conditions that were used for testing a great variety of CC (with T) calculations by Cioslowski and Watts.[54] The simultaneous two bond stretching in SiH_2 ($^1A_1$) has also been included since it contains a third period atom and FCI reference calculations by Bauschlicher and Taylor[55] are available.

The equilibrium geometries used in the calculations for these molecules are summarized in Table VIII. The DZP (six d functions) basis sets for BH, HF, and H_2O have been taken from Table 1 of Ref. 54. For the SiH_2 molecule the basis set for H was the scaled $(4s)/(2s)$ basis given by Dunning[47,48] with one set of p polarization functions.[55] For Si, the $(12s8p/5s3p)$ contraction given by McLean and Chandler[56]

TABLE VIII. Molecular geometries used in calculations (atomic units).

	r_e	$1.5*r_e$	$2.0*r_e$
BH	(0, 0, 2.330 03)	(0, 0, 3.495 04)	(0, 0, 4.660 06)
HF	(0, 0, 1.732 88)	(0, 0, 2.599 32)	(0, 0, 3.465 76)
H_2O	(±1.494 19, 0, 1.156 92)	(±2.241 28, 0, 1.735 39)	(±2.988 37, 0, 2.313 85)
SiH_2	(±2.093 87, 0, 1.91868)	(±3.140 82, 0, 2.87 801)	(±4.187 74, 0, 3.837 35)

was used, with five *d* polarization functions.[55] One MO was frozen at the correlation steps for BH, HF, and H_2O and 5 MOs for SiH_2. The number of correlated electrons was 4, 8, 8, and 6, respectively.

The results are included in Tables IX to XII. In the case of single bond breaking (BH and HF) the MVTD energies are closer to CCSDT than CCSDT-1b or CCSD(T) at all distances. The simultaneous breaking of two equivalent single bonds is a much more difficult problem because of the weight of a quadruple excitation, i.e., a determinant of the external space, becomes very important in the wave function. In this cases (H_2O and SiH_2) the effect of the implicit consideration of linked quadruples effects on the coefficients of doubles which is present in CCSD and iterative-triples CC methods favours more accurate results at $2.0r_e$ geometries.

Additional tests for the good results at long distances for single-bond breaking can be obtained from the dissociation potential curves in the next section.

Overall, the high quality of the MVTD results that was observed in the previous section is confirmed for the equilibrium geometries and for single bond stretching geometries. However, significant deviations amounting to a few mhartree from the CCSDT[54] or FCI[55] energies can occur at long distances in simultaneous stretching of two single bonds as in H_2O or SiH_2 molecules, because the SDCI model space for the $(SC)^2CI$ procedure becomes less realistic.

V. ENERGY CURVES AND SPECTROSCOPIC PROPERTIES

Four molecules that represent different chemical situations have been studied along their potential curves and with large basis sets. Li_2 and LiNa are two examples of homolytic bond breaking with significantly different number of electrons, while the differences in electronegativity between the atoms are null or very close to zero. NeH^+ and $LiBe^+$ are different examples of heterolytic bond breaking. The first one is a strong bond while the second is a weak van der Waals interaction. The last two molecules dissociate to closed shell systems and calculations with the Boys' and Bernardi's[57] counterpoise correction to the basis set superposition error (BSSE) have been included. In all cases some spectroscopic properties have been calculated that can be used as additional tests for the MVTD method.

The basis sets are ANOs from Widmark *et al.* $[14s9p4d3f]/(6s5p3d2f)$ for Li and Be,[58] and $[17s12p5d4f]/(7s6p4d3f)$ for Na.[59] The basis set for NeH^+ was the Dunning's aug-cc-pVTZ[60,61] that uses $[11s6p3d2f]/(5s4p3d2f)$ and $[6s3p2d]/(4s3p2d)$ contractions for Ne and H, respectively. The $1s$ core MO was excluded from the correlation calculations in LiNa and NeH^+ as well as the highest virtual MOs in LiNa. The CC calculations in this section were performed with the methods described in Refs. 62 and 28.

The potential energy curves have been calculated at SCF, SDCI, $(SC)^2$SDCI, $(SC)^2$(T), MVTD, CCSD(T), and CCSDT-1b levels of the theory. In Figs. 1 to 3 are shown the results with the four latest methods for the Li containing molecules Li_2, LiNa, and $LiBe^+$.

The correlation problem in Li_2 is basically a two electron problem because the four core electrons lie very deep in energy and configure a hardly polarizable charge cloud. In fact, the correlation energy for the six electron system is estimated about -0.08 a.u. in the present calculations, i.e., about two times the exact correlation energy in H_2 (-0.0409 hartree).[63] Hence, the correlation effects due to triples and quadruples are not expected to be large in this

TABLE IX. Summary of total energies for BH molecule.

	E (hartree)		
	r_e	$1.5*r_e$	$2.0*r_e$
SCF	−25.125 225	−25.062 371	−24.988 191
SDCI	−25.209 764	−25.156 781	−25.101 623
$(SC)^2$SDCI	−25.211 333	−25.159 184	−25.109 067
$(SC)^2$(T)	−25.212 983	−25.161 596	−25.113 559
MVTD	−25.213 907	−25.162 934	−25.114 092
CCSD[a]	−25.212 265	−25.160 381	−25.108 682
CCSDT-1b	−25.213 505	−25.162 291	−25.112 601
CCSD(T)[a]	−25.213 555	−25.162 361	−25.113 131
CCSDT[a]	−25.213 885	−25.162 881	−25.113 651

[a]Reference 54.

TABLE X. Summary of total energies for HF molecule.

	E (hartree)		
	r_e	$1.5*r_e$	$2.0*r_e$
SCF	−100.047 688	−99.933 664	−99.818 140
SDCI	−100.242 072	−100.147 604	−100.055 605
$(SC)^2$SDCI	−100.248 125	−100.154 530	−100.070 789
$(SC)^2$(T)	−100.250 901	−100.158 733	−100.078 815
MVTD	−100.253 479	−100.162 118	−100.082 100
CCSD[a]	−100.250 498	−100.157 464	−100.073 160
CCSDT-1b	−100.253 408	−100.162 144	−100.082 890
CCSD(T)[a]	−100.253 178	−100.161 764	−100.083 240
CCSDT[a]	−100.253 308	−100.161 994	−100.082 310

[a]Reference 54.

TABLE XI. Summary of total energies for H_2O molecule.

