*Regular article*

# Static electric properties of LiH: explicitly correlated coupled cluster calculations*

**Daniel Tunega, Jozef Noga**

Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84236 Bratislava, Slovakia

**Abstract.** Explicitly correlated MBPT-R12 and coupled cluster [up to CCSD(T)-R12] methods have been used in calculations of various (vibrationless) electrical properties for the LiH molecule, including the dipole and quadrupole moments, dipole and quadrupole polarizability tensors, dipole hyperpolarizability tensors, and the second dipole hyperpolarizability tensors. Generally, with extension of the basis set the R12 method did not lead to faster convergence for the calculated properties towards the basis limit. Nevertheless, R12 calculations serve as useful indicators to judge the reliability of the results, and substantially help in determining the accuracy. Results obtained with the $11s8p6d5f/9s8p6d5f$ basis and CCSD(T)-R12 calculated within this work should be close to the basis set limit.

**Key words:** Coupled-cluster theory – Explicitly correlated – Electric properties – Hyperpolarizability – Basis set limit

## 1 Introduction

Reliable knowledge of higher-order electric properties is of great importance for the design and development of novel nonlinear optical materials. Though conceptually an easy task, an accurate and reliable prediction of second- and higher-order polarizabilities of molecules remains a great challenge to theoretical chemists. On one hand, problems arise owing to the necessity of using extremely accurate correlated methods with rather extensive basis sets; on the other hand, the calculation is complicated owing to the lack of higher-order analytical derivative methods for highly correlated approaches. Developments in the analytical response

methods concerning the hyperpolarizability calculations have been recently reviewed by Luo et al. [1].

Using simple well-established finite difference techniques (see e.g. [2]) instead of the analytical derivatives again amplifies the computational demands by a necessity to achieve much higher numerical stability than is usually required, for example in the study of chemical reactivity or even weak intermolecular interactions.

Experience with calculations of higher-order electrical properties reveals that the prerequisite of reliable results is the use of flexible enough basis sets which include functions with higher angular momentum quantum numbers needed to properly describe the deformation in the charge distribution under the influence of the electric field (field gradient).

Of course, this aspect has to be separated from the generally slow convergence of the conventional configuration interaction (CI) expansion when the basis set is increased toward the completeness and which is caused by the inability of the CI wave functions to describe the correlation cusp [2] correctly. It was clear a long time ago [4, 5] that as soon as the inter-electronic coordinate $r_{12}$ is explicitly introduced into the wave function, the convergence toward the limit value is speeded up dramatically. Nevertheless, owing to the occurrence of many-electron integrals or other conceptual or computational problems, methods which treat this problem are not widely used. An excellent review concerning this topic has been recently written by Klopper [6]. To such methods also belongs the family of explicitly correlated, so called R12, methods whose origin goes back to the work of Kutzelnigg [7]. These basically start from the usual conventional one-electron basis sets and the many-electron integrals are essentially eliminated – though not "free of charge" (vide infra). Recently, we have implemented this idea within the coupled cluster (CC) theory [8, 9]. Using such an approach for a four-electron system like LiH, it was possible to achieve accuracy of the calculated energy within about 50 μE$_h$ from the estimated limit value [10]. In the latter case we used CCSDT1-R12 (the R12 analog of CCSDT-1[11]) with the $11s8p6d5f/9s8p6d5f$ GTO basis set. With the same

basis set the conventional CC result has been off by about 1 mE$_h$. When $f$ functions on both atoms were disregarded, the CCSDT1-R12 error in the energy remained within 0.15 mE$_h$, whereas the conventional energy was off by more than 2 mE$_h$.

Encouraged by the above-mentioned results, in this study our aim was to obtain predictions of static electrical properties for the LiH molecule which approach what can be assigned to the basis set limit value. This motivation has been strongly enhanced by the dissipation of values currently available from the literature. The long list of results was summarized some time ago by Karlström et al. [12] and very recently by Papadopoulos et al. [13]. The majority of the papers deal with the dipole moment and the dipole polarizability; less is available for the dipole hyperpolarizability [13–19], and very scarce are the predictions for the second dipole hyperpolarizability [13, 17, 20]. In the present study we have extended the number of investigated properties to quadrupole moments and quadrupole polarizability tensors which were earlier calculated using the point charge method and multi-configuration self-consistent field [16].

For higher-order electrical properties one could hardly expect the same convergence behavior with extension of the basis by higher angular momenta as for the absolute energy. Nevertheless, in this line, our recent results for the polarizability of Be [21] have shown a substantial improvement in favor of the R12 method. Hence, such an investigation of the convergence pattern with a systematic extension of the basis is also included in this study, together with the convergence pattern in the hierarchy of many-body perturbation theory (MBPT) methods.

