Comment on ''Response to 'Comment on ''Frequency-dependent equation-of-motion coupled cluster hyperpolarizabilities: Resolution of the discrepancy between theory and experiment for HF?'' ' '' [J. Chem. Phys. 109, 9201 (1998)]

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(Received 14 August 1998; accepted 18 August 1998)

[S0021-9606(98)30344-X]

In the communication by Rozyczko and Bartlett[1] (referred to as RB1) a one-term formula was given for the calculation of equation-of-motion coupled cluster (EOM-CC) hyperpolarizabilities. This formula contained a resolvent where the manifold **h** was not explicitly specified. Therefore, we had to assume that the authors used the manifold **h** and the resolvent defined in their previous paper, Ref. 2, containing the ''manifold of singly and doubly excited determinants,'' and excluding the reference state.

With this definition of the resolvent renormalization terms are missing in the hyperpolarizability expression. We pointed this out in the comment to RB1 and gave the generic correct expressions for the hyperpolarizabilities. In their reply to our comment (referred to as RB2) Rozyczko and Bartlett write that obviously the manifold **h** in RB1 contained both the excited states and the reference state and that the fact that we used their previous (and at that time only) definition ''shows a decided lack of flexibility by Hättig *et al.*''

In a scientific paper there must be consistency between the reported results and the presented formula. As we will show below, the calculations reported in RB1 neglected the renormalization terms and are in agreement with Eq. (1) of RB1 only if the resolvent does not contain the reference state, as we anticipated.

In RB2 Rozyczko and Bartlett reference two methods, which have not been introduced before:

(1) EOM(1) which is an approximation to the EOM-CCSD method where renormalization terms are neglected. This approximation is identical to the formula we assumed that Rozyczko and Bartlett used in RB1.
(2) EOM(2) which is the one where renormalization terms are included properly and which is identical to the formula we derived in our comment.

The EOM(1) static $\beta_{\|}$ and $\gamma_{\|}$ for the HF/POL1++ basis in Table I of RB2 is -8.03 and 511, respectively, and are identical to the static $\beta_{\|}$ and $\gamma_{\|}$ for the HF/POL1++ basis in Table I of RB1. Therefore, the calculations in RB1 were EOM(1) calculations and Rozyczko and Bartlett used the equation we assumed they did and a manifold **h** which did not contain the reference state.

At the time where Rozyczko and Bartlett received our private communication, later published as comment in JCP,[3] they had another paper[4] reporting results for *trans*-butadiene. In that paper[4] the numerical results and the equations were changed without reference to comply with the equations in our private communication.

The effect the neglect of renormalization terms will have on the size extensivity was also discussed in our comment. For the HF molecule we estimated the error introduced by neglecting the renormalization terms for $\beta_{zzz}(0)$ in the t-aug-cc-pVTZ basis to be of the order 0.65 a.u. or 6% of the total value. This estimate is in agreement with the differences between the EOM(1) and EOM(2) results for $\beta_{\|}$ for smaller basis sets in Table I of RB2. We consider 6% a large error for a ten electron system keeping in mind that the percentage error will increase linearly with the number of electrons.

We pointed out that the one-term expression for the hyperpolarizability given in RB1 does not satisfy time reversal symmetry. Rozyczko and Bartlett state in RB2 that it does because the equations of Butcher[5] and Bishop,[6] which they use, do so. However, Rozyczko and Bartlett forget that the assumptions of Butcher and Bishop are different. They used that bra states are the conjugate of the ket states (to get real average values) which is not fulfilled in EOM-CC. Time reversal symmetry must therefore be imposed explicitly in the EOM-CC formula as Rozyczko and Bartlett write that they have done in their reported calculations.

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