	E (hartree)		
	r_e	$1.5*r_e$	$2.0*r_e$
SCF	−76.040 749	−75.800 736	−75.582 632
SDCI	−76.245 423	−76.042 423	−75.877 903
$(SC)^2$SDCI	−76.251 127	−76.055 260	−75.912 085
$(SC)^2$(T)	−76.254 956	−76.063 451	−75.931 876
MVTD	−76.258 001	−76.069 709	−75.949 492
CCSD[a]	−76.254 259	−76.062 836	−75.932 322
CCSDT-1b	−76.257 939	−76.071 236	−75.956 842
CCSD(T)[a]	−76.257 819	−76.071 196	−75.958 612
CCSDT[a]	−76.257 999	−76.071 386	−75.956 352

[a]Reference 54.

system, even at very long bond distances. In fact, the triples contributions range between −0.5 to −2.0 mhartree along the dissociation curve. Of course, the dominant triples effects are the linked ones as expected. It can be seen from Fig. 1 that both $(SC)^2$(T) and MVTD curves are very coincident, even at long bond distances. This clearly indicates the little contribution of linked quadruples all along the curve (cf. Sec. VII). Besides this, the MVTD curve follows very closely the CCSDT-1b one, in coincidence with the accurate behavior of MVTD shown in the previous sections for single bonds.

In Table XIII we have summarized some spectroscopic properties calculated from the potential energies. It is to be noted that CCSD(T), which deviates from the *a priori* more accurate CCSDT-1b curve at long distances, apparently converges to a better estimate of D_e. However, the CCSDT-1b and MVTD energies calculated at $r=100$ Å are −14.9124 hartree which gives an energy for each Li atom of −7.4562 hartree, a value that compares well to the CCSDT (i.e., FCI) result for Li atom (−7.4564 hartree).[64] On the other hand, CCSD(T) at $r=100$ Å gives −14.9144 hartree, so predicting −7.4572 hartree for the Li atom. Of course, a better value of the energy of Li can be obtained at the CCSD(T) level from an open shell calculation[64] which gives the accurate value of −7.4564 a.u. Consequently, the apparent better CCSD(T) estimation of the D_e value from $E(r_{\text{large}})-E(r_e)$ would come from an underestimation of E at large values of r.

TABLE XII. Summary of total energies for SiH_2 molecule.

	E (hartree)		
	r_e	$1.5*r_e$	$2.0*r_e$
SCF	−289.994 434	−289.851 193	−289.683 400
SDCI	−290.102 754	−289.977 487	−289.858 453
$(SC)^2$SDCI	−290.106 255	−289.984 418	−289.878 207
$(SC)^2$(T)	−290.108 906	−289.990 220	−289.891 337
MVTD	−290.110 094	−289.993 752	−289.904 961
CCSD	−290.107 434	−289.987 789	−289.893 359
CCSDT-1a	−290.109 510	−290.992 786	−289.907 614
FCI[a]	−290.110 207	−289.994 384	−289.908 071

[a]Reference 55.

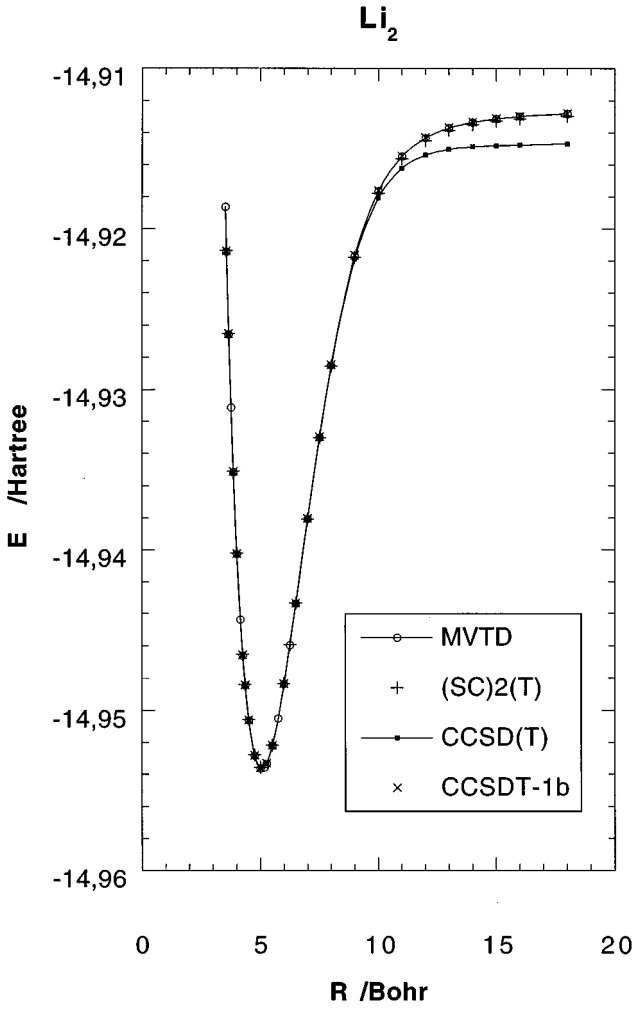

FIG. 1. Potential energy curves for Li_2. The energies and distances are in atomic units. See the text for the meaning of the method labels.

In the MVTD curve of Li_2 the little hump at intermediate distances larger than r_e that had been reported for larger diatomics in previous works[34,36] does not appear. The occurrence of this hump has been related to the perturbative estimate of the coefficients of the triples in the total dressing step. Its absence can be due to the relatively small contribution of triples in Li_2. In any case, and likely due to the overestimated steepness of the potential curve after the equilibrium distance, MVTD tends to slightly overestimate the first anarmonicity constant $\omega_e x_e$. In this calculation, all the spectroscopic properties (apart from D_e discussed above) are reasonably predicted by all the methods with a similar accuracy in good agreement with the detailed experimental data.[65,66] Note again the agreement between the MVTD and CCSDT-1 results.

The dissociation process of the LiNa molecule is similar to that of Li_2. Correlation calculations involve 12 electrons in 114 MOs. Despite the inclusion of eight electrons of the L shell of Na (the K shell was frozen) the correlation energy at equilibrium distances is only about −0.092 hartree. As shown in Fig. 2, the MVTD and CCSDT-1 potential energy curves run very close all along the dissociation process,

TABLE XIII. Comparison of the theoretical spectroscopic constants of Li_2.

	r_e(Å)	D_e(eV)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	$\omega_e y_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})	γ_e(cm^{-1})	δ_e(cm^{-1})	β_e(cm^{-1})
SCF	2.784	2.494	337.60	−1.886	0.0071	0.6200	0.0055	1.8*e*−05	8.4*e*−06	−1.6*e*−08
SDCI	2.681	1.591	354.74	−2.240	0.0002	0.6683	0.0064	−5.1*e*−06	9.5*e*−06	1.4*e*−08
$(SC)^2$SDCI	2.673	1.155	351.99	−2.416	−0.0089	0.6724	0.0067	−3.3*e*−05	9.8*e*−06	4.3*e*−08
SC^2(T)	2.671	1.111	351.50	−2.439	−0.0110	0.6735	0.0068	−3.8*e*−05	9.9*e*−06	4.8*e*−08
MVTD	2.671	1.116	351.87	−2.452	−0.0089	0.6737	0.0068	−3.8*e*−05	9.8*e*−06	4.7*e*−08
CCSD(T)	2.670	1.062	351.80	−2.447	−0.0095	0.6738	0.0068	−3.8*e*−05	9.9*e*−06	4.8*e*−08
CCSDT-1b	2.671	1.116	351.84	−2.440	−0.0094	0.6737	0.0068	−3.7*e*−05	9.8*e*−06	4.7*e*−08
Expt.[a]	2.673	1.059	351.42	−2.583	−0.0064	0.6724	0.0071	−2.7*e*−05	9.7*e*−06	3.1*e*−08
Expt.[b]	2.673	1.056	351.39	−2.578	−0.0065	0.6726	−0.0070	−3.6*e*−05	9.8*e*−06	5.7*e*−08