## 2 Method and computational details

In the present calculations we have used both conventional CC and explicitly correlated coupled cluster theory (CC-R12) currently implemented in the direct integral driven code DIRCCR12-95 [22] which uses the R12 adopted [23] modified version of the HERMIT program [24–26] to provide the necessary integrals. A comprehensive summary of the conventional CC approach has been recently given [27]. CC-R12 theory in full detail can be found elsewhere [9, 28].

A common feature of single-reference CC theories is that the wave operator $\Omega$ which transforms the independent particle model wave function $\Phi$, describing the non-degenerate ground state of some many-electron system, into the exact wave function $\Psi$ can be expressed as an exponential of the so-called cluster operator ($S$), i.e.

$$\Psi = \Omega\Phi = e^S\Phi \tag{1}$$

In a *conventional* ansatz [29], $S \equiv T$ is the usual global cluster excitation operator

$$T = T_1 + T_2 + T_3 + \cdots \tag{2}$$

$$T_1 = \sum_{i,a} t_a^i a_i^a; \quad T_2 = \frac{1}{4}\sum_{\substack{i,j \\ a,b}} t_{ab}^{ij} a_{ij}^{ab}; \quad T_3 = \frac{1}{36}\sum_{\substack{i,j,k \\ a,b,c}} t_{abc}^{ijk} a_{ijk}^{abc} \tag{3}$$

With $\Phi$ being a Slater determinant, $i$, $j$, …, and $a$, $b$, … denote the occupied and virtual molecular spin-orbitals, respectively. $a_{ij\ldots}^{ab\ldots}$ are particular excitation (replacement) operators which create the usual excited determinants in the conventional configuration space.

In the explicitly correlated CC-R12, the inter-electronic distance operator is essentially introduced into the wave operator via putting

$$S = T + \mathscr{R} \tag{4}$$

$$\mathscr{R} = \frac{1}{8}\sum_{\substack{i,j \\ k,l}} c_{\mathbf{kl}}^{ij}\left(\sum_{\alpha,\beta} \bar{r}_{\alpha\beta}^{kl}\tilde{a}_{ij}^{\alpha\beta} - \sum_{a,b} \bar{r}_{ab}^{kl}\tilde{a}_{ij}^{\alpha\beta}\right) \tag{5}$$

$$\bar{r}_{rs}^{pq} = \langle pq|r_{12}|rs\rangle - \langle pq|r_{12}|sr\rangle \tag{6}$$

where $\alpha$, $\beta$ refer to virtual spin orbitals in a *complete* basis, while $p$, $q$, $r$, $s$ refer to arbitrary spin orbitals. Obviously $\mathscr{R}$ represents a basis set incompleteness correction. This operator basically creates *unconventionally* substituted determinants in which a pair of occupied spin orbitals $ij$ is replaced by another pair of occupied spin orbitals $kl$ multiplied by the inter-electronic distance operator, and from the resulting function only the orthogonal complement to the *conventional* excitation space is preserved. The weight of such a substituted determinant in the final wave function expansion is related to the amplitude $c_{\mathbf{kl}}^{ij}$.

We will not go further into detail here. Let us just mention that in the working equations the summations over the complete basis can be treated by a systematic introduction of completeness insertions known as the standard approximation [30]. Then the difficult many-electron integrals can be eliminated from the calculation, provided that the basis set is (quasi) saturated for the lower angular momenta. This is the price to pay mentioned in the introduction. For details the reader is referred elsewhere [9, 28, 30]. We note that the validity of the standard approximation has been shown for externally unperturbed systems (i.e. the standard Fock matrix). Nevertheless, one can find [30] that the parts of the Fock operator which commute with $r_{12}$ do not influence the final forms, which holds for the dipole and quadrupole operators introduced in our calculations (vide infra).

From the beginning we have used the finite field technique [2] to calculate all the properties, i.e. the dipole ($\mu$) and quadrupole ($\Theta$) moments, dipole polarizability ($\alpha$), dipole hyperpolarizability ($\beta$), second dipole hyperpolarizability ($\gamma$), and the quadrupole polarizability ($C$). As external perturbations we have used homogeneous electric fields of strengths from $\pm0.00005$ to $\pm0.005$ au and field gradients of strengths from $\pm0.0001$ to $\pm0.005$ au. Values for the calculated properties were obtained from polynomial fits from the energy expansion with respect to the applied electric field (field gradient) strength [31]:

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta - \cdots$$
$$\quad - \frac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} - \frac{1}{6}C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} - \cdots$$
$$\vdots \tag{7}$$

Cartesian coordinates are denoted as $\alpha, \beta$, and $\gamma$ suffixes and sums over all possible components are implicitly understood. $F_\alpha$ and $F_{\alpha\beta}$ are the electric field and the electric field gradient, respectively. We took a polynomial by one order higher than the highest investigated property in the series, i.e. of fifth order for the expansion with respect to the electric field, and third order with respect to the field gradient. The number of points in the fit was at least twice the number of fitted parameters.

