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On the difference between the transition properties calculated with linear response- and equation of motion-CCSD approaches

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In this work, we quantitatively investigate the difference between the linear response (LR) and the equation of motion (EOM) coupled cluster (CC) approaches in the calculation of transition properties, namely, dipole and oscillator strengths, for the most widely used truncated CC wave function, which includes single and double excitation operators. We compare systems of increasing size, where the size-extensivity may be important. Our results suggest that, for small molecules, the difference is small even with large basis sets. The difference increases with the size of the system, but it is numerically small until hundreds of electron pairs are correlated. Although these calculations may be possible in a few years, at present the EOM approach is more advantageous, albeit more approximate, because it is computationally less demanding. © 2009 American Institute of Physics. [doi:10.1063/1.3255990]

I. INTRODUCTION

Two approaches were developed to calculate transition properties within the single reference coupled cluster (CC) theory,¹ namely, the linear response (LR)^{2,3} and the equation of motion (EOM).⁴⁻⁶ These two formulations are equivalent for the exact wave function, which consider all the possible excitation clusters, both for excitation energies and transition properties. This is not the case when the wave operator is truncated at a certain order, as happens in production calculations. The two formalisms are still equivalent for the definition of the transition energies, but they differ for the transition properties (for instance oscillator and rotational strength).⁷

The difference is that the LR approach rigorously considers the relaxation contribution of the ground state cluster amplitudes induced by the perturbation that produces the electronic excitation.^{2,7} On the other hand, the EOM approach considers “frozen” ground state amplitudes and includes the contribution of the reference determinant to the transition properties.⁴ As a result, the former formalism provides size-intensive transition properties, whereas the latter does not. The counterbalance is the larger computational cost of the LR approach compared to the EOM one, as the ground state relaxation must be calculated for each excitation. Quoting Bartlett: “It is a failing of standard CC theory that there are two ways to define second- and higher-order properties that are equivalent in the limit.”¹

The purpose of this work is to quantitatively investigate such difference for the most used truncated CC wave function, which includes single and double excitation operators: CCSD. We compare dipole and oscillator strengths calculated at EOM-CCSD and LR-CCSD level for systems of increasing size, where the size extensivity may be important. The goal is to determine whether the LR approach is worth

the extra computational effort, or whether the cheaper EOM approach provides numerically acceptable results.

This work is organized as follows. Section II reports calculations on a series of noninteracting LiH molecules. Section III reports calculations on a series of all-trans linear polyenes of increasing size. Section IV reports calculations on a series of linear polyenes with a donor and an acceptor groups connected at each end of the chain. Section V contains some concluding remarks. All the calculations are performed with a development version of the Gaussian suite of programs,⁸ in which the EOM-CCSD and LR-CCSD methods have been recently implemented.

II. NONINTERACTING LIH MOLECULES

This model system was studied in a paper by Koch *et al.*,⁷ which first pointed out the failure of the EOM approach to provide size-intensive transition properties. We revisit the same system in order to get more information. It consists of a series of noninteracting LiH molecules. In the original paper, the Li–H internuclear distance is 4 a.u., and we retain it. The molecules are aligned along the *Y* axis (also the molecular bond lies on the same axis) at an intermolecular distance of 5000 a.u. In the original paper a Dunning’s double zeta basis set is used,⁹ which includes *s* type functions only, reported in Table I.

We did not manage to reproduce the self-consistent field (SCF) energy from Ref. 7, probably because of a difference in the basis set actually used in the paper. We converge to a different (lower) SCF energy than in Ref. 7: our SCF energy is $-7.956\ 759\ 012\ 65$ a.u., whereas in Ref. 7 it is $-7.945\ 08$ a.u. Since the SCF is different, the post-SCF results are also different, but this is not a serious concern because it is the qualitative behavior which is of interest here. We also note that, at this bond length, the Hartree-Fock (HF) wave function has a singlet-triplet instability. We repeat the calculations on the same system with many other basis sets,

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TABLE I. Dunning basis set used in the LiH calculation (s functions) (Ref. 9).