[a]Reference 65.
[b]Reference 66.

while the CCSD(T) curve separates at long distances. The contribution of linked quadruples effects is very small (less than −0.0002 hartree at very short distances) so that the $(SC)^2$(T) curve which is also shown in Fig. 2 remains always very close to the MVTD and CCSDT-1 curves. In fact, for $r=5.25$ bohr, near the curves minima, the difference between CCSD (−169.385 186) and $(SC)^2$SDCI (−169.385 413) is only 0.000 23 hartree, indicating even a small positive (unstabilizing) effect of linked quadruples. Their contribution is very small anyway.

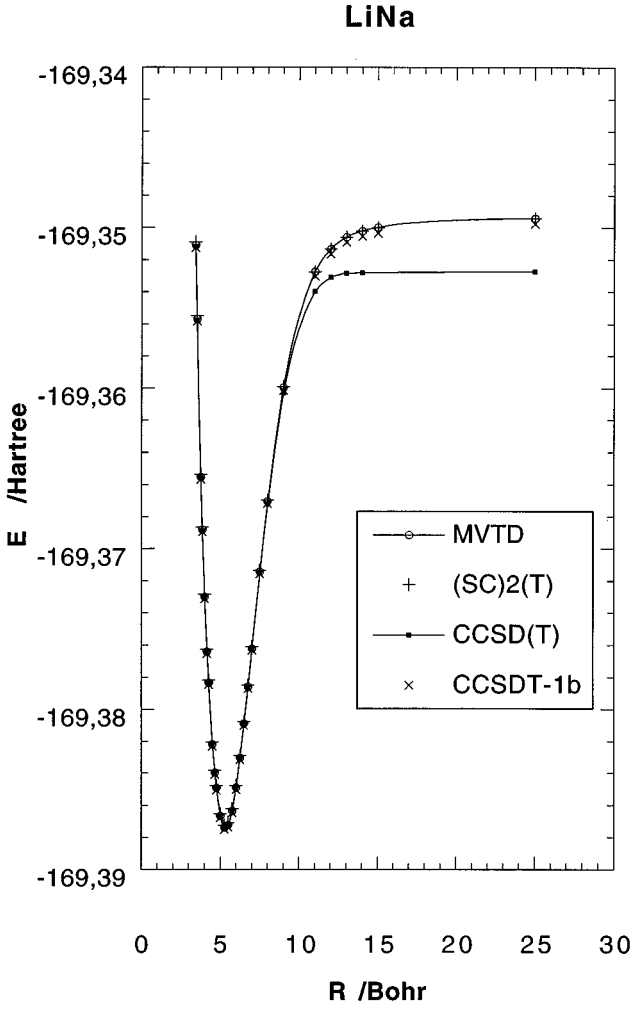

FIG. 2. Potential energy curves for LiNa. The energies and distances are in atomic units. See the text for the meaning of the method labels

The calculated spectroscopic properties are shown in Table XIV as well as some experimental data. As for Li_2, the best estimate of the dissociation energy as a difference $E(r_{\text{large}})-E(r_e)$ is provided by CCSD(T) while CCSDT-1b and MVTD overestimate it by more than 0.1 eV. It is also noticeable that the error in the estimate of the equilibrium distances (and consequently, of the rotational constants) amounts to about 0.07 Å. Less important but also significant is the error in the estimate of vibrational frequency that is 1.1 cm^{-1}. The equilibrium distance is the spectroscopic parameter which is more sensitive to insufficient account of the core–valence correlation in molecules with atoms of the second or higher rows.[59] The large deviation from experimental results in the bond distance can be due to the difficulties of the basis set to properly account for the Na core polarization in the presence of the Li atom, and also, in part, to the exclusion of effects of the frozen 1*s* core electrons. It must be noted, however, that Widmark *et al.*[59] calculated the ANOs basis set for Na from the average density matrix obtained through SDCI calculations of the Na_2 molecule, its positive and negative ions, and the molecule in a homogeneous electric field. Notwithstanding, their best estimate of the polarizability of the Na atom (all electrons considered) was 190.5 a.u. to be compared to the experimental value of 159.2 a.u.[67] In addition, our results are correct for Li_2, discarding spurious effects from Li basis.

$LiBe^+$ is isoelectronic to Li_2 but the dissociation process is different $[LiBe^+(^1S)\rightarrow Be(^1S)+Li^+(^1S)]$. Because the two main bonding electrons do not separate, the nondynamical correlation does not significantly affect the process, and good results can be expected with a single-reference method as MVTD. The interaction is much weaker than in the former cases, and must be treated as a van der Waals interatomic interaction, where the interatomic correlation at long distances is expected to play an important role. For this kind of problem, dynamic correlation oriented methods as (single reference) CC ones and MVTD are methods of choice. The results shown in Fig. 3 do not include the counterpoise correction and show that for this six electrons system, dissoci-

TABLE XIV. Comparison of the theoretical spectroscopic constants of LiNa.

	r_e(Å)	D_e(eV)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	$\omega_e y_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})	γ_e(cm^{-1})	δ_e(cm^{-1})	β_e(cm^{-1})
SCF	3.001	2.386	248.42	−1.096	0.0024	0.3483	0.0023	4.8e−06	2.7e−06	2.6e−09
SDCI	2.833	1.582	261.75	−1.723	0.0127	0.3908	0.0008	−3.6e−05	3.5e−06	1.2e−07
(SC)^{2}SDCI	2.824	1.091	257.27	−1.871	0.0115	0.3930	0.0006	−5.6e−06	3.7e−06	1.5e−07
SC^2(T)	2.821	1.030	255.61	−1.857	0.0091	0.3941	0.0005	−7.6e−05	3.8e−06	1.47e−07
MVTD	2.819	1.034	255.91	−1.921	0.0154	0.3942	0.0006	−6.4e−05	3.8e−06	1.52e−07
CCSD(T)	2.818	0.945	255.67	−1.768	0.0	0.3942	0.0005	−6.7e−05	3.8e−06	1.50e−06
CCSDT-1b	2.818	1.029	255.76	−1.761	0.0	0.3942	0.0005	−6.6e−05	3.8e−06	1.4e−07
Expt.[a]	2.885	0.876	257.00	−1.66		0.3770	0.0038			

[a]Reference 82.

ating to closed shells, the curves of $(SC)^2(T)$, MVTD, CCSD(T), and CCSDT-1b are nearly coincident.