All calculations have been performed for the equilibrium internuclear separation of 3.015 au, which is both an experimental and optimal value with our best method and basis set. Naturally, we have used here the same GTO basis sets which led to the very accurate energies [10] mentioned in the introduction, namely $14s8p6d5f/11s8p6d5f$ for the lithium and $12s8p6d5f/9s8p6d5f$ for the hydrogen atom.

Besides the absolute energy, also the spectroscopic constants and the binding energy for the LiH molecule were extremely accurate [10]. We believe that those basis sets are flexible enough for the pertinent calculations of the polarizabilities. Though it is clear that an $sp$ set can hardly provide accurate polarizabilities even with the R12 method, we were curious if there is at all any improvement using the latter. Therefore, we have also performed calculations

with the *sp* and *spd* subsets of the initial basis for both atoms. We have not discriminated between Li and H, because essentially the LiH molecule tends to be an ion pair $Li^{\delta+}H^{\delta-}$ where both atoms resemble two-electron systems. Unlike previously [10], spherical harmonics have now been used since in the meantime we have adopted our program in this way. Despite the energy differences being very small (at the level of about 10 $\mu E_h$), the recalculated energies are collected in Table 1, for completeness.

As can be seen, the highest level correlated method which we use in this study is CCSD(T) [32] or alternatively CCSD(T)-R12. Our previous results on the energy clearly proved that it was ineffective to go further in the hierarchy of CC methods. With iterative treatment of triple excitations within CCSDT-1 the energy differs by only 2 $\mu E_h$. To be certain, we have calculated the dipole moment and the $\alpha_{zz}$ polarizability using CCSDT-1, but within the figures given below there was no difference. To show the convergence pattern in the hierarchy of correlated methods we have included the MBPT results up to fourth order, and the CCSD[T] = CCSD + T(CCSD) [33].

All calculations had an adjusted integral threshold of $10^{-14}$, and all the CC results were converged to $10^{-10}$ for the amplitudes, what means at least $10^{-11}$ $E_h$ for the energy.

## 3 Results and discussion

Prior to discussing the results we have to note that they are not vibrationally averaged. As one can see from the recent work by Papadopoulos et al. [13], vibrational contributions are rather large even for the vibrational ground-state. For hyperpolarizabilitties the vibrational corrections are of the order of the magnitude of the pure electronic contributions. On the other hand, correlation effects were only accounted for via MBPT(4) [13], which is clearly not enough, as follows from the results below. Hence our study can serve as a complementary useful information to [13].

Calculated dipole moments and related polarizabilities are collected in Tables 2–5. There is a solid point to which one can eventually compare at the SCF level, namely the fully numerical calculation by Laaksonen et al. [34]. Our SCF energy is higher just by 13 $\mu E_h$ and the dipole moment agrees within 0.0002 au. It is clear from Table 2 that including the *d* functions into the basis set is not more important than to fully account for the correlation effects, which is – with the given basis set – accomplished at the CCSD(T) level. Practically negligible differences between the CCSD[T] and CCSD(T) values just confirms the previous statement.

Unlike the energy, for the dipole moments we can hardly say that the R12 method is superior. Neither could we say that the result is converged to the limit when the R12 and conventional values are almost the same. This simply reflects the fact that it is not the improper description of the correlation cusp which plays the crucial role, but instead the lack of higher angular momenta needed in the wave function to be able to describe the charge distribution properly. *f* functions contribute very little to the dipole moment, as expected.

There is, however, an indicator to estimate how the basis set for the given property is saturated, namely the difference between the MBPT(2)-R12 results obtained with the more slowly converging *standard approximation* "A" and faster convergent *standard approximation* "B" [9, 28, 30]. The latter is a default for higher-level calculations; therefore we have only denoted "A" in the table. The closeness of the results from both methods is a good indication for the convergence. With the largest basis set this difference is about 0.001 au for the dipole moment, while using the *sp* basis set the deviation is 0.015 au. In view of the convergence pattern both for the conventional and R12 results, the limiting value at the CCSD(T) level will fall slightly below 2.2935 au, in ex-