Li		H	
s exponents	Coefficients	s exponents	Coefficients
1783.0	0.000 824	33.640	0.025 374
267.1	0.006 403	5.058	0.189 684
60.07	0.033 239	1.147	0.852 933
16.78	0.126 621
5.403	0.337 749	0.3211	1.0
1.906	0.575 669
0.2634	0.062 311	0.1013	1.0
...	...		
0.7179	1.0		
...	...		
0.077 16	1.0		
...	...		
0.028 54	1.0		

namely, STO-3G, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z. The first one is a minimum basis set, but it is larger than that in Table I. The second one is often considered a good choice for production calculations at CC level. The others are included to study basis set convergence. The lowest A_g transition is considered (one excited state per molecule).

The results for the dipole strength, as a function of the number of LiH molecules, are reported in Fig. 1. The evident flaw of the EOM approach is that, with a sufficient number of LiH molecules, the dipole strength eventually becomes negative, which is unphysical. However, this breakdown occurs differently for the various basis sets. For the Dunning basis set this will occur at the 28th molecule (at the 19th in Ref. 7). With the STO-3G basis, the dipole strength will become negative at the 45th molecule (note that the starting point is very different between the two basis sets), whereas with the aug-cc-pVDZ this will occur at the 184th molecule. With larger basis sets, the crossing occurs with more than 200 molecules. Note that we explicitly include up to 22 molecules with the smallest basis set, 18 with STO-3G, 9 with

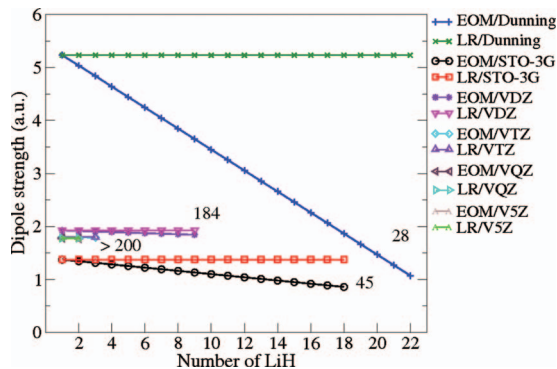


FIG. 1. Dipole strength (a.u.) as a function of the number of noninteracting LiH molecules, calculated with EOM-CCSD and LR-CCSD with various basis sets. The Li–H distance is 4.0 a.u. as in Ref. 7. At this distance the HF wave function has a singlet-triplet instability. The label Dunning refers to the Dunning's basis set reported in Table I. The numbers inside the plot indicate the number of LiH when the EOM dipole strength becomes negative.

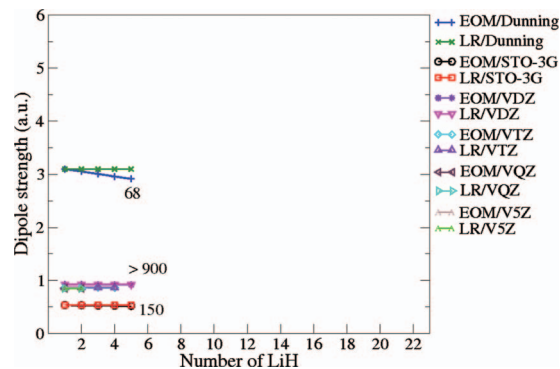


FIG. 2. Dipole strength (a.u.) as a function of the number of noninteracting LiH molecules, calculated with EOM-CCSD and LR-CCSD with various basis sets. The Li–H distance is 3.004 465 89 a.u., optimized at B3LYP/aug-cc-pVTZ level. At this distance the HF wave function is stable. The label Dunning refers to the Dunning's basis set reported in Table I. The numbers inside the plot indicate the number of LiH when the EOM dipole strength becomes negative.

aug-cc-pVDZ, 3 with aug-cc-pVTZ, 2 with aug-cc-pVQZ and aug-cc-pV5Z, and then extrapolate the value of the property, considering the fact that it changes linearly with the number of molecules.