The spectroscopic properties reported in Table XV have been calculated after performing counterpoise corrections to avoid the BSSE. The effects of triples and quadruples affect only the Be atom and the effects of linked quadruples are negligible (never greater than 0.08 mhartree) so that $(SC)^2(T)$ and MVTD results are largely coincident. The calculated dissociation energy is nearly 0.60 eV and similar results are expected for CCSD(T) or CCSDT-1 due to the coincidence of the curves. The results are similar to those of Boldyrev *et al.*[68] who reported 2.629 Å for r_e and 320 cm^{-1} for ω_e from an MP2 calculation using 6-311+G* basis set. The same authors estimate the bonding energy as 0.573 eV with QCISD(T) and the 6-311+G($2df$) basis set.

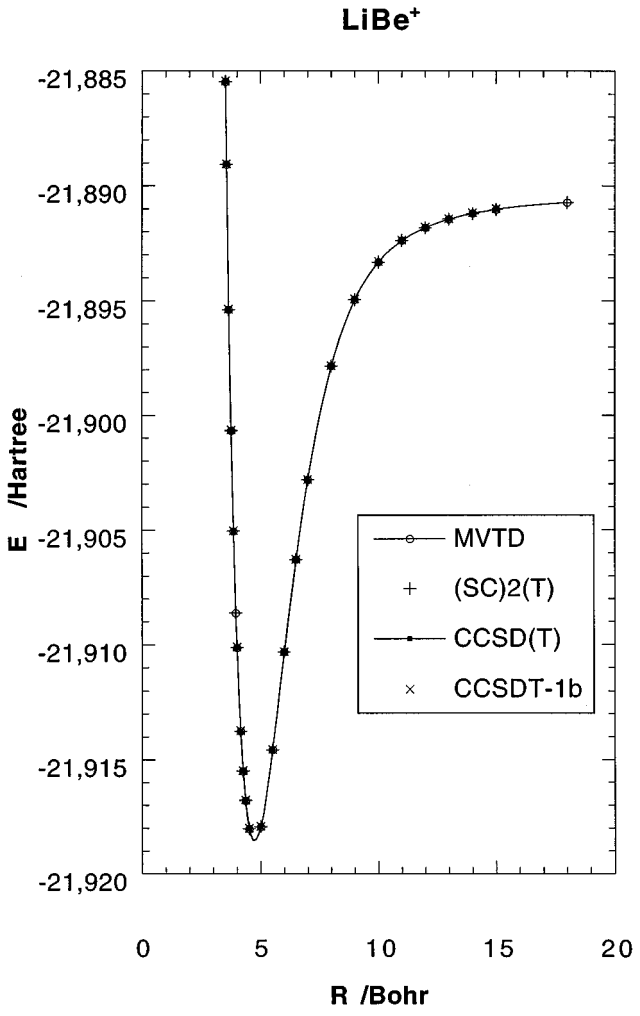

FIG. 3. Potential energy curves for $LiBe^+$. The energies and distances are in atomic units. See the text for the meaning of the method labels.

The interaction in NeH^+ is strong, but the molecule dissociates to a closed shell plus a proton $[NeH^+(^1S) \rightarrow Ne(^1S) + H^+]$. The BSSE effects on the correlation energy can be approximatively calculated and calculations with the counterpoise method have been performed.

The results for the spectroscopic properties are summarized in Table XVI with and without the CP correction. Some experimental data[69–71] and theoretical results from other authors at CCSD and CCSD(T) level[72] are also shown as reference results. The theoretical results in Ref. 72 used in all cases UHF molecular orbitals, while we have used RHF ones. However, no significant differences must be expected in the SCF energies due to the heterolytic nature of the bond cleavage. In spite of this, some differences occur in the SCF spectroscopic constants in relation to the reference values, which can be partly due to the different methods used in the spectroscopic analysis. The Simons–Parr–Finlan method[73] was used in Ref. 72. In the present work we used Hutson's method.[74] Similar results for equilibrium distances are obtained from CCSD and $(SC)^2$SDCI for both CP corrected and uncorrected calculations. The same can be said for CCSD(T) and MVTD. It is to be noted that the less accurate CCSD and $(SC)^2$SDCI methods seem to agree better with the experimental distance obtained from Refs. 69 and 70 (0.991 195 and 0.9913 Å, respectively), while the methods including linked triples slightly overestimate r_e, especially after CP correction. In general the agreement with experiment of the spectroscopic properties calculated with CP corrected MVTD is similar, or even better (see, e.g., ω_e) than the same properties calculated with CCSD(T). In particular, the agreement of the CP-MVTD vibrational results and the experimental data from Fourier transform emission spectroscopy by Ram *et al.*[69] is remarkable. The effect of CP correction is specially noticeable in the case of the calculated D_e which otherwise would be, for CCSD(T) and MVTD, out of the experimental error range determined by Lorentzen *et al.*[71]

TABLE XV. Comparison of the theoretical spectroscopic constants of $LiBe^+$.

	r_e(Å)	D_e(eV)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	$\omega_e y_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})	γ_e(cm^{-1})	δ_e(cm^{-1})	β_e(cm^{-1})
SCF	2.649	0.632	317.52	−4.815	−0.006	0.609	0.013	−0.000 07	8.9e−06	1.1e−07
SDCI	2.610	0.604	321.93	−4.837	−0.019	0.627	0.013	−0.000 10	9.4e−06	1.2e−07
$(SC)^2$SDCI	2.616	0.595	319.15	−4.807	−0.021	0.624	0.013	−0.000 11	9.4e−06	1.4e−07
SC^2(T)	2.615	0.597	319.85	−4.857	−0.017	0.625	0.013	−0.000 12	9.4e−06	1.4e−07
MVTD	2.615	0.597	319.76	−4.856	−0.016	0.625	0.013	−0.000 11	9.4e−06	1.4e−07

VI. A "TOUCH STONE" TEST ON THE POSSIBILITIES AND LIMITATIONS OF THE MVTD METHOD: OZONE

It is well known that the theoretical study of the ozone molecule potential energy surface demands a multireference description, mainly because of the strong mixing of the $^1A_1$ ground state determinant with those obtained by redistributing the electrons in the π system along with large $\sigma-\pi$ repolarization effects that occur even with small geometrical distortion. A particularly important example of such multireference character is the calculation of the harmonic frequencies, which constitutes a challenge to theoretical chemistry methods due to the largely nondynamical nature of the correlation problem.[75,76] The multireference character becomes specially challenging in the C_s distortions that determine the asymmetrical stretching mode ω_3.[75] The balanced treatment of correlation in both the C_{2v} and C_s subspaces, whose multireference character is very different, is then required for a proper account of ω_3. However, only the moderately multireference C_{2v} subspace must be treated properly to obtain the symmetric modes (ω_1 stretching and ω_2 bending) as well as the C_{2v} equilibrium geometry.