**Table 1.** Total energies for the LiH molecule (in $E_h$)

| Basis | *sp* | | *spd* | | *spdf* | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| SCF | −7.98710265 | | −7.98733093 | | −7.98733914 | |
| MBPT(2) | −8.04931568 | −8.05849971 | −8.05655489 | −8.05999941 | −8.05830397 | −8.06015346 |
| MBPT(3) | −8.05969693 | −8.06693477 | −8.06555451 | −8.06732371 | −8.06655497 | −8.06734074 |
| MBPT(4) | −8.06212690 | −8.06889569 | −8.06767119 | −8.06953799 | −8.06867105 | −8.06963001 |
| CCSD | −8.06288727 | −8.06959983 | −8.06834248 | −8.07024640 | −8.06935229 | −8.07031265 |
| CCSD[T] | −8.06299463 | −8.06970187 | −8.06849781 | −8.07039927 | −8.06951849 | −8.07047764 |
| CCSD(T) | −8.06299329 | −8.06970040 | −8.06849588 | −8.07039732 | −8.06951644 | −8.07047563 |

**Table 2.** Dipole moment $\mu$ calculated for LiH using various methods (in au)

| Basis | *sp* | | *spd* | | *spdf* | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| SCF | 2.3615 | | 2.3621 | | 2.3620 | |
| MBPT(2) | 2.3358 | 2.3430 | 2.3274 | 2.3277 | 2.3258 | 2.3262 |
| MBPT(2)/A | – | 2.3279 | – | 2.3261 | – | 2.3252 |
| MBPT(3) | 2.3292 | 2.3238 | 2.3152 | 2.3146 | 2.3138 | 2.3138 |
| MBPT(4) | 2.3223 | 2.3184 | 2.3064 | 2.3067 | 2.3051 | 2.3054 |
| CCSD | 2.3104 | 2.3108 | 2.2967 | 2.2971 | 2.2957 | 2.2960 |
| CCSD[T] | 2.3083 | 2.3088 | 2.2944 | 2.2949 | 2.2934 | 2.2937 |
| CCSD(T) | 2.3084 | 2.3089 | 2.2945 | 2.2951 | 2.2935 | 2.2939 |
| CCSDT-1A | 2.3085 | 2.3089 | 2.2946 | 2.2951 | 2.2936 | 2.2939 |

**Table 3.** Static dipole polarizability ($\alpha$) tensor componets calculated for the LiH molecule using various methods (in au)

| Basis | sp | | spd | | spdf | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| $\alpha_{zz}$ | | | | | | |
| SCF | | 21.89 | | 21.88 | | 21.88 |
| MBPT(2) | 24.07 | 23.62 | 23.57 | 23.35 | 23.49 | 23.42 |
| MBPT(3) | 24.83 | 24.18 | 24.32 | 24.11 | 24.26 | 24.13 |
| MBPT(4) | 25.42 | 24.73 | 24.92 | 24.71 | 24.95 | 24.83 |
| CCSD | 26.68 | 25.71 | 25.87 | 25.61 | 25.78 | 25.69 |
| CCSD[T] | 26.68 | 25.84 | 25.99 | 25.73 | 25.90 | 25.81 |
| CCSD(T) | 26.67 | 25.83 | 25.98 | 25.71 | 25.88 | 25.79 |
| $\alpha_{xx}$ | | | | | | |
| SCF | | 24.50 | | 25.24 | | 25.41 |
| MBPT(2) | 25.68 | 25.32 | 26.94 | 26.41 | 27.07 | 26.92 |
| MBPT(3) | 26.49 | 25.90 | 27.96 | 27.82 | 28.04 | 27.97 |
| MBPT(4) | 26.97 | 26.55 | 28.59 | 28.36 | 28.68 | 28.58 |
| CCSD | 27.71 | 27.42 | 29.51 | 29.34 | 29.60 | 29.53 |
| CCSD[T] | 27.80 | 27.42 | 29.55 | 29.39 | 29.64 | 29.57 |
| CCSD(T) | 27.80 | 27.42 | 29.54 | 29.38 | 29.63 | 29.57 |

**Table 4.** Dipole hyperpolarizability ($\beta$) tensor components calculated for the LiH molecule using various methods (in au)

| Basis | sp | | spd | | spdf | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| $\beta_{zzz}$ | | | | | | |
| SCF | | −328 | | −308 | | −310 |
| MBPT(2) | −506 | −454 | −433 | −408 | −426 | −411 |
| MBPT(3) | −557 | −507 | −477 | −460 | −471 | −458 |
| MBPT(4) | −604 | −548 | −520 | −499 | −514 | −518 |
| CCSD | −604 | −548 | −520 | −499 | −514 | −518 |
| CCSD[T] | −764 | −688 | −646 | −622 | −624 | −633 |
| CCSD(T) | −765 | −685 | −649 | −619 | −639 | −630 |
| $\beta_{xxz}$ | | | | | | |
| SCF | | −137 | | −131 | | −132 |
| MBPT(2) | −174 | −156 | −161 | −152 | −158 | −152 |
| MBPT(3) | −192 | −174 | −177 | −171 | −175 | −170 |
| MBPT(4) | −208 | −188 | −193 | −186 | −190 | −192 |
| CCSD | −262 | −231 | −236 | −225 | −232 | −230 |
| CCSD[T] | −262 | −237 | −240 | −231 | −238 | −235 |
| CCSD(T) | −263 | −236 | −241 | −230 | −237 | −234 |

