LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1998 issue.

COMMENTS

Comment on ''Frequency-dependent equation-of-motion coupled cluster hyperpolarizabilities: Resolution of the discrepancy between theory and experiment for HF?'' [J. Chem. Phys. 107, 10823 (1997)]

Christof Hättig, Henrik Koch, and Poul Jørgensen
Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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In a recent communication[1] Rozyczko and Bartlett announce the implementation and application of the equation-of-motion coupled cluster method for frequency-dependent hyperpolarizabilities of any order and any process. Their formulation is based on an open-ended formula for the equation-of-motion coupled cluster hyperpolarizability, which was presented without derivation or reference:

$$\begin{aligned}\langle\langle q_0;q_1,\cdots,q_n\rangle\rangle^{\mathrm{RB}}_{\omega_1,\cdots,\omega_n}&=\hat{P}(0,\cdots,n)\langle 0|(1+\Lambda)\tilde{q}_0^T|\mathbf{h}\rangle\\&\times\mathbf{R}(-\omega_1\cdots-\omega_n)\langle\mathbf{h}|\tilde{q}_1^T|\mathbf{h}\rangle\\&\times\mathbf{R}(-\omega_2\cdots-\omega_n)\cdots\mathbf{R}(-\omega_n)\langle\mathbf{h}|\tilde{q}_n^T|0\rangle.\end{aligned}\tag{1}$$

The resolvent was defined as $\mathbf{R}(\omega)=\langle\mathbf{h}|E_0-H_0+\omega|\mathbf{h}\rangle$ and the configuration manifold $\mathbf{h}$ was in a preceding paper by the authors[2] defined as ''manifold of singly and doubly excited determinants'' (not including the ground state 0). $\hat{P}(0,\cdots,n)$ is a permutation operator that symmetrizes with respect to the $(n+1)!$ permutations of the operator/frequency pairs (q_i/ω_i). The similarity transformed operators q_i^T are defined as $e^{-T}q_ie^T$ and $\tilde{q}_i^T=q_i^T-\langle 0|(1+\Lambda)q_i^T|0\rangle$, with $\Lambda=\Sigma_\mu\zeta_\mu\hat{\tau}_\mu^\dagger$. Using a more explicite notation Eq. (1) can thus be rewritten as

$$\begin{aligned}\langle\langle q_0;q_1,\cdots,q_n\rangle\rangle^{\mathrm{RB}}_{\omega_1,\cdots,\omega_n}&=\hat{P}(0,\cdots,n)\sum_{\substack{\nu_1\cdots\nu_n\\ \mu_0\mu_1\cdots\mu_{n-1}}}\langle 0|\left(1+\sum_\mu\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_0^T|\mu_0\rangle\\&\times R^{\mathrm{CC}}_{\mu_0\nu_1}(-\omega_1-\cdots-\omega_n)\langle\nu_1|\tilde{q}_1^T|\mu_1\rangle\\&\times R^{\mathrm{CC}}_{\mu_1\nu_2}(-\omega_2-\cdots-\omega_n)\cdots R^{\mathrm{CC}}_{\mu_{n-1}\nu_n}(-\omega_n)\langle\nu_n|\tilde{q}_n^T|0\rangle,\end{aligned}\tag{2}$$

with the summations μ_i, ν_i over the manifold of single and double excitations with respect to the Hartree–Fock reference state $(|\mu)=\hat{\tau}_\mu|0\rangle$, $\langle\nu|=\langle 0|\hat{\tau}_\nu^\dagger)$ and $R^{\mathrm{CC}}_{\mu\nu}(\omega)=[-(\mathbf{A}-\omega\mathbf{1})^{-1}]_{\mu\nu}$, where $\mathbf{A}$ is the coupled cluster Jacobian.

In the following we show that beyond linear response Eq. (1) is incompatible with the generic definition of EOM-CC response properties, that in the limit of a complete cluster expansion the correct full CI result is not reproduced with Eq. (1) beyond linear response, and that the results obtained by Eq. (1) are strongly nonsize extensive. Furthermore, we point out the fact that Eq. (1) breaks the time-reversal symmetry and we discuss the implications.

In the CI-like equation-of-motion coupled cluster method[3] frequency-dependent properties maybe generically defined[4,5] by replacing in the exact state expressions the ground state ket and bra wave functions by the coupled cluster wave function $|\mathrm{CC}\rangle$ and its biorthogonal counterpart $\langle 0|(1+\Sigma_\mu\zeta_\mu\hat{\tau}_\mu^\dagger)e^{-T}$ and the frequency-dependent reduced resolvent operator,

$$\hat{R}(\omega)=\sum_{k\neq 0}|k\rangle(\omega-\omega_{0k})^{-1}\langle k|\tag{3}$$

by its EOM-CC approximation:[5]

$$\begin{aligned}\hat{R}^{\mathrm{EOMCC}}(\omega)=e^T\Bigg(\sum_{\nu\mu}(\hat{\tau}_\nu-\zeta_\nu)|0\rangle\\\times[-(\mathbf{A}-\omega\mathbf{1})^{-1}]_{\nu\mu}\langle 0|\hat{\tau}_\mu^\dagger\Bigg)e^{-T}.\end{aligned}\tag{4}$$

With the reduced resolvent operator defined in Eq. (3), the linear, quadratic, and cubic response functions for an exact state[6–8] can be written as:[9]

$$\langle\langle q_0;q_1\rangle\rangle_{\omega_1}=\hat{P}(0,1)\langle 0|q_0\hat{R}(\omega_1)q_1|0\rangle,\tag{5}$$

$$\begin{aligned}\langle\langle q_0;q_1,q_2\rangle\rangle_{\omega_1,\omega_2}\\=\hat{P}(0,1,2)\langle 0|q_0\hat{R}(\omega_1+\omega_2)\overline{q_1}\hat{R}(\omega_2)q_2|0\rangle,\end{aligned}\tag{6}$$

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$$\langle\langle q_0;q_1,q_2,q_3\rangle\rangle_{\omega_1,\omega_2,\omega_3}$$
$$=\hat{P}(0,1,2,3)\{\langle 0|q_0\hat{R}(\omega_1+\omega_2+\omega_3)\overline{q_1}\hat{R}(\omega_2+\omega_3)$$
$$\times\overline{q_2}\hat{R}(\omega_3)q_3|0\rangle-\langle 0|q_0\hat{R}(\omega_1+\omega_2+\omega_3)$$
$$\times\hat{R}(\omega_1)q_1|0\rangle\langle 0|q_2\hat{R}(\omega_3)q_3|0\rangle\}, \quad (7)$$

where $\overline{q_i}=q_i-\langle 0|q_i|0\rangle$. Applying the recipe described above, one obtains for the EOM-CC linear response function:

$$\langle\langle q_0;q_1\rangle\rangle_{\omega_1}^{\mathrm{EOMCC}}=\hat{P}(0,1)\sum_{\mu_0\nu_1}\langle 0|\left(1+\sum_{\mu}\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_0^T|\mu_0\rangle R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_1)\langle\nu_1|q_1^T|0\rangle,$$
$$\times\tilde{q}_0^T|\mu_0\rangle R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_1)\langle\nu_1|q_1^T|0\rangle, \quad (8)$$

which is compatible with Eq. (1) and the expressions given in Refs. 4 and 5. For the quadratic and cubic response functions we obtain:

$$\langle\langle q_0;q_1,q_2\rangle\rangle_{\omega_1,\omega_2}^{\mathrm{EOMCC}}=\hat{P}(0,1,2)\sum_{\mu_0\nu_1\mu_1\nu_2}\langle 0|\left(1+\sum_{\mu}\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_0^T|\mu_0\rangle R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_1+\omega_2)$$
$$\times\langle\nu_1|\tilde{q}_1^T(\hat{\tau}_{\mu_1}-\zeta_{\mu_1})|0\rangle R^{\mathrm{CC}}_{\mu_1\nu_2}(\omega_2)\langle\nu_2|q_2^T|0\rangle, \quad (9)$$

and

$$\langle\langle q_0;q_1,q_2,q_3\rangle\rangle_{\omega_1,\omega_2,\omega_3}^{\mathrm{EOMCC}}=\hat{P}(0,1,2,3)\times\left\{\sum_{\substack{\mu_0\mu_1\mu_2\\ \nu_1\nu_2\nu_3}}\langle 0|\left(1+\sum_{\mu}\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_0^T|\mu_0\rangle R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_1+\omega_2+\omega_3)\langle\nu_1|\tilde{q}_1^T(\hat{\tau}_{\mu_1}-\zeta_{\mu_1})|0\rangle\right.$$
$$\times R^{\mathrm{CC}}_{\mu_1\nu_2}(\omega_2+\omega_3)\langle\nu_2|\tilde{q}_2^T(\hat{\tau}_{\mu_2}-\zeta_{\mu_2})|0\rangle R^{\mathrm{CC}}_{\mu_2\nu_3}(\omega_3)\langle\nu_3|q_3^T|0\rangle-\sum_{\mu_0\nu_1\nu_2}\langle 0|\left(1+\sum_{\mu}\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_0^T|\mu_0\rangle$$
$$\left.\times R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_1+\omega_2+\omega_3)R^{\mathrm{CC}}_{\nu_1\nu_2}(\omega_1)\langle\nu_2|q_1^T|0\rangle\sum_{\mu_0\nu_1}\langle 0|\left(1+\sum_{\mu}\zeta_\mu\hat{\tau}_\mu^\dagger\right)\tilde{q}_2^T|\mu_0\rangle R^{\mathrm{CC}}_{\mu_0\nu_1}(\omega_3)\langle\nu_1|q_3^T|0\rangle\right\}. \quad (10)$$

Apart from the signs of the frequency arguments, the generic EOM-CC quadratic and cubic response functions differ from Eq. (1) in two points:

(1) In Eqs. (9) and (10) appear matrix elements of the form $\langle\nu_i|\tilde{q}_i^T(\hat{\tau}_{\mu_i}-\zeta_{\mu_i})|0\rangle$, whereas in formula (1) or (2) the matrix elements $\langle\nu_i|\tilde{q}_i^T\hat{\tau}_{\mu_i}|0\rangle$ are used;

(2) Formula (1) neglects renormalization terms which appear in the exact state and the generic EOM-CC response functions beyond quadratic response [the second term in Eqs. (7) and (10)].

The terms neglected in Eq. (1) are usually nonvanishing. This is easily seen, if one considers the static hyperpolarizabilities $\beta_{zzz}(0)$ and $\gamma_{zzz}(0)$. If we define the vectors $\hat{\eta}_\mu^z=\langle 0|(1+\Sigma_\nu\zeta_\nu\hat{\tau}_\nu^\dagger)\tilde{z}^T|\mu\rangle$ and

$$\tilde{t}_\mu^{z\ldots z}=\sum_{\substack{\nu_1\ldots\nu_n\\ \mu_1\ldots\mu_{n-1}}}R^{\mathrm{CC}}_{\mu\nu_1}(0)\langle\nu_1|\tilde{z}^T|\mu_1\rangle$$
$$\times R^{\mathrm{CC}}_{\mu_1\nu_2}(0)\cdots R^{\mathrm{CC}}_{\mu_{n-1}\nu_n}(0)\langle\nu_n|z^T|0\rangle \quad (11)$$

the static EOM-CC hyperpolarizabilities can be written as:

$$\beta_{zzz}^{\mathrm{EOMCC}}(0)=6\sum_{\mu}\tilde{\eta}_\mu^z\tilde{t}_\mu^{zz}-3\alpha_{zz}^{\mathrm{EOMCC}}(0)\sum_{\mu}\zeta_\mu\tilde{t}_\mu^z, \quad (12)$$

and

$$\gamma_{zzzz}^{\mathrm{EOMCC}}(0)=24\sum_{\mu}\tilde{\eta}_\mu^z\tilde{t}_\mu^{zzz}-4\beta_{zzz}^{\mathrm{EOMCC}}(0)$$
$$\times\sum_{\mu}\zeta_\mu\tilde{t}_\mu^z-12\alpha_{zz}^{\mathrm{EOMCC}}(0)$$
$$\times\left[\sum_{\mu}\zeta_\mu\tilde{t}_\mu^{zz}+\sum_{\nu\mu}\tilde{\eta}_\nu^zR^{\mathrm{CC}}_{\nu\mu}(0)\tilde{t}_\mu^z\right]. \quad (13)$$

Equation (1) includes for both properties only the first term: $\beta_{zzz}^{\mathrm{RB}}(0)=6\Sigma_\mu\tilde{\eta}_\mu^z\tilde{t}_\mu^{zz}$ and $\gamma_{zzzz}^{\mathrm{RB}}(0)=24\Sigma_\mu\tilde{\eta}_\mu^z\tilde{t}_\mu^{zzz}$. The neglected terms will usually be nonvanishing: $\Sigma_\mu\zeta_\mu\tilde{t}_\mu^z$ will be nonzero for molecules with a nonzero z component of the dipole moment and the third term for $\gamma_{zzzz}^{\mathrm{EOMCC}}(0)$ persists even for systems with spherical symmetry. The neglected terms can also not be expected to be small: For the hydrogen fluoride molecule we have computed $\Sigma_\mu\zeta_\mu t_\mu^z$ using a CCSD wave function and the t-aug-cc-pVTZ basis[10] ($R_{\mathrm{HF}}=1.7328$ a.u.) and obtained a result of 0.034. If this is combined with the experimental value for the static polarizability $\alpha_{zz}(0)=6.4$ a.u.,[11] one obtaines for the term neglected in

$\beta^{\mathrm{RB}}_{zzz}(0)$ an estimate of $3\times0.034\times6.4$ a.u.$=0.65$ a.u. Compared to the result for $\beta_{zzz}(0)$ in the t-aug-cc-pVTZ basis (9.84 a.u.) given in Ref. 1, this means an error of $\approx$6% in addition to the intrinsic errors of the EOM-CCSD method and basis set errors.

In the limit of a complete cluster expansion, the generic EOM-CC response functions converge to the full CI result. Since the terms neglected in Eq. (1) are generally nonvanishing, this expression must converge to a wrong limit when the cluster expansion approaches completeness. The terms neglected in Eq. (1) are not size extensive. Thus in the generic EOM-CC expressions these terms cancel against nonsize extensive contributions in the first term. The latter nonsize extensive contributions are included in Eq. (1). Therefore, this approximation is strongly nonsize extensive. The terms neglected in β and γ scale with $N^2_{\mathrm{electrons}}$. Assuming the same prefactor as for HF one might expected already for medium-sized organic molecules like benzene or butadiene, with about 30 electrons, errors of $\approx$20%.

For a truncated cluster expansion already the generic EOM-CC response functions are not size extensive, as is demonstrated in Ref. 5. In addition, for a truncated cluster expansion the coupled cluster state $|\mathrm{CC}\rangle$ and the biorthogonal state $\langle 0|(1+\Lambda)\rangle e^{-T}$ are not each others complex conjugate and the EOM-CC resolvent operator $\hat{R}^{\mathrm{EOMCC}}(\omega)$ and the matrix $\mathbf{R}^{\mathrm{CC}}(\omega)$ are not hermitian (nor are they the similarity transformed of hermitian operators and matrices). As a consequence, the EOM-CC response functions and also the response functions defined by Eq. (1) will not obey the time-reversal symmetry,[12,13] i.e.,

$$\langle\langle q_0;q_1,\ldots,q_n\rangle\rangle^{\mathrm{EOMCC/RB}}_{-\omega_1,\ldots,-\omega_n}\neq(\langle\langle q_0;q_1,\ldots,q_n\rangle\rangle^{\mathrm{EOMCC/RB}}_{\omega_1,\ldots,\omega_n})^*; \tag{14}$$

for frequency-dependent hyperpolarizabilities this means f.x. $\beta^{\mathrm{SHG}}_{\parallel}(\omega)=\beta_{\parallel}(-2\omega;\omega,\omega)\neq\beta^{\mathrm{SHG}}_{\parallel}(-\omega)$

In addition to our concern about the inadequacy of Eq. (1) for the calculation of frequency-dependent hyperpolarizabilities, we have two comments to more detailed points of the letter by Rozyzcko and Bartlett:

Rozyczko and Bartlett mention twice in Ref. 1 that orbital relaxation effects vanish in a complete basis, but conclude that they ''do not seem to approach that in the current calculations, even in the p-aug-cc-pVTZ basis,'' implying that this effect would vanish in the one-particle basis set limit. We note that orbital relaxation effects are not related to basis set insufficiency but are rather a correlation problem, as has also many times previously been pointed out by one of the authors of Ref. 1. The effects of orbital relaxation persist in the complete one-electron basis set limit, but vanish in the full CI limit since the full CI wave function is invariant under orthogonal transformations of the orbital basis.

In Table II of Ref. 1 the authors list static hyperpolarizabilities for various basis sets which according to the table caption and the explanation in the text are CCSD and CCSD(T) finite field results obtained with relaxed and unrelaxed orbitals. The unrelaxed CCSD results are also listed in Table I in the rows for $\beta_{\parallel}(0)$ and $\gamma_{\parallel}(0)$. The text to Table I states that the results in Table I were obtained using Eq. (1) and we expect that the unrelaxed CCSD results in Table II were obtained using Eq. (1). This, however, raises the question about the meaning of the unrelaxed CCSD(T) results as in the unrelaxed approach the Hartree–Fock orbitals are not canonical when a field is applied and canonical orbitals are assumed in the definition of the CCSD(T) model.

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