Calculations were done using the same DZP basis set used in previous works.[75,76] Optimization was carried out until the gradient was less than 10^{-4} a.u. using internal coordinates, which corresponds to error less than 0.0002 Å and 0.03° in bond lengths and angles, respectively. Finally, the harmonic frequencies were calculated using the FG method of Wilson *et al.*,[77] using numerically calculated hessians in terms of the symmetry coordinates recommended by Graybeal.[78] In order to test the precision of the method, the SCF frequencies were calculated giving errors of less than 5 cm^{-1} compared to those reported in Ref. 75.

The results are shown in Table XVII. One immediately sees that MVTD keeps better performances than CCSDT-1a with respect to CCSDT in those properties that depend mainly on the C_{2v} subspace, while the asymmetric ω_3 is clamorously overestimated. This overestimation can be easily traced to the bad treatment of linked triples from the similar result of $(SC)^2$(T). The lack of adaptation of the singles and doubles coefficients to the important contributions of some triple excitations is a serious difficulty in this case. It seems that a steepest rise of T_1 amplitudes occurs when the geometry is distorted, as has been discussed by Stanton *et al.*[75] In spite of this, the accuracy in the equilibrium energy of MVTD is still remarkable. The accuracy of the CCSD(T) approach compared to full CCSDT is striking in this case, a result that can be considered somehow fortuitous, as has been discussed in detail by Watts *et al.*[76]

TABLE XVI. Comparison of the theoretical spectroscopic constants of NeH^+.

	r_e(Å)	D_e(eV)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})	γ_e(cm^{-1})	δ_e(cm^{-1})	β_e(cm^{-1})
SCF	0.977	2.196	3063.8	−133.04	18.550	1.178	−0.0061	0.0027	5.1e−05
SDCI	0.987	2.308	2994.7	−120.41	18.029	1.087	−0.0031	0.0026	2.0e−05
$(SC)^2$SDCI	0.989	2.319	2978.4	−119.28	17.957	1.081	−0.0028	0.0026	1.7e−05
$(SC)^2$(T)	0.991	2.315	2954.3	−116.56	17.882	1.085	0.0013	0.0026	9.1e−06
MVTD	0.993	2.311	2944.8	−115.83	17.843	1.079	0.0008	0.0026	8.1e−06
SCF+CP	0.977	2.186	3060.9	−133.22	18.532	1.171	−0.0083	0.0027	5.3e−05
SDCI+CP	0.991	2.257	2955.2	−118.69	17.903	1.082	−0.0038	0.0026	1.9e−05
$(SC)^2$SDCI+CP	0.992	2.264	2935.5	−117.06	17.830	1.079	−0.0027	0.0026	1.4e−05
$(SC)^2$(T)+CP	0.995	2.267	2913.2	−114.57	17.749	1.079	0.0005	0.0026	5.3e−06
MVTD+CP	0.996	2.266	2904.1	−113.82	17.712	1.076	0.0008	0.0026	4.1e−06
SCF[a]	0.973	2.194	3053.0	−135.60	18.420	1.180			
CCSD[a]	0.989	2.312	2964.0	−120.10	17.820	1.082			
CCSD(T)[a]	0.992	2.318	2936.0	−118.90	17.720	1.079			
SCF+CP[a]	0.973	2.183	3050.0	−134.20	18.410	1.173			
CCSD+CP[a]	0.992	2.261	2924.0	−118.30	17.700	1.085			
CCSD(T)+CP[a]	0.996	2.265	2894.0	−116.90	17.590	1.082			
Expt.[b]	0.991		2903.8	−113.36	17.880	1.097			
Expt.[c]	0.991		2900.0	−111.00	17.880	1.080			
Expt.[d]		2.276±0.032							

[a]Reference 72.
[b]Reference 69.
[c]Reference 70.
[d]Reference 71.

TABLE XVII. Equilibrium geometrical parameters, harmonic frequencies and energies for O_3.

	r(Å)	θ(deg)	ω_1(cm^{-1})	ω_2(cm^{-1})	ω_3(cm^{-1})	E(hartree)
$(SC)^2$SDCI	1.260	117.5	1262	750	781	−224.897 580
$(SC)^2$(T)	1.276	116.7	1201	732	1851	−224.927 791
MVTD	1.283	116.8	1173	718	1834	−224.940 527
CCSD[c]	1.263	116.5	1256	748	1240	−244.906 346
CCSD+T(CCSD)[c]	1.293	117.0	1097	685	128*i*	−224.944 831
CCSD(T)[d]	1.287	116.8	1129	703	976	−224.941 382
CCSDT-1a[c]	1.295	116.6	1076	674	680	−224.945 859
CCSDT[d]	1.286	116.7	1141	705	1077	−224.941 197
Exp	1.272[a]	116.8[a]	1135[b]	716[b]	1089[b]	

[a]Reference 83.
[b]Reference 84.
[c]Reference 75.
[d]Reference 76.

VII. LINKED AND NONLINKED CONTRIBUTIONS ALONG THE DISSOCIATION CURVES

As was indicated in Eq. (8), the MVTD calculations provide a detailed analysis of the contributions to the correlation energy which are related to the MBPT diagrams passing through triples and quadruples.

The contributions of linked and unlinked triples (ΔE_L^T, ΔE_{NL}^T) and linked and unlinked quadruples (ΔE_L^Q, ΔE_{NL}^Q) for Li_2, LiNa, $LiBe^+$, and NeH^+ are shown in Figs. 4 to 7. A similar plot is shown in Fig. 8 for Be_2 coming from a 4 electron calculation with a $3s2p1d$ basis set. This plot is included as an additional reference for a dissociation to closed shell fragments. The CP corrected plots for $LiBe^+$ and NeH^+ are shown in Figs. 9 and 10.

All these curves illustrate the little quantitative contribution of linked quadruple diagrams. In spite of this, their importance for an accurate calculation of bond distances and spectroscopic properties has been shown above in Sec. III on the basis of the different results of CCSD vs $(SC)^2$SDCI and MVTD vs $(SC)^2$(T).

Li_2 and LiNa show contribution profiles that correspond to a typical homolytic cleavage of single bonds. Similar behavior had been found for linked triples and unlinked quadruples for F_2 and HF.[36] The behavior of the unlinked triples contribution is similar in Li_2 and LiNa, and similar to that found previously for HF. This would indicate the relative importance of the coefficients of the singles in these systems. The contrary is found sometimes, e.g., ΔE_{NL}^T was found to be very small in F_2, indicating that the coefficients of singles are relatively small in this system.

The curves of $LiBe^+$ are shown in Fig. 6. They can be compared to those of Be_2 shown in Fig. 8. A few different features can be remarked. Both ΔE_{NL}^Q and ΔE_L^T show a behavior that can be considered typical of a dissociation towards two closed shell fragments. They show more important contributions at short bond distances than in the dissociation limit. It is important to note that this behavior persists in ΔE_L^T after the CP correction, i.e., after the removal (along with the extended basis effects) of the local effects in the fragments. Instead, the profile of the ΔE_{NL}^Q contribution changes remarkably (see Fig. 9). Also noticeable is the important contribution of linked quadruples in Be_2, while in $LiBe^+$ their contribution is negligible. Remember, however, that Be_2 is a very special case where important degeneracies are expected in the bond region and nondynamical correlation is more important than in $LiBe^+$.