cellent agreement with the vibrationless estimate (2.293 au) determined using molecular-beam spectroscopy by Rothstein [35]. It is also very close to rather accurate value of 2.2921 au obtained by Roos and Sadlej [36] using a rather extensive basis set and CAS-SCF. The vibrational contribution calculated at the SCF level by Papadopoulos et al. [12] was 0.025 au. The latter authors used evidently less saturated basis sets and the deviation of the SCF dipole moment from the numerical HF limit was larger than in our case. Nevertheless, the vibrational correction can be expected around the given value. Actually this correction coincides with the difference between the mentioned vibrationless estimate and other experimental values of $2.314 \pm 0.001$ au [37] and 2.3145 au [38].

In Table 3 we display the calculated dipole polarizability tensor components. Again, similar trends are encountered as for the dipole moment. However, the effect of electron correlation is much more pronounced. Unfortunately, in the course of the calculations we did not think about the usefulness of MBPT(2)-R12/A for polarizabilities. The pertinent energy has been standardly printed out with too few decimal places in order to be able to provide numerically plausible values. Therefore we have not included them in the table. Nevertheless, let us just mention that for the $\alpha_{zz}$ the differences between MBPT(2)-R12/A and MBPT(2)-R12/B are roughly 0.6, 0.1, and 0.02 au, for sp, spd, and spdf basis sets, respectively. Larger were the differences for $\alpha_{xx}$ (1, 0.5, 0.15 au). If we take into consideration that with the more accurate correlated methods the results converge faster to the limit, as follows from the results, we can safely estimate the value of $25.80 \pm 0.03$ au as the CCSD(T)-R12 $\alpha_{zz}$ limit. Perhaps with a little more uncertainty the limiting value for the $\alpha_{xx}$ tensor component can be estimated as $29.60 \pm 0.05$ au. The vibrationally uncorrected anisotropy is then $\Delta\alpha = -3.8$ au. It should be mentioned here that the vibrational correction can even change the sign for $\Delta\alpha$ [13]. Finally, the average polarizability $\bar{\alpha}$[1] should lie within 28.35–28.45 au. The SCF vibrational correction makes as much as almost 20% for $\alpha_{zz}$, and,

---

[1] $\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz});\ \bar{\beta} = \frac{3}{5}(2\beta_{xxz} + \beta_{zzz});\bar{\gamma} = \frac{1}{5}(\frac{8}{3}\gamma_{xxxx} + \gamma_{zzzz} + 4\gamma_{xxzz})$

naturally, much less (by an order of magnitude) for $\alpha_{xx}$ [13].

Tensor components for the dipole hyperpolarizabilty $\beta$ and the second dipole hyperpolarizability $\gamma$ are given in Tables 4 and 5. In the case of the hyperpolarizability $\beta$, with nonzero components $\beta_{zzz}$ and $\beta_{xxz}$, it is much more important to properly account for the correlation energy than to extend the basis. Indeed, the correlation contributions comprise as much as 50% of the total values, but beyond MBPT(4) the contributions alone cover about one third of the total correlation effects. The vibrational correction, as given in [13], has an opposite sign and a value of 373 au for $\beta_{zzz}$. Based on the fact that results using conventional and explicitly correlated methods systematically approach each other if one extends the basis by $d$ and $f$ functions, we can predict a vibrationless $\beta_{zzz} = -630$ au and $\beta_{xxz} = -234$ au with an estimated error bar of about 2% . These values correspond to an average around $\bar{\beta} = -660$ au.

Unlike the hyperpolarizability, the second dipole hyperpolarizability $\gamma$ is much more sensitive to extension of the basis set, but still the correlation effects account for a substantial part of the tensor component values. Of course, the $sp$ basis is too poor. However, it is quite interesting to note that even if the SCF values with different basis sets differ considerably, as soon as $d$ functions are included, at the level of correlated calculations, the differences are much smaller. Again, with $spdf$ basis sets the conventional and R12 values are rather close, which is valid generally from MBPT(2) to CCSD(T). Hence, the corresponding CCSD(T)-R12 values are our predictions. Using these we arrive at an average value of $\bar{\gamma} = 111 \times 10^3$ au.

Perhaps it is worth noting that by adding more diffuse $s$ and $p$ functions to our basis for Li, the above-mentioned final results remain the same within slight changes in the last printed digit. We have checked this using the $spd$ basis set and the CCSD-R12 method, because our original set did not include as diffuse $s$ and $p$ functions as some other basis sets used in previous calculations of polarizabilities. From our study it follows that for LiH it seems to be more important to have a "diffuse" basis set for H, in accord with the ionic character ($Li^{\delta+}H^{\delta-}$) of this molecule.