Although the EOM approach will eventually yield a negative dipole strength even with an infinite basis set, Fig. 1 shows how the difference between the two approaches is smaller with larger basis sets. This figure shows that at present, the limit of the size of the system that can be treated with a reasonably large basis set at an acceptable computational time is reached long before the numerical difference between the two approaches is appreciable. Even if one can afford to calculate 28 molecules with the aug-cc-pVDZ basis set, which is the crossover point for the smallest basis set, the difference in the dipole strength between EOM and LR would be 0.2857 a.u. (the LR value is 1.9267 a.u.), but the cost of the latter calculation would roughly be 1.5 times larger than the former. Also, for the small basis sets (Dunning and STO-3G), the absolute value of the oscillator strength is far from the basis set limit, and the difference between EOM and LR is of no practical significance. Additionally, the single reference CCSD wave function may not be able to properly describe even the ground state of a system with stretched bonds.

We repeated the calculation of this transition property with the same basis sets at the equilibrium geometry of a single LiH molecule (3.004 465 89 a.u.). The optimization was carried out at B3LYP/aug-cc-pVTZ level. The results are reported in Fig. 2. The first important consideration is that the HF wave function is stable at this bond distance and this represents a far more common situation in production calculations. Figures 1 and 2 are scaled the same to facilitate the comparison. The absolute value of the dipole strength becomes smaller with all the basis sets. Nevertheless, the number of LiH molecules necessary to obtain an unphysical negative dipole strength with EOM increases considerably with all the basis sets. With the correlation consistent basis sets the crossover point is located at more than 900 LiH molecules. This means that the difference between the two approaches is negligible in the range of molecules that can

TABLE II. Dipole strengths for the noninteracting LiH molecules. Li–H internuclear distance is 4.0 a.u.

Number of LiH molecules	<i>s functions</i>		STO-3G		aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pV5Z	
	EOM	LR	EOM	LR	EOM	LR	EOM	LR	EOM	LR	EOM	LR
1	5.2343	5.2308	1.3751	1.3746	1.9272	1.9267	1.8061	1.8043	1.7817	1.7794	1.7816	1.7789
2	5.0362	5.2308	1.3448	1.3746	1.9166	1.9267	1.7973	1.8043	1.7729	1.7794	1.7728	1.7790
3	4.8380	5.2308	1.3143	1.3746	1.9060	1.9267	1.7886	1.8043				
4	4.6399	5.2308	1.2840	1.3746	1.8954	1.9266						
5	4.4417	5.2308	1.2536	1.3746	1.8849	1.9266						
6	4.2435	5.2308	1.2232	1.3746	1.8743	1.9266						
7	4.0454	5.2308	1.1928	1.3746	1.8637	1.9267						
8	3.8472	5.2308	1.1624	1.3746	1.8532	1.9267						
9	3.6491	5.2308	1.1320	1.3746	1.8426	1.9267						
10	3.4509	5.2308	1.1016	1.3746								
11	3.2527	5.2308	1.0712	1.3746								
12	3.0546	5.2308	1.0408	1.3746								
13	2.8564	5.2308	1.0104	1.3746								
14	2.6583	5.2308	0.9800	1.3746								
15	2.4601	5.2308	0.9496	1.3746								
16	2.2619	5.2308	0.9192	1.3746								
17	2.0638	5.2308	0.8888	1.3746								
18	1.8656	5.2308	0.8585	1.3746								
19	1.6675	5.2308										
20	1.4693	5.2308										
21	1.2711	5.2308										
22	1.0730	5.2308										

be realistically considered nowadays. Moreover, also at this geometry the effect of the basis set (Dunning and STO-3G with respect to the correlation consistent ones) is larger than the difference between EOM and LR.

However, it is fair to note that the value of the EOM dipole strength degrades long before it reaches a negative value. If we consider a 30% difference with respect to the proper LR value, the EOM approach provides poor results when about 60 and 300 electron pairs are considered for the stretched and the equilibrium geometry, respectively, and the large basis sets. Although these numbers are beyond the present capabilities, they may become routine in a few years.

The numerical values of dipole strength plotted in Figs. 1 and 2 are reported in Tables II and III, since they are difficult to access in the figures.