The profiles of the linked and unlinked contributions in the NeH^+ molecule are shown, before and after CP correction, in Figs. 7 and 10, respectively. The shape of these profiles is very singular, remembering those of typical potential energy curves. This shape corresponds to the formation of a strong bond at short distances while, in the limit of dissociation, the system accommodates to a closed shell fragments

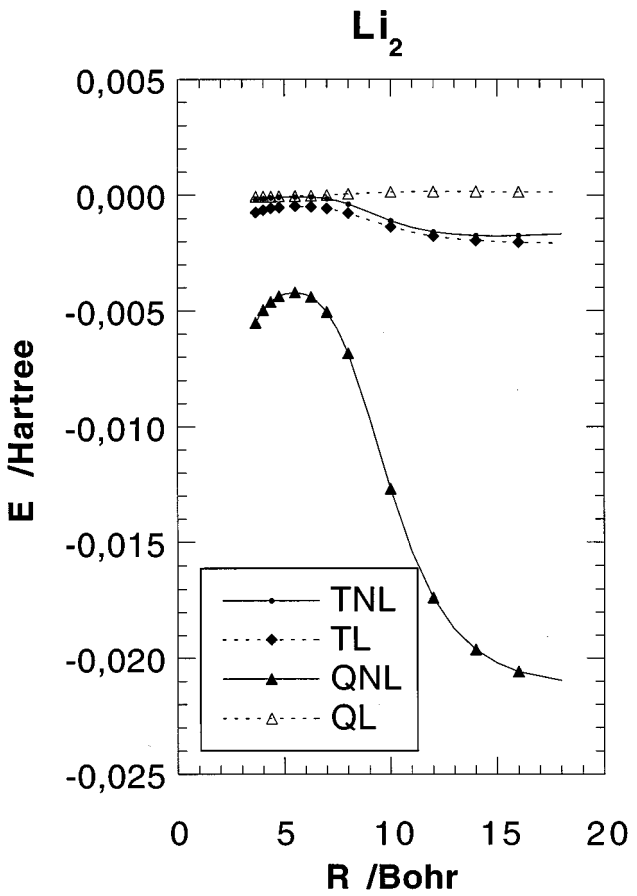

FIG. 4. Linked and unlinked contributions from triples (TL and TNL, respectively) and quadruples (QL and QNL) to the MVTD correlation energy along the dissociation curve for Li_2. See the text for details.

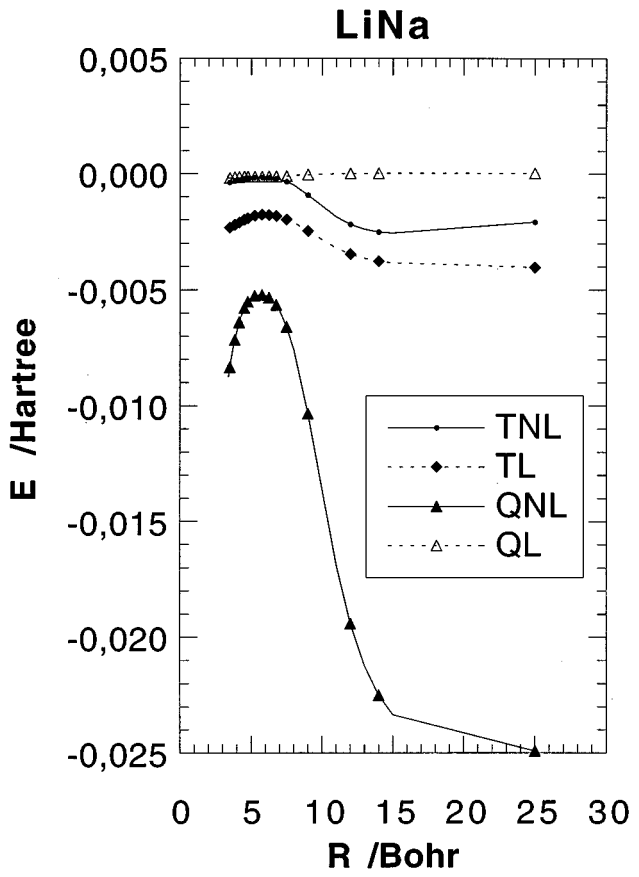

FIG. 5. Linked and unlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for LiNa. See caption of Fig. 4 for details.

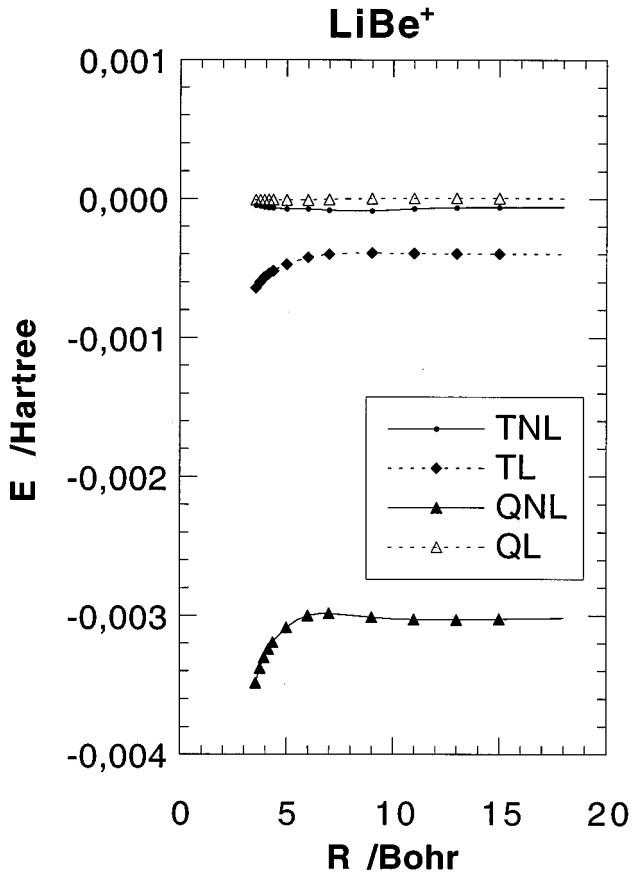

FIG. 6. Linked and unlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for $LiBe^+$. See caption of Fig. 4 for details.

dissociation. Consider, e.g., the curve corresponding to ΔE_L^T, which in the dissociation limit corresponds, essentially, to the linked triples contribution of the Ne atom. At distances shorter than 5 bohr, a true bond begins to form and at distances shorter than ≈ 2.5 bohr, the curve has the same shape that was found in typical single bonds (Li_2, LiNa, F_2, or HF).

Also noticeable is the fact that the CP correction reduces in 1 order of magnitude the linked and unlinked contributions to the bond, as well as the fact that at short distances, the CP corrected contributions are positive, indicating that they are more negative in the Ne atom with its basis set enlarged with the functions of the H than in the NeH^+ molecule.