**Table 5.** Second dipole hyperpolarizability ($\gamma$) tensor components calculated for the LiH molecule using various methods (in $10^3$ au)

| Basis | $sp$ | | $spd$ | | $spdf$ | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| $\gamma_{zzzz}$ | | | | | | |
| SCF | | 61.1 | | 53.1 | | 73.5 |
| MBPT(2) | 83.7 | 68.4 | 76.5 | 71.2 | 75.2 | 73.5 |
| MBPT(3) | 91.3 | 81.0 | 83.7 | 80.2 | 82.4 | 79.3 |
| MBPT(4) | 98.7 | 88.2 | 90.7 | 86.8 | 84.7 | 83.7 |
| CCSD | 126.6 | 112.3 | 124.1 | 108.3 | 111.3 | 109.5 |
| CCSD[T] | 128.4 | 114.3 | 126.9 | 110.8 | 113.8 | 111.9 |
| CCSD(T) | 128.4 | 114.3 | 126.6 | 110.3 | 113.3 | 111.5 |
| $\gamma_{xxzz}$ | | | | | | |
| SCF | | 14.3 | | 25.5 | | 34.1 |
| MBPT(2) | 22.4 | 21.1 | 39.5 | 35.8 | 40.2 | 40.2 |
| MBPT(3) | 23.3 | 22.9 | 42.3 | 41.5 | 43.0 | 43.1 |
| MBPT(4) | 24.3 | 23.9 | 45.2 | 43.1 | 45.4 | 44.9 |
| CCSD | 25.2 | 24.9 | 49.4 | 48.4 | 49.8 | 49.3 |
| CCSD[T] | 25.2 | 24.9 | 49.6 | 48.5 | 49.9 | 49.3 |
| CCSD(T) | 25.3 | 24.9 | 49.6 | 48.5 | 49.9 | 49.3 |
| $\gamma_{xxxx}$ | | | | | | |
| SCF | | 30.9 | | 50.7 | | 70.0 |
| MBPT(2) | 46.3 | 43.6 | 74.8 | 67.8 | 75.9 | 75.9 |
| MBPT(3) | 47.8 | 46.7 | 80.1 | 78.6 | 81.1 | 81.5 |
| MBPT(4) | 48.9 | 48.0 | 83.6 | 79.8 | 84.7 | 83.7 |
| CCSD | 50.6 | 50.0 | 91.4 | 89.5 | 92.9 | 91.8 |
| CCSD[T] | 50.6 | 50.0 | 91.7 | 89.8 | 93.1 | 92.1 |
| CCSD(T) | 50.6 | 50.0 | 91.7 | 89.7 | 93.1 | 92.0 |

**Table 6.** Quadrupole moment $\Theta$ calculated for the LiH molecule with respect to the center of mass (in au)

| Basis | $sp$ | | $spd$ | | $spdf$ | |
|---|---|---|---|---|---|---|
| Method | Conv | R12 | Conv | R12 | Conv | R12 |
| SCF | | 3.373 | | 3.379 | | 3.379 |
| MBPT(2) | 3.299 | 3.365 | 3.239 | 3.243 | 3.230 | 3.240 |
| MBPT(3) | 3.269 | 3.243 | 3.180 | 3.174 | 3.173 | 3.172 |
| MBPT(4) | 3.240 | 3.219 | 3.142 | 3.143 | 3.137 | 3.142 |
| CCSD | 3.198 | 3.192 | 3.105 | 3.104 | 3.103 | 3.105 |
| CCSD[T] | 3.192 | 3.186 | 3.097 | 3.097 | 3.095 | 3.097 |
| CCSD(T) | 3.193 | 3.186 | 3.098 | 3.097 | 3.096 | 3.097 |

**Table 7.** Quadrupole polariz-ability (*C*) tensor components calculated for the LiH molecule using various methods (in au)