III. POLYENES

This section collects the results for a series of all-trans linear polyenes of increasing size, starting from two up to seven conjugated double bonds. Two basis sets are considered for the different molecules, 6-31+G* and aug-cc-pVDZ.

The former is smaller but has a set of diffuse functions on the carbons, which are important to properly describe an electronic transition. The latter is larger and, as pointed out in the previous section, more suitable for production of EOM-CCSD calculations. For the smallest system, butadiene, we also include the results with larger basis sets, namely, aug-cc-pVTZ, aug-cc-pVDZ with a double set of diffuse functions (denoted aug-cc-pVDZ+), and aug-cc-pVTZ with a double set of diffuse functions (denoted aug-cc-pVTZ+). With the larger basis sets (the triple ζ and the double diffuse) the core orbitals are frozen. The geometries were optimized at B3LYP/6-31G* level and can be found in the supporting information.¹⁰

We focus mainly on the lowest transition of B_u symmetry because it has the largest oscillator strength. For the first four systems (up to five double bonds), the experimental transition energies in gas phase are known.^{11–19} Table IV reports the experimental as well as the calculated vertical transition energies. Figure 3 shows the shift in the transition energies with respect to butadiene. EOM and LR formalisms provide the same transition energies, as discussed in Sec. I.

TABLE III. Dipole strengths for the noninteracting LiH molecules. Li–H internuclear distance is 3.004 465 89 a.u. (optimized geometry).

Number of LiH molecules	<i>s functions</i>		STO-3G		aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pV5Z	
	EOM	LR	EOM	LR	EOM	LR	EOM	LR	EOM	LR	EOM	LR
1	3.0977	3.0962	0.5340	0.5339	0.9238	0.9235	0.8666	0.8659	0.8503	0.8494	0.8499	0.8489
2	3.0510	3.0962	0.5304	0.5339	0.9228	0.9236	0.8657	0.8659	0.8494	0.8494	0.8489	0.8489
3	3.0043	3.0962	0.5267	0.5339	0.9218	0.9235	0.8647	0.8659				
4	2.9577	3.0962	0.5231	0.5339	0.9208	0.9235	0.8638	0.8659				
5	2.9110	3.0962	0.5195	0.5339	0.9198	0.9235						

TABLE IV. Transition energies (eV) for the polyenes from 2 to 5 conjugated double bonds. The experimental data are from Refs. 11–19.

Number of double bonds	Expt.	EOM	
		6-31+G*	aug-cc-pVDZ
2	5.91	6.55	6.37
3	4.95	5.67	5.48
4	4.41	5.04	4.87
5	4.02	4.59	4.43

Table IV shows that the larger basis set yields results closer to experiment, but Fig. 3 shows a very good agreement with experiment as far as the trend is concerned. This indicates that both basis sets give a correct qualitative description of this transition for all the systems.

Figures 4 and 5 show the change of the oscillator strength as a function of the transition energy and number of double bonds, respectively, calculated with the two approaches and the two basis sets. With the larger basis set, we calculate up to five double bonds before the computational cost becomes too demanding. We note that these calculations are among the largest on these systems, very close to the limit of what it can be afforded on common machines. Both figures show that the oscillator strength increases with the size of the molecule and that the EOM and LR results start to diverge. Figure 5 shows a quite linear increase in oscillator strength with the number of double bonds, and that the difference between the basis sets is small for this property. The difference between EOM and LR is small compared to the absolute value of the property, even for the largest molecule.

Another way to increase the size of the system is to keep the same molecular structure and increase the basis set. This is an important issue for CC theory, since it shows considerable sensitivity to the choice of the basis set. For butadiene we examined in detail the effect of the basis set on a larger part of the spectrum, considering five states per symmetry, since the experimental UV spectrum in gas phase is available.¹¹ Only states of symmetry A_u and B_u are active in the UV. The simulated spectrum is obtained by the oscillator strengths adding Gaussian functions through the Harada–Nakanishi equation:

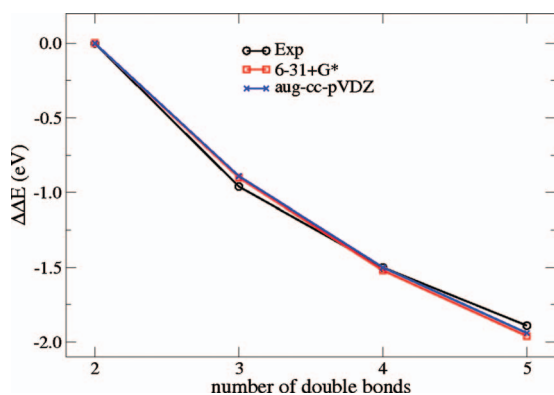


FIG. 3. Experimental and calculated (at EOM-CCSD level with two basis sets) transition energies (eV) relative to butadiene.

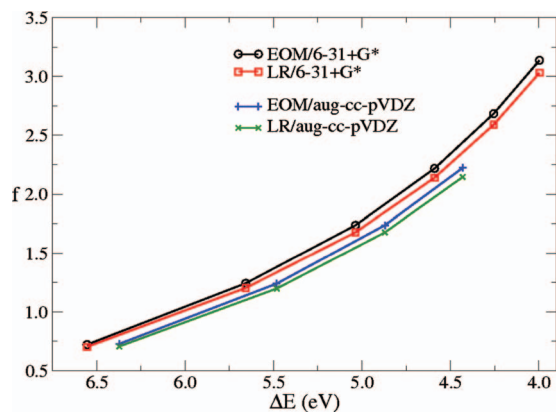


FIG. 4. Oscillator strength as a function of the transition energy for the linear polyenes of increasing size. EOM and LR approaches with two basis sets are used in the calculation.

$$\varepsilon(\nu) = \frac{f_i}{\text{const} \sqrt{\pi} \sigma} e^{-\left(\frac{\nu - \nu_i}{\sigma}\right)^2}. \quad (1)$$

The spectrum, reported in Fig. 6, qualitatively reproduces the experimental one¹¹ with all the basis sets, although it is shifted toward higher energies. The Pople basis set, the smallest one, has the largest shift. The other basis sets agree on the first transition but show different features on higher states. From our comparison, the important fact is that there is not a large difference between the EOM and the LR spectra for all the basis sets. The largest difference is found for the first transition (B_u), which is also the one with the largest value of oscillator strength.

Figure 7 shows the change with the basis set of the oscillator strength for this transition. This figure shows that the difference between EOM and LR is quite small and similar between the various basis sets. Even when there is a large change due to the extra diffuse functions, the two formalisms are still close to each other.

IV. DONOR-ACCEPTOR POLYENES (DA-POLYENES)

This final set of molecules consists of all-trans planar polyenes with a carbonyl group attached at one end and an amino group at the other, in order to create a polarization of

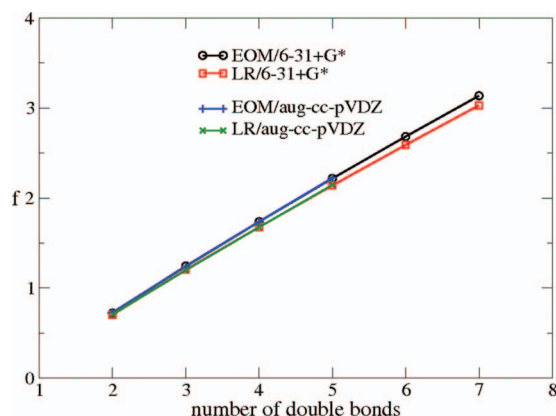


FIG. 5. Oscillator strength as a function of the number of conjugated double bonds for the linear polyenes of increasing size. EOM and LR approaches with two basis sets are used in the calculation.