VIII. GENERAL DISCUSSION

In the present work we have considerably enlarged the number of test calculations performed with MVTD and its simpler approach $(SC)^2(T)$. The average is clearly good, with MVTD results in the equilibrium region lying closer to the CCSDT than other less complete CC(with T) approaches. The spectroscopic properties discussed in Sec. V show a remarkable accuracy unless for LiNa where CC methods face similar difficulties, a fact that could be attributed to limitations in the ANOs basis set. Instead, the results on Li_2 with the ANOs basis set of Widmark *et al.*[58] are good when compared to experiment.

Some inaccuracies must however be pointed out. (1) Single bond dissociation curves, even though not showing a hump at intermediate distances for the systems here considered, tends to overestimate D_e energies giving results similar to CCSDT-1. (2) Situations where quadriexcitations become degenerate with ϕ_0 such as the simultaneous breaking of two equivalent single bonds show deviations in the MVTD energies in relation with full CCSDT or FCI greater than CCSD(T) or CCSDT-1a. (3) Overestimation in the bond length as compared to CCSDT occurs in the triple bond system CN^+. A small deviation of the average accuracy in the MVTD bond lengths is found in the BeO system. (4) MVTD does not manages properly the largely multireference problem of the asymmetrical stretching of ozone, where some $\pi-\pi^*$ and $\sigma-\sigma^*$ single excitations acquire large weight under very small geometrical distortion.

There are some reasons to believe that these problems come mainly from the perturbational-like estimation of the coefficients of the triples provided by Eq. (4). (1) In a previous work it was shown that the linked triples term is responsible of the occurrence of the little hump at intermediate distances in the dissociation energy curves of F_2 and HF.[36]

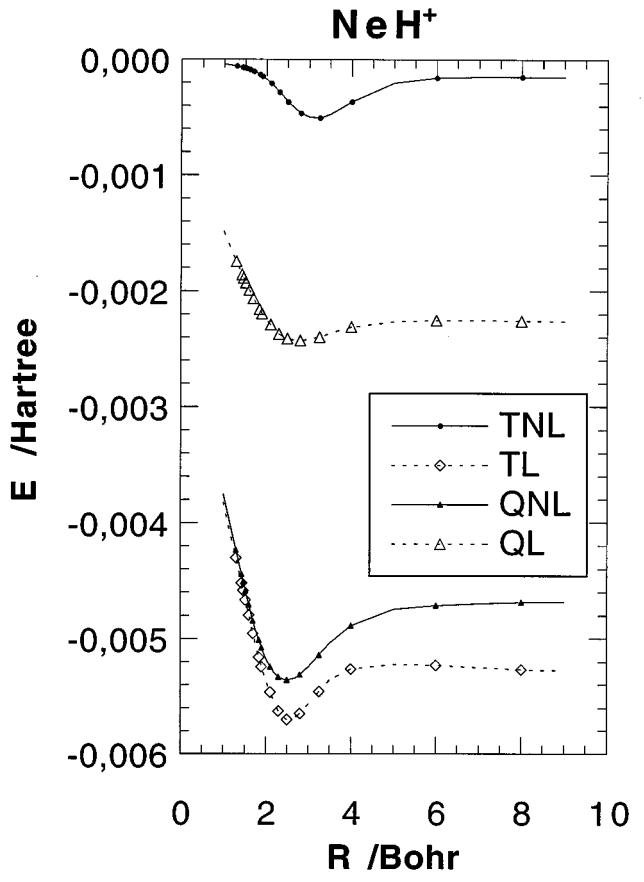

FIG. 7. Linked and unlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for NeH^+. See caption of Fig. 4 for details.

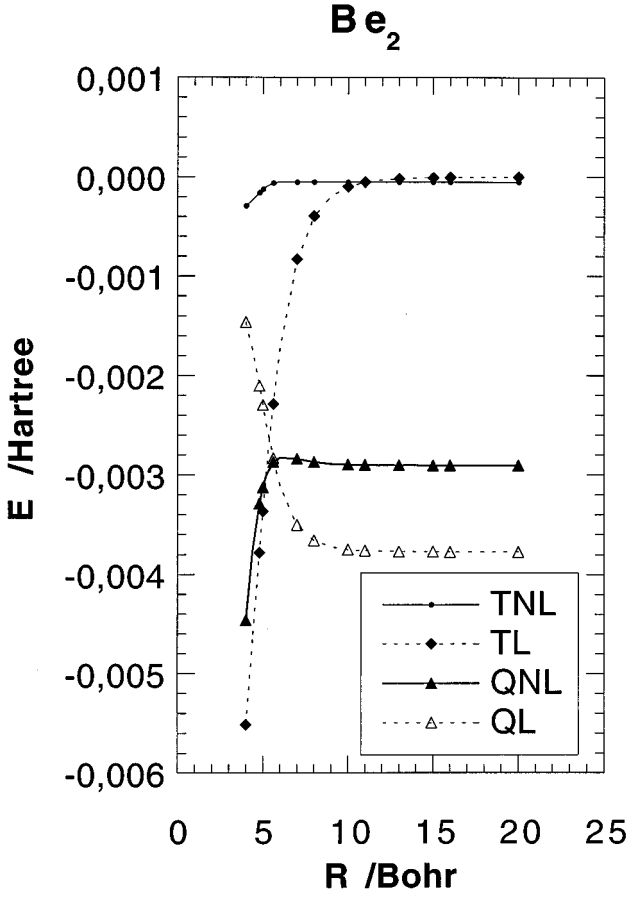

FIG. 8. Linked and unlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for Be_2. See caption of Fig. 4 for details.

(2) Both in SiH_2 and H_2O the differences in the energy with CCSDT and FCI at $2*r_e$ are by far larger in $(SC)^2(T)$ than in MVTD (cf. Tables XI and XII). (3) The deviation of the r_e predicted by $(SC)^2(T)$ for CN^+ (1.220 Å) in relation to those of $(SC)^2SDCI$ ($r_e = 1.172$ Å) and CCSD ($r_e = 1.198$ Å) clearly points toward a bad behavior of the linked triples contribution. (3) The overestimation of ω_3 in ozone is clearly related to the $(SC)^2(T)$ contribution.

So, we can conclude that further work could be done in the calculation of linked triples to improve the yet remarkable accuracy of the MVTD method. First of all, the calculation of the c_α coefficients of triples might be improved calculating them as two separate contributions. One of them would correspond to the disconnected diagrams and can be calculated from products of singles and doubles coefficients in a way similar to that used for quadruples coefficients in Eq. (5). The second contribution would correspond to the connected diagrams and can be calculated perturbatively.