| Basis Method | sp | | spd | | spdf | |
|---|---|---|---|---|---|---|
| | Conv | R12 | Conv | R12 | Conv | R12 |
| $C_{zz,zz}$ | | | | | | |
| SCF | | 290.1 | | 299.6 | | 298.8 |
| MBPT(2) | 300.3 | 291.5 | 309.2 | 289.6 | 307.7 | 307.3 |
| MBPT(3) | 306.3 | 297.9 | 315.5 | 311.5 | 313.8 | 312.5 |
| MBPT(4) | 310.2 | 303.0 | 319.5 | 312.7 | 317.9 | 316.9 |
| CCSD | 315.3 | 308.3 | 323.9 | 318.1 | 329.9 | 329.9 |
| CCSD[T] | 315.6 | 308.5 | 324.1 | 318.3 | 329.7 | 330.7 |
| CCSD(T) | 315.6 | 308.5 | 324.1 | 318.3 | 330.0 | 331.1 |
| $C_{xz,xz}$ | | | | | | |
| SCF | | 138.2 | | 147.7 | | 142.3 |
| MBPT(2) | 142.3 | 138.2 | 146.5 | 137.4 | 145.8 | 145.6 |
| MBPT(3) | 145.2 | 141.2 | 149.5 | 147.6 | 148.7 | 148.1 |
| MBPT(4) | 147.0 | 143.6 | 151.4 | 148.2 | 150.7 | 150.2 |
| CCSD | 150.2 | 146.8 | 154.2 | 151.1 | 157.2 | 156.8 |
| CCSD[T] | 150.3 | 146.9 | 154.3 | 152.0 | 157.1 | 157.4 |
| CCSD(T) | 150.3 | 146.9 | 154.3 | 151.7 | 157.1 | 157.4 |
| $C_{xx,xx}$ | | | | | | |
| SCF | | 210.2 | | 217.1 | | 217.5 |
| MBPT(2) | 222.4 | 215.9 | 229.0 | 214.5 | 227.9 | 227.6 |
| MBPT(3) | 226.9 | 220.0 | 233.6 | 230.7 | 232.4 | 231.5 |
| MBPT(4) | 229.8 | 224.5 | 236.6 | 233.1 | 235.5 | 234.8 |
| CCSD | 237.1 | 231.7 | 243.6 | 239.2 | 248.0 | 247.6 |
| CCSD[T] | 237.3 | 231.9 | 243.8 | 239.4 | 248.1 | 248.6 |
| CCSD(T) | 237.3 | 231.9 | 243.7 | 239.3 | 248.1 | 248.9 |

Calculated field gradient properties, the quadrupole moment, and the quadruple polarizability tensor are given in Tables 6 and 7. Quadrupole moments were calculated with respect to the center of mass. At the SCF level the quadrupole moment agrees very well with the numerical SCF value of 3.3701 au [39]. Surprisingly low is the sensitivity of the results to the inclusion of higher angular momentum funtions in the basis set. Relative contributions from electron correlation effects are similar, as for the dipole moment and the dipole polarizability. Our best estimate for the quadrupole moment is 3.097 au, in a fairly good agreement with a high-level CI calculated value by Bishop and Cheung [40, 41] of 3.0655 au.

As for the dipole polarizabilities, the conventional and explicitly correlated results for the quadrupole polarizability tensor are almost identical for the *spdf* basis sets; hence the corresponding CCSD(T)-R12 values are our best predictions. Our values differ from those reported by Bishop and Lam [16], however, calculated with much smaller basis sets. Using the point charge technique at the MC SCF level they obtained 222, 118, and 94 au for $C_{zz, zz}$, $C_{xz, xz}$, and $C_{xx, xx}$, respectively. Also, we have observed much less sensitivity of $C_{xx, xx}$ when *d* functions were added.

It is somewhat disappointing that with extending the basis up to *f* functions the R12 method did not converge faster to the limiting value. For the dipole moment the *spd* basis in a way corresponds to the *sp* basis for the energy, so, as mentioned above, with the *sp* basis an improvement was not really expected. Another factor which plays an important role in the R12 calculations is justification of the standard approximation. For atoms it is rather straightforward. For instance, if only *s* orbitals are occupied in the reference wave function, a saturated

*sp* basis set is appropriate. With *s* and *p* orbitals occupied in the reference, one should have a saturated *spdf* basis set.

Let us consider the beryllium atom whose occupied orbitals in the reference state only involve *s* functions. However, when an external electric field is applied, then also *p* functions are partially involved in occupied orbitals. Consequently, the standard approximation is less justified with the *sp* set only. This may cause an additional numerical imbalance. Although the error caused by this imbalance might be negligible for absolute energies, for delicate numerical differences which occur in calculations of polarizabilities, even small disturbances can cause large errors. Similar considerations can be applied to molecules, including our case. Essentially, both factors mentioned above shift the "full" reliability of the R12 results toward basis sets with higher angular momenta. Indeed, one can see this trend for the beryllium atom where we were able to go as far as to *h* functions [21]. So it is probable that a clear convergence trend in favor of R12 would start from the *spdf* basis set toward more extended basis sets, i.e. toward further refinement of the results. Unfortunately, computational demands for such a study are extremely high.

## 4 Conclusions

Although using explicitly correlated methods we cannot see a substantial improvement in the convergency of calculated electric properties toward the basis set limit value, it is certainly a useful tool to judge if the results are close to the limiting values. Namely, when the conventional and explicitly correlated values in the whole range of correlated methods differ just very

slightly, this is a good indication for (quasi) saturation of the basis set. A similar indication is the small difference between the two variants of the standard approximation at the MBPT(2) level. For the polarizability of atoms (Be [21] and F$^-$ [42]), however, we have found clearly faster convergency for explicitly correlated methods.

The results definitely show that even for such a small molecule as LiH, in order to obtain reliable result it is equally important to account for infinite order effects (via CCSD) and to add higher angular momentum functions. The effect of triple excitations is practically negligible, as can be expected. We believe our results have decreased the uncertainty in the dissipation of calculated predictions for static polarizabilities and hyperpolarizabilities of this molecule.

## References

1. Luo Y, Ågren H, Jorgensen P, Mikkelsen KV (1995) Adv Quantum Chem 26:165
2. Dykstra CE, Liu S-Y, Malik DJ (1989) Adv Chem Phys 75:37
3. Kato T (1957) Commun Pure Appl Math 10:151
4. Hylleraas EA (1929) Z Phys 54:347
5. Hylleraas EA (1930) Z Phys 65:209
6. Klopper W (1998) In:Schleyer PvR, Allinger NL, Clark T, Gasteiger J, Kollman PA, Schaefer HF III, Schreiner PR (eds) The Encyclopedia of Computational Chemistry. Wiley, Chichester (in press)
7. Kutzelnigg W (1985) Theor Chim Acta 68:445
8. Noga J, Kutzelnigg W, Klopper W (1992) Chem Phys Lett 199:497
9. Noga J, Kutzelnigg W (1994) J Chem Phys 101:7738
10. Noga J, Tunega D, Klopper W, Kutzelnigg W (1995) J Chem Phys 103:309
11. Lee YS, Kucharski SA, Bartlett RJ (1984) J Chem Phys 81:5906
12. Karlström G, Roos BO, Sadlej AJ (1982) Chem Phys Lett 86:374
13. Papadopoulos MG, Willetts A, Handy NC, Underhill AE (1996) Mol Phys 88:1063
14. Lazzaretti P, Zanasi R (1981) J Chem Phys 74:5216
15. Lazzaretti P, Rossi E, Zanasi R (1982) J Phys B 15:521
16. Bishop DM, Lam B (1985) Chem Phys Lett 120:69
17. Maroulis G, Bishop DM (1986) Theor Chim Acta 69:161
18. Vrbik J, Legare DA, Rothstein SM (1990) J Chem Phys 92:1221
19. Rérat M, Mérawa M, Pouchan C (1992) Phys Rev A 46:5471
20. Hyams PA, Gerratt J, Cooper DL, Raimondi M (1993) J Chem Phys 100:4417
21. Tunega D, Noga J, Klopper W (1997) Chem Phys Lett 269:435
22. Noga J, Klopper W (1995) DIRCCR12-95:a direct AO integral driven CC-R12 program (unpublished)
23. Klopper W, Röhse R (1992) Theor Chim Acta 83:441
24. Helgaker TU (1986) HERMIT program (unpublished)
25. Helgaker TU, Almlöf J, Jensen HJA, Jørgensen P (1986) J Chem Phys 84:6266
26. Helgaker TU, Taylor PR (1992) Theor Chim Acta 83:177
27. Bartlett RJ (1995) In:Yarkony DA (ed) Modern electronic structure theory, Part I. World Scientific, Singapore, p 1047
28. Noga J, Klopper W, Kutzelnigg W (1997) In:Bartlett RJ (ed) Recent advances in computational chemistry, vol 2. World Scientific, Singapore, p 1
29. Čížek J (1969) Adv Chem Phys 14:35
30. Kutzelnigg W, Klopper W (1991) J Chem Phys 94:1985
31. Buckingham AD (1967) Adv Chem Phys 12:107
32. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
33. Urban M, Noga J, Cole SJ, Bartlett RJ (1985) J Chem Phys 83:404
34. Laaksonen L, Sundholm D, Pyykkö P (1984) Chem Phys Lett 105:573
35. Rothstein E (1969) J Chem Phys 50:1899
36. Roos BO, Sadlej AJ (1985) Chem Phys 94:43
37. Wharton L, Gold LP, Klemperer W (1962) J Chem Phys 37:2149
38. Lovas FJ, Tiemann E (1974) J Phys Chem Ref Data 3:609
39. Sundholm D, Pyykkö P, Laaksonen L, Sadlej AJ (1984) Chem Phys Lett 112:1
40. Bishop DM, Cheung LM (1983) J Chem Phys 78:1396
41. Bishop DM, Cheung LM (1983) J Chem Phys 79:2945
42. Müller H et al. (unpublished)