Supporting Information for
“Linear and Nonlinear Optical Properties from TDOMP2 Theory”

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Abstract

The Supporting Information gives algebraic expressions for the closed-shell spin-restricted OMP2 method, molecular geometries, electronic ground-state energies and dipole moments, and a comparison of TDCC2 absorption spectra with those from LRCC2 theory from 0–930 eV.
1 Closed-shell spin-restricted OMP2 expressions

We now assume closed-shell systems where each orbital is doubly occupied. Then the expression for the fock matrix is given by

\[ f_{pq}^p = h_{pq}^p + 2u_{pq}^j - u_{jq}^p. \]  

(1)

Using the following biorthogonal parameterization of \( \hat{\Lambda}, \hat{T}, \)

\[
\hat{T}_2 = \frac{1}{2} \sum_{abij} \tau_{ij}^{ab} \hat{E}_i^a \hat{E}_j^b, \\
\hat{\Lambda}_2 = \frac{1}{2} \sum_{abij} \lambda_{ij}^{ab} \left( \frac{1}{3} \hat{E}_j^b \hat{E}_i^a + \frac{1}{6} \hat{E}_i^b \hat{E}_j^a \right),
\]

the derivatives of the OMP2 Hamilton function w.r.t \( (\lambda_{ij}^{ab}, \kappa_i^a) \) are given by

\[
\frac{\partial H}{\partial \lambda_{ij}^{ab}} = u_{ij}^{ab} + P_{ij}^{ab} \left( f_{cij}^{ac} - f_{kij}^{kab} \right), \\
\frac{\partial H}{\partial \kappa_i^a} = h_{i}^{b} \gamma_{b}^{a} - h_{j}^{a} \gamma_{i}^{j} + u_{pq}^{ir} \Gamma_{pq}^{ar} - u_{rs}^{aq} \Gamma_{iq}^{rs},
\]

(2)

(3)

Furthermore, one can show that

\[
\lambda_{ij}^{ab} = 2(2\tau_{ij}^{ab} - \tau_{ji}^{ab})^*. 
\]

(4)

The expressions for the one- and two-body density matrices are given by

\[
\gamma_{i}^{j} = 2\delta_{i}^{j} + (\gamma_{c})_{i}^{j}, \quad (\gamma_{c})_{i}^{j} = -\lambda_{ab}^{kj} \tau_{ki}^{ab}, \\
\gamma_{a}^{b} = \lambda_{ac}^{ij} \tau_{ij}^{bc}
\]

(5)

(6)
\[ \Gamma_{ij}^{kl} = 4\delta_i^k \delta_j^l - 2\delta_i^l \delta_j^k + \hat{P}_{ij}^{kl} \left( -2\delta_i^k (\gamma_c)_j^l + \delta_i^l (\gamma_c)_j^k \right), \] (7)

\[ \Gamma_{ij}^{ab} = 2(2\tau_{ij}^{ab} - \tau_{ji}^{ab}), \] (8)

\[ \Gamma_{ij}^{ab} = \lambda_{ij}^{ab} = 2(2\tau_{ij}^{ab} - \tau_{ji}^{ab})^* = (\Gamma_{ij}^{ab})^*, \] (9)

\[ \Gamma_{ia}^{jb} = 2\delta_i^j \gamma_a^b = \Gamma_{ia}^{jb}, \] (10)

\[ \Gamma_{ia}^{jb} = -\delta_i^j \gamma_a^b = \Gamma_{ai}^{jb}. \] (11)


## 2 Molecular geometries

Table 1 lists the molecular geometries used in the main article.

Table 1: Molecular geometries (Cartesian coordinates, in Bohr).

| Molecule | Atom | X | Y | Z |
|----------|------|---|---|---|
| HF       | H    | 0.0 | 0.0 | 0.0 |
|          | F    | 0.0 | 0.0 | 1.7328795 |
| H₂O      | O    | 0.0 | 0.0 | -0.1239093563 |
|          | H    | 0.0 | 1.4299372840 | 0.9832657567 |
|          | H    | 0.0 | -1.4299372840 | 0.9832657567 |
| NH₃      | N    | 0.0 | 0.0 | 0.2010 |
|          | H    | 0.0 | 1.7641 | -0.4690 |
|          | H    | 1.5277 | -0.8820 | -0.4690 |
|          | H    | -1.5277 | -0.8820 | -0.4690 |
| CH₄      | C    | 0.0 | 0.0 | 0.0 |
|          | H    | 1.2005 | 1.2005 | 1.2005 |
|          | H    | -1.2005 | -1.2005 | 1.2005 |
|          | H    | -1.2005 | 1.2005 | -1.2005 |
|          | H    | 1.2005 | -1.2005 | -1.2005 |
3 Ground-state energies and electric dipole moments

Table 2 lists ground-state energies and the $z$-component of the electric dipole moments computed with the d-aug-cc-pVDZ basis set for Ne and the aug-cc-pVDZ basis set for the remaining molecules.

Table 2: Ground-state energies (a.u.) and electric dipole moments (a.u.) for Ne, HF, $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{CH}_4$.

|          | $E_0$            | $\mu_z$ |
|----------|------------------|---------|
| Ne       | CCSD $-128.708\,821\,187\,1$ | 0.0     |
| Ne       | OMP2 $-128.707\,014\,780\,2$ | 0.0     |
| Ne       | CC2 $-128.707\,468\,246\,7$  | 0.0     |
| HF       | CCSD $-100.261\,508\,470\,8$ | $-0.703\,237\,143\,6$ |
| HF       | OMP2 $-100.260\,190\,513\,7$ | $-0.700\,524\,169\,9$ |
| HF       | CC2 $-100.260\,558\,712\,4$  | $-0.689\,047\,761\,5$ |
| $\text{H}_2\text{O}$ | CCSD $-76.270\,767\,643\,3$ | 0.729\,092\,066\,3 |
| $\text{H}_2\text{O}$ | OMP2 $-76.265\,470\,576\,8$ | 0.724\,729\,427\,6 |
| $\text{H}_2\text{O}$ | CC2 $-76.265\,519\,413\,7$  | 0.716\,397\,141\,7 |
| $\text{NH}_3$ | CCSD $-56.421\,326\,271\,4$ | $-0.575\,380\,861\,1$ |
| $\text{NH}_3$ | OMP2 $-56.408\,134\,740\,5$ | $-0.570\,946\,397\,5$ |
| $\text{NH}_3$ | CC2 $-56.408\,016\,476\,4$  | $-0.568\,898\,057\,1$ |
| $\text{CH}_4$ | CCSD $-40.394\,143\,335\,9$ | 0.0     |
| $\text{CH}_4$ | OMP2 $-40.371\,768\,987\,0$ | 0.0     |
| $\text{CH}_4$ | CC2 $-40.371\,657\,899\,0$  | 0.0     |

4 Comparison of absorption spectra from TDCC2 and LRCC2 theory

Figure 1 shows the agreement between spectra from TDCC2 simulations and from LRCC2 calculations using the Lanczos-chain-driven algorithm described by Coriani et al.$^{1,2}$ as implemented in the Dalton quantum chemistry program.$^{3,4}$ The same geometries and basis sets as above were used.
Figure 1: Absorption spectra from TDCC2 simulations and LRCC2 calculations for Ne, HF, H$_2$O, NH$_3$ and CH$_4$. 


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