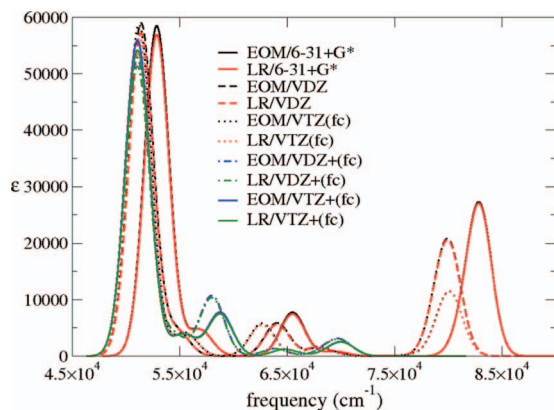


FIG. 6. UV spectrum for butadiene obtained with different basis sets and the EOM and LR oscillator strengths. The experimental spectrum is in Ref. 11.

the π electronic cloud. In this case, we consider one to four double bonds (excluding the carbonyl), with the same basis sets used in Sec. III. We consider the first transition of A' symmetry, which is the one with the largest oscillator strength. The geometries were optimized at B3LYP/6-31G* level and can be found in the supporting information.¹⁰

Figures 8 and 9 report the oscillator strength as a function of the transition energy and of the number of C=C bonds for the 6-31+G* and the aug-cc-pVDZ basis sets. As in Sec. III, this set of molecules shows very close results between the two formalisms, although the difference increases with the size of the molecule. The basis sets, even with different absolute values, show a very similar trend.

The effect of the basis set is explicitly addressed for the smallest of the molecules, and it is reported in Fig. 10. It is shown that, although the basis set has an observable effect on the absolute value of the oscillator strength, with a maximum $\Delta f=0.05$, the difference between EOM and LR remains rather constant.

V. CONCLUSIONS

The examples considered in this work show that EOM and LR-CCSD provide nonequivalent oscillator strengths and that the difference increases with the size of the molecule, as it is expected.⁷ However, the size of the system when this difference becomes numerically relevant is very large and far from the present computational possibilities.

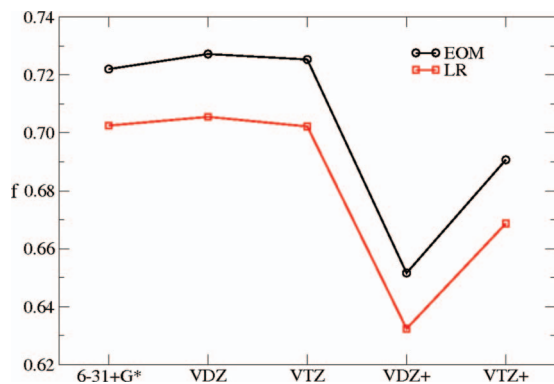


FIG. 7. Oscillator strength as a function of the basis set for the first B_u transition of butadiene.

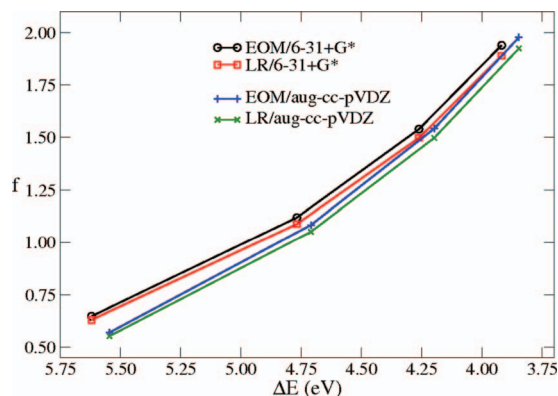


FIG. 8. Oscillator strength as a function of the transition energy for the DA-polyenes of increasing size. EOM and LR approaches with two basis sets are used in the calculation.

Even for the noninteracting LiH molecules, when a production level basis set is used, the difference of the two formalisms is small in the range of size that can be explicitly calculated at present. This does not cover the fact that eventually EOM yields an unphysical result when the proper number of molecules is considered. In fact, the EOM dipole strength becomes 70% of the LR value around 300 molecules with large basis sets, and thus it becomes negative for more than 900 molecules.

When the molecule is small (one LiH, butadiene, or the smallest DA-polyene) the difference is negligible. Increasing the size of the basis set seems not to influence significantly the difference between the two formalisms.

Since a larger computational effort is required for the size-intensive formalism, the question is how much larger this effort is. In order to calculate the relaxation of the ground state amplitudes (Z_{LR}), a system of equations very similar to the ground state Z vector (Z_{GS})^{20,21} must be solved (apart from an expensive constant term in the LR system that is calculated only once before the first step of the iterative cycle) for each excited state. The quantities necessary to obtain transition energies and properties are the ground state T amplitudes, the Z_{GS} amplitudes, the left (L) and right (R) eigenvectors, and the Z_{LR} amplitudes.^{2,4} If we assume that

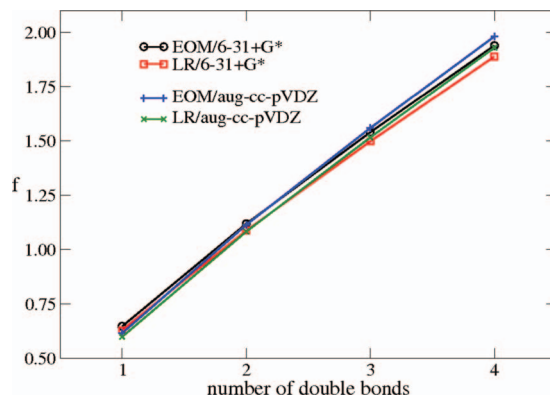


FIG. 9. Oscillator strength as a function of the number of conjugated CC double bonds for the DA-polyenes of increasing size. EOM and LR approaches with two basis sets are used in the calculation.

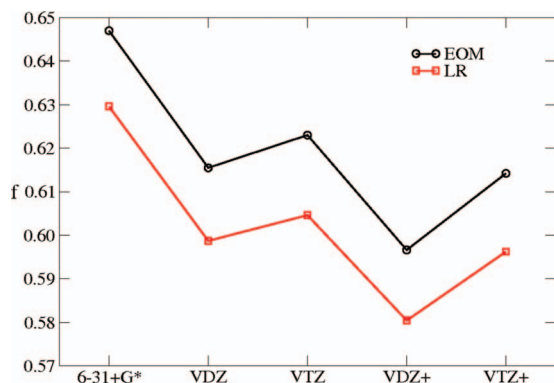


FIG. 10. Oscillator strength as a function of the basis set for the first A' transition of the smallest DA-polyene.

the cost to compute these quantities for one state is roughly the same, then the computational cost can be approximated as

$$T + Z_{GS} + nL + nR + n'Z_{LR}, \quad (2)$$

where n is the number of excited states and n' is the number of states for which we compute the size-intensive properties ($n \geq n'$). Thus, if $n=1$, LR is 25% more expensive than EOM. If $n \gg 1$ and $n=n'$, LR is 50% more expensive than EOM. However, if $n \gg 1$ and $n'=1$, for instance if one is only interested in the oscillator strength of the fifth state, the added cost of the LR calculation is small.

We have seen in this paper that for a small molecule the two approaches are numerically very close, thus even when the extra effort for each state is relatively small, the final result is not going to change considerably. If the number of states is large, then the extra effort becomes roughly equivalent to half the effort to compute the excited state eigenvectors. When a large basis set is used, even for a small molecule and one state, the extra computational time can be significant, whereas the change in the property small. The effect can be large on a relatively small system (like the stretched LiH molecules) only when an extremely small basis set is used, but in this case the results are poor independently on the chosen approach.

In the conclusions in Ref. 7 it is stated: “We found that for 19 or more noninteracting LiH systems the transition

strength becomes negative. This is, of course, an absurd result that makes it questionable to use the EOMCC approach for larger systems, in spite of the fact that the test calculations on single smaller molecules (LiH, CH^+ , and C_4) have all given close agreement between CCLR and EOMCC dipole transition strengths.” However, the results we report suggest that, despite the more rigorous formulation of the transition properties in the LR approach than in the EOM, we are still far from the possibility to study molecular systems that are large enough to show a significant numerical gap. Therefore, for practical purposes, at the present time the EOM approach is more advantageous. However, when the computational power will allow the treatment of several hundreds of electron pairs at this level of theory, the EOM transition properties will not be accurate enough, and a LR approach will become necessary.

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