The use of the Epstein–Nesbet denominators in the perturbative-like estimation of the coefficients of triples might be also reconsidered. In general, the MP Hamiltonian partition gives better convergence behavior of perturbative series than the EN one due to the larger values of the MP denominators.[79] However, single reference fourth order EN provides lower energies[79,42] than MP4. The actual role that the EN shifting plays in our model leads to lower final energies and, consequently, closer in general to CCSDT or FCI ones. It is true that sometimes this results in total energies under the FCI limit, but the excessive shifting in the denominators could be additionally corrected including EPV contributions as it has been done in fully iterative matrix dressing methods elsewhere.[80] It can be argued also, concerning the use of the EN denominators in Eq. (4), that they introduce a lack of invariance under an arbitrary rotation of degenerate orbitals.[81] However, in the MVTD model such a lack of invariance comes mainly from the CEPA character of the $(SC)^2SDCI$ step and would not be corrected by the use of MP denominators. Whether the same quality of results can be obtained using the MP partition and this could help to improve the results in the difficult cases, is the subject of work in progress.

As pointed out in the introduction, MVTD or $(SC)^2(T)$ offer the possibility in most cases of improving, in one noniterative step, the $(SC)^2SDCI$ results that are close to CCSD ones to a quality close to that of CCSDT. One advantage of performing this improvement in a noniterative step, that has been few exploited in other methods that include noniterative steps, as, e.g., CCSD(T), is the additional flexibility that they incorporate. One could take, e.g., a reduced space of natural

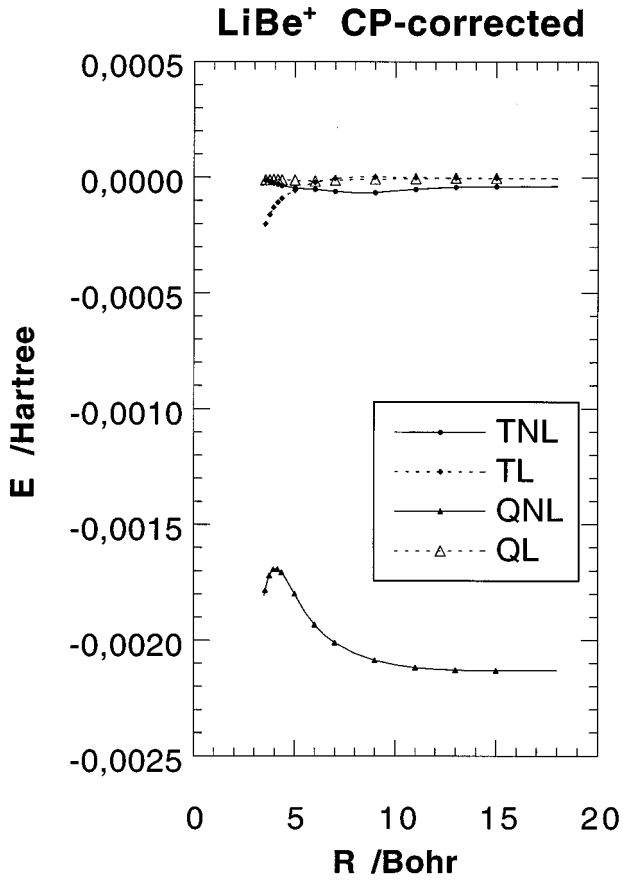

FIG. 9. Linked and unlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for $LiBe^+$ after CP correction. See caption of Fig. 4 for details.

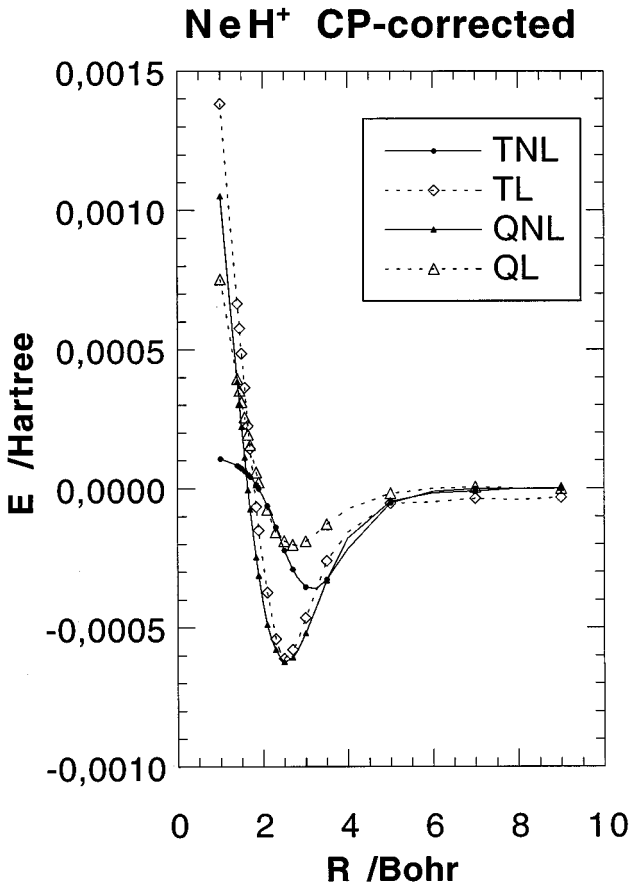

FIG. 10. Linked and nonlinked contributions from triples and quadruples to the MVTD correlation energy along the dissociation curve for NeH^+ after CP correction. See caption of Fig. 4 for details.

MO to calculate the last costly loop, and this would reduce significantly the calculation time without an important loss in the energy improvement.

IX. CONCLUSIONS

The test calculations reported in the present work show that, except for a few cases discussed above, the results provided by the MVTD concerning energy, bond distances and spectroscopic properties are very good, lying close to CCSDT or CCSDT-1. The exceptions are the most difficult cases where simultaneous dissociation of two equivalent single bonds are concerned or the multireference character of the problem concerns two or more single excitation, so that the weight of some triple or quadruple excitations in the wave function become very important. Of course, CC methods are expected to show more flexibility to deal with these situations, mainly the approaches that include iteratively (more or less approximately) the interactions between triples amplitudes and singles and doubles ones, and consequently with quadruples amplitudes through T_2T_2 and with triples amplitudes through T_1T_2 operators.

The analysis of the $(SC)^2(T)$ results suggests that the estimation of the coefficients of triples in the dressing operator needs to be revisited to improve the results in the most difficult cases discussed in Sec. VII. Nevertheless, in most cases where the contribution of linked quadruples is small, the $(SC)^2(T)$ provides good energies and spectroscopic properties at a moderate cost. The relative importance of quadruples can be ascertained from differences in the CCSD and $(SC)^2SDCI$ curves near the well bottom.

The potential energy curves calculated with MVTD follow very closely the CCSDT-1b curves, even at the dissociation limit. Significant deviations from the experimental values of bond length found for LiNa was unexpected and could be related to the limited ability of the ANOs basis set to reproduce the polarizability of atomic Na.

The analysis of contributions of linked and unlinked diagrams by means of the partition of the MVTD energy provided by the implementation of the method can be used to characterize the nature of the bond and to better understand its formation as exemplified in the case of the bond in the NeH^+ molecule. This could represent an interesting bond analysis tool for chemists.

The authors consider that the overall results are very encouraging and contribute to assess future and more involved calculations with MVTD as well as they show clearly the points that would help to improve the method.

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