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CORRECTION

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Correction: Visualizing and characterizing excited states from time-dependent density functional theory

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Correction for 'Visualizing and characterizing excited states from time-dependent density functional theory' by John M. Herbert *et al.*, *Phys. Chem. Chem. Phys.*, 2024, **26**, 3755–3794, **https://doi.org/10.1039/D3CP04226J**.

My recent review[1] on visualization and characterization methods in time-dependent density functional theory (TD-DFT) contains a sign error in the definition of the natural transition orbitals. This affects eqn (3.1) and (3.2) and the accompanying text in the same paragraph. The corrected equations are

$$\mathbf{U}_{\mathrm{o}}^{\dagger}\left(\Delta\mathbf{P}^{\mathrm{hole}}\right)\mathbf{U}_{\mathrm{o}} = \underbrace{\begin{pmatrix} -\lambda_1^2 & 0 & 0 & \cdots \\ 0 & -\lambda_2^2 & 0 & \cdots \\ & & \ddots & 0 \\ 0 & \cdots & 0 & -\lambda_{n_{\mathrm{occ}}}^2 \end{pmatrix}}_{-\boldsymbol{\Lambda}^2} \tag{3.1}$$

and

$$\mathbf{U}_{\mathrm{v}}^{\dagger}\left(\Delta\mathbf{P}^{\mathrm{elec}}\right)\mathbf{U}_{\mathrm{v}} = \begin{pmatrix} \boldsymbol{\Lambda}^2 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \tag{3.2}$$

These eigenvalues differ in sign from what was (erroneously) published in ref. 1. The text accompanying these equations should suggest that $\Delta\mathbf{P}^{\mathrm{elec}}$ is positive semidefinite (eigenvalues $\lambda_i^2 \geq 0$) whereas $\Delta\mathbf{P}^{\mathrm{hole}}$ is negative semidefinite (eigenvalues $-\lambda_i^2$). This is consistent with the signs in eqn (2.12) that defines $\Delta\mathbf{P}^{\mathrm{elec}}$ and $\Delta\mathbf{P}^{\mathrm{hole}}$, and with remarks made concerning the attachment and detachment densities in eqn (2.17).

In addition, eqn (2.13) for the normalization of the electron and hole densities holds only when the Tamm–Dancoff approximation (TDA) is invoked. A more general statement is that

$$\mathrm{tr}(\Delta\mathbf{P}^{\mathrm{elec}}) = -\mathrm{tr}(\Delta\mathbf{P}^{\mathrm{hole}})$$

always, consistent with the eigenvalues given above, whereas

$$\mathrm{tr}\left(\Delta\mathbf{P}^{\mathrm{elec}}\right) \overset{\mathrm{TDA}}{=} 1$$

holds only within the TDA. Note that

$$\mathrm{tr}\left(\Delta\mathbf{P}^{\mathrm{elec}}\right) = \sum_{ia}\left(|x_{ia}|^2 + |y_{ia}|^2\right)$$

according to eqn (2.12), whereas the normalization condition for linear response TD-DFT is $\sum_{ia}\left(|x_{ia}|^2 + |y_{ia}|^2\right) = 1$ [eqn (2.4)]. Therefore, $\mathrm{tr}(\Delta\mathbf{P}^{\mathrm{elec}})$ can exceed unity for full linear response TDDFT. Typically $||\mathbf{y}|| \sim 10^{-3}$ for small molecules, so the deviation from the TDA result is not large.

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The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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Notes and references

1 J. M. Herbert, Visualizing and characterizing excited states from time-dependent density functional theory, *Phys. Chem. Chem. Phys.*, 2024, **26**, 3755–3794.