Electronic Supplementary Information
Part I

Practical computation of electronic excitation in solution: vertical excitation model

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Prepared on 22nd July 2011

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1. Appendix to Section 2

1.1 Note

All the quantities and notations used in this document are the same as those defined in the main text. This document cites the following references (which are also cited in the main text):

(A1) M. Cossi and V. Barone, *J. Phys. Chem. A*, 2000, **104**, 10614.

(A2) G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110.

(A3) F. Lipparini, G. Scalmani, B. Mennucci, E. Cancès, M. Caricato and M. J. Frisch, *J. Chem. Phys.*, 2010, **133**, 014106.

(A4) S. Miertuš, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117.

(A5) S. Miertuš and J. Tomasi, *Chem. Phys.*, 1982, **65**, 239.

1.2 The proof of eqn (21)

Using eqns (10), (15), and (18), one can obtain the following equations

$$\overline{\overline{\mathbf{Q}}}^{el} = -\mathbf{D}_{\varepsilon_{opt}}^{-1}\,\overline{\overline{\mathbf{b}}} + \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1}\,\mathbf{D}_{\varepsilon_{opt}}^{-1}\,\,\mathbf{\Omega}\,\mathbf{D}_{\varepsilon_0}^{-1}\,\overline{\mathbf{b}} \tag{A1}$$

$$\overline{\mathbf{Q}}^{or} = -\frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1}\,\mathbf{D}_{\varepsilon_0}^{-1}\,\overline{\mathbf{b}} \tag{A2}$$

Using eqns (10), (16), (17), and (19), one can obtain the following equations

$$\overline{\overline{\mathbf{Q}}}^{dyn} = -\mathbf{D}_{\varepsilon_{opt}}^{-1}\,\overline{\overline{\mathbf{b}}} \tag{A3}$$

$$\overline{\mathbf{Q}}^{in} = -(\mathbf{D}_{\varepsilon_0}^{-1} - \mathbf{D}_{\varepsilon_{opt}}^{-1})\,\overline{\mathbf{b}} \tag{A4}$$

Subtraction then yields

$$\overline{\overline{\mathbf{Q}}}^{el} - \overline{\overline{\mathbf{Q}}}^{dyn} = \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1}\,\mathbf{D}_{\varepsilon_{opt}}^{-1}\,\,\mathbf{\Omega}\,\mathbf{D}_{\varepsilon_0}^{-1}\,\overline{\mathbf{b}} \tag{A5}$$

$$\overline{\mathbf{Q}}^{in} - \overline{\mathbf{Q}}^{or} = \left(\frac{1 - \varepsilon_{opt}}{\varepsilon_0 - 1}\,\mathbf{D}_{\varepsilon_0}^{-1} + \mathbf{D}_{\varepsilon_{opt}}^{-1} \right)\overline{\mathbf{b}} =$$

$$= \frac{1}{\varepsilon_0 - 1} \mathbf{D}_{\varepsilon_{\text{opt}}}^{-1} \left[(\varepsilon_0 - 1) \mathbf{D}_{\varepsilon_0} - (\varepsilon_{\text{opt}} - 1) \mathbf{D}_{\varepsilon_{\text{opt}}} \right] \mathbf{D}_{\varepsilon_0}^{-1} \, \overline{\mathbf{b}} \qquad (A6)$$

In CPCM, the matrix $\mathbf{\Omega}$ satisfies the following equations:

$$\mathbf{D}_{\varepsilon_0} = \frac{\varepsilon_0}{\varepsilon_0 - 1} \mathbf{\Omega} \qquad (A7)$$

$$\mathbf{D}_{\varepsilon_{\text{opt}}} = \frac{\varepsilon_{\text{opt}}}{\varepsilon_{\text{opt}} - 1} \mathbf{\Omega} \qquad (A8)$$

Applying eqns (A7) and (A8) to the expression in brackets in eqn (A6), one can prove that the right-hand side of eqn (A6) is equivalent to the right-hand side of eqn (A5), thereby proving eqