RESEARCH ARTICLE

Anatomy of molecular properties evaluated with explicitly correlated electronic wave functions

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1. Detailed expressions for direct MP2-F12 one-electron density and contributions to right-hand side of Z-vector equations

For closed-shell systems, the matrix elements of the direct (unrelaxed) one-electron density of MP2-F12 are given in terms of spin-free (not antisymmetrized) integrals as follows:

$$\begin{aligned}
 D_j^i = & 2 (t_{\text{MP1}})_{ab}^{ik} (t_{\text{MP1}})_{jk}^{ab} - (t_{\text{MP1}})_{ab}^{ki} (t_{\text{MP1}})_{jk}^{ab} \\
 & + \frac{C_0^2 + 3C_1^2}{2} A_{ab}^{ik} A_{jk}^{ab} + \frac{C_0^2 - 3C_1^2}{2} A_{ab}^{ki} A_{jk}^{ab} \\
 & + \frac{C_0 + 3C_1}{2} \left((t_{\text{MP1}})_{ab}^{ik} A_{jk}^{ab} + A_{ab}^{ik} (t_{\text{MP1}})_{jk}^{ab} \right) \\
 & + \frac{C_0 - 3C_1}{2} \left((t_{\text{MP1}})_{ab}^{ki} A_{jk}^{ab} + A_{ab}^{ki} (t_{\text{MP1}})_{jk}^{ab} \right) \\
 & + \frac{C_0^2 + 3C_1^2}{2} X_{jk}^{ik} + \frac{C_0^2 - 3C_1^2}{2} X_{jk}^{ki},
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 D_b^a = & 2 (t_{\text{MP1}})_{ij}^{ac} (t_{\text{MP1}})_{bc}^{ij} - (t_{\text{MP1}})_{ij}^{ca} (t_{\text{MP1}})_{bc}^{ij} \\
 & + \frac{C_0^2 + 3C_1^2}{2} A_{ij}^{ac} A_{bc}^{ij} + \frac{C_0^2 - 3C_1^2}{2} A_{ij}^{ca} A_{bc}^{ij} \\
 & + \frac{C_0 + 3C_1}{2} \left((t_{\text{MP1}})_{ij}^{ac} A_{bc}^{ij} + A_{ij}^{ac} (t_{\text{MP1}})_{bc}^{ij} \right) \\
 & + \frac{C_0 - 3C_1}{2} \left((t_{\text{MP1}})_{ij}^{ca} A_{bc}^{ij} + A_{ij}^{ca} (t_{\text{MP1}})_{bc}^{ij} \right) \\
 & + \frac{C_0^2 + 3C_1^2}{2} r_{ij}^{ac} r_{bc}^{ij} + \frac{C_0^2 - 3C_1^2}{2} r_{ij}^{ca} r_{bc}^{ij},
 \end{aligned} \tag{2}$$

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$$\begin{aligned}
D_{\beta'}^a = & r_{\beta'c}^{ij} \left(\frac{C_0 + 3C_1}{2} (t_{\text{MP1}})_{ij}^{ac} + \frac{C_0 - 3C_1}{2} (t_{\text{MP1}})_{ij}^{ca} \right. \\
& + \frac{C_0^2 + 3C_1^2}{2} A_{ij}^{ac} + \frac{C_0^2 - 3C_1^2}{2} A_{ij}^{ca} \Big) \\
& + \frac{C_0^2 + 3C_1^2}{2} r_{\beta'c}^{ij} r_{ij}^{ac} + \frac{C_0^2 - 3C_1^2}{2} r_{\beta'c}^{ij} r_{ij}^{ca}, \tag{3}
\end{aligned}$$

$$D_{\beta'}^{\alpha'} = \frac{C_0^2 + 3C_1^2}{2} r_{\beta'c}^{ij} r_{ij}^{\alpha'c} + \frac{C_0^2 - 3C_1^2}{2} r_{\beta'c}^{ij} r_{ij}^{c\alpha'}. \tag{4}$$

Intermediates in X_{am} in terms of spin-free (not antisymmetrized) integrals are as follows:

$$\bar{g}_{mk}^{al} D_l^k = \left(2g_{mk}^{al} - g_{km}^{al} \right) D_l^k, \tag{5}$$

$$\begin{aligned}
\bar{g}_{m\gamma}^{a\beta} D_{\beta}^{\gamma} = & \bar{g}_{mc}^{ab} D_b^c + \bar{g}_{mc}^{a\beta'} D_{\beta'}^c + \bar{g}_{m\gamma'}^{ab} D_b^{\gamma'} + \bar{g}_{m\gamma'}^{a\beta'} D_{\beta'}^{\gamma'} \\
= & \left(2g_{mc}^{ab} - g_{kc}^{ab} \right) D_b^c + \left(2g_{mc}^{a\beta'} - g_{kc}^{a\beta'} \right) D_{\beta'}^c \\
& + \left(2g_{m\gamma'}^{ab} - g_{k\gamma'}^{ab} \right) D_b^{\gamma'} + \left(2g_{m\gamma'}^{a\beta'} - g_{k\gamma'}^{a\beta'} \right) D_{\beta'}^{\gamma'}, \tag{6}
\end{aligned}$$

$$\begin{aligned}
\frac{1}{2} \bar{g}_{bc}^{al} t_{il}^{bc} = & g_{bc}^{al} \left(2 (t_{\text{MP1}})_{il}^{bc} - (t_{\text{MP1}})_{li}^{bc} \right. \\
& + \frac{C_0 + 3C_1}{2} A_{il}^{bc} + \frac{C_0 - 3C_1}{2} A_{li}^{bc} \Big), \tag{7}
\end{aligned}$$

$$\begin{aligned}
C_{\alpha'c}^{al} t_{il}^{bc} = & f_b^{\alpha'} r_{\alpha'c}^{al} \left(\frac{C_0 + 3C_1}{2} (t_{\text{MP1}})_{il}^{bc} + \frac{C_0 - 3C_1}{2} (t_{\text{MP1}})_{li}^{bc} \right. \\
& + \frac{C_0^2 + 3C_1^2}{2} A_{il}^{bc} + \frac{C_0^2 - 3C_1^2}{2} A_{li}^{bc} \Big) \\
& + f_b^{\alpha'} r_{cb}^{al} \left(\frac{C_0 + 3C_1}{2} (t_{\text{MP1}})_{il}^{cb} + \frac{C_0 - 3C_1}{2} (t_{\text{MP1}})_{li}^{cb} \right. \\
& + \frac{C_0^2 + 3C_1^2}{2} A_{il}^{cb} + \frac{C_0^2 - 3C_1^2}{2} A_{li}^{cb} \Big), \tag{8}
\end{aligned}$$

$$\begin{aligned}
\frac{1}{2} \bar{g}_{mb}^{kl} t_{kl}^{ab} = & g_{mb}^{kl} \left(2 (t_{\text{MP1}})_{kl}^{ab} - (t_{\text{MP1}})_{kl}^{ba} \right. \\
& + \frac{C_0 + 3C_1}{2} A_{kl}^{ab} + \frac{C_0 - 3C_1}{2} A_{kl}^{ba} \Big), \tag{9}
\end{aligned}$$

$$F_m^{\alpha'} \bar{r}_{\alpha'b}^{kl} t_{kl}^{ab} = f_m^{\alpha'} r_{\alpha'b}^{kl} \left(\frac{C_0 + 3C_1}{2} (t_{\text{MP1}})_{kl}^{ab} + \frac{C_0 - 3C_1}{2} (t_{\text{MP1}})_{kl}^{ba} \right. \\ \left. + \frac{C_0^2 + 3C_1^2}{2} A_{kl}^{ab} + \frac{C_0^2 - 3C_1^2}{2} A_{kl}^{ba} \right), \quad (10)$$

$$F_b^{\alpha'} \bar{r}_{m\alpha'}^{kl} t_{kl}^{ab} = f_b^{\alpha'} r_{m\alpha'}^{kl} \left(\frac{C_0 + 3C_1}{2} (t_{\text{MP1}})_{kl}^{ab} + \frac{C_0 - 3C_1}{2} (t_{\text{MP1}})_{kl}^{ba} \right. \\ \left. + \frac{C_0^2 + 3C_1^2}{2} A_{kl}^{ab} + \frac{C_0^2 - 3C_1^2}{2} A_{kl}^{ba} \right), \quad (11)$$

$$\frac{1}{2} \bar{r}_{a\gamma'}^{kl} \bar{g}_{kl}^{m\gamma'} = \left(\frac{C_0 + 3C_1}{2} r_{a\alpha'}^{kl} + \frac{C_0 - 3C_1}{2} r_{a\alpha'}^{lk} \right) g_{m\alpha'}^{kl}, \quad (12)$$

$$\frac{1}{2} \bar{r}_{m\gamma'}^{kl} \bar{g}_{kl}^{a\gamma'} = \left(\frac{C_0 + 3C_1}{2} r_{m\alpha'}^{kl} + \frac{C_0 - 3C_1}{2} r_{m\alpha'}^{lk} \right) g_{a\alpha'}^{kl}, \quad (13)$$

$$\frac{1}{2} (F_k^k + F_l^l) \bar{r}_{m\beta'}^{kl} \bar{r}_{kl}^{a\beta'} = \left(f_k^j r_{mb}^{jl} + f_l^j r_{mb}^{kj} \right) \\ \left(\frac{C_0^2 + 3C_1^2}{2} r_{kl}^{a\beta'} + \frac{C_0^2 - 3C_1^2}{2} r_{lk}^{a\beta'} \right), \quad (14)$$

$$\frac{1}{2} F_m^{\alpha'} \bar{r}_{\alpha'\beta'}^{kl} \bar{r}_{kl}^{a\beta'} = f_m^{\alpha'} r_{\alpha'b}^{kl} \left(\frac{C_0^2 + 3C_1^2}{2} r_{kl}^{a\beta'} + \frac{C_0^2 - 3C_1^2}{2} r_{lk}^{a\beta'} \right), \quad (15)$$

$$\frac{1}{2} F_{\alpha'}^{\beta'} \bar{r}_{m\gamma'}^{kl} \bar{r}_{kl}^{a\beta'} = f_{\beta'}^{\alpha'} r_{m\alpha'}^{kl} \left(\frac{C_0^2 + 3C_1^2}{2} r_{kl}^{a\beta'} + \frac{C_0^2 - 3C_1^2}{2} r_{lk}^{a\beta'} \right), \quad (16)$$

$$\frac{1}{2} \bar{r}_{m\gamma'}^{kl} F_{\beta'}^a \bar{r}_{kl}^{\beta\gamma'} = r_{m\gamma'}^{kl} \left(\frac{C_0^2 + 3C_1^2}{2} f_b^a r_{kl}^{b\gamma'} + \frac{C_0^2 - 3C_1^2}{2} f_b^a r_{lk}^{b\gamma'} \right. \\ \left. + \frac{C_0^2 + 3C_1^2}{2} f_{\beta'}^a r_{kl}^{\beta'\gamma'} + \frac{C_0^2 - 3C_1^2}{2} f_{\beta'}^a r_{lk}^{\beta'\gamma'} \right). \quad (17)$$

2. Results for x^2 and y^2 components of H₂O quadrupole moment from MP2 calculations

Table 1. The derivations of the triple- ζ F12 calculations of Θ_{xx} and Θ_{yy} (a.u.) for H₂O with respect to the estimated basis set limits.^a

Method	Basis	Θ_{xx}	Θ_{yy}
MP2-F12 ^b	aug-cc-pVTZ	−0.00065	−0.00157
	cc-pVTZ-F12	0.01130	−0.00957
MP2-F12 _C ^b	aug-cc-pVTZ	−0.00067	−0.00187
	cc-pVTZ-F12	0.01128	−0.00955
Basis set limit			
MP2	—	−1.84402	1.95318

^aThe basis set limits were the HF/aug-cc-pV6Z values plus the extrapolated MP2 correlation contributions from the aug-cc-pVQZ and aug-cc-pV5Z values.

^bThe CABS singles correction was included in the calculations.

Figure 1. The direct one-electron density (D^{dir}) and orbital response (D^{or}) contributions from the CABS singles and correlation corrections to Θ_{xx} and Θ_{yy} for H₂O. F12 and F12_C refer to the F12 correlation corrections with and without the coupling from the MP2 and F12 corrections.

Figure 2. Basis set convergence of MP2 correlation contributions to Θ_{xx} for H_2O . MP2-F12 and MP2-F12_c refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.

Figure 3. Basis set convergences of MP2 correlation contributions to Θ_{yy} for H_2O . MP2-F12 and MP2-F12_c refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.

3. Basis set convergence of various MP2 correlation contributions to z components of dipole moment

Figure 4. Basis set convergence of MP2 correlation contributions to μ_z for BH. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the boron atom while the aug-cc-pVXZ basis sets were used for the hydrogen atom.

Figure 5. Basis set convergence of MP2 correlation contributions to μ_z for the HF molecule. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the fluorine atom while the aug-cc-pVXZ basis sets were used for the hydrogen atom.

Figure 6. Basis set convergence of MP2 correlation contributions to μ_z for H_2O . MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.

4. Basis set convergences of various MP2 correlation contributions to z^2 components of quadrupole moment

Figure 7. Basis set convergences of MP2 correlation contributions to Θ_{zz} for BH . MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the boron atom while the aug-cc-pVXZ basis sets were used for the hydrogen atom.

Figure 8. Basis set convergences of MP2 correlation contributions to Θ_{zz} for the HF molecule. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets are used for the fluorine atom while the aug-cc-pVXZ basis sets were used for the hydrogen atom.

Figure 9. Basis set convergence of MP2 correlation contributions to Θ_{zz} for H₂O. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets are used for the hydrogen atoms.

5. F12-corrected correlation contributions to the components of the H₂O quadrupole moment, r_{α}^2 , with different basis sets

Figure 10. Basis set convergence of F12-corrected correlation contributions to $\langle x^2 \rangle$ for H₂O. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.

Figure 11. Basis set convergence of F12-corrected correlation contributions to $\langle y^2 \rangle$ for H₂O. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.

Figure 12. Basis set convergence of F12-corrected correlation contributions to $\langle z^2 \rangle$ for H₂O. MP2-F12 and MP2-F12_C refer to the F12-corrected correlation contributions with and without the coupling from the MP2 and F12 corrections. The (aug-)cc-pVXZ-F12 basis sets denote that the cc-pVXZ-F12 basis sets were used for the oxygen atom while the aug-cc-pVXZ basis sets were used for the hydrogen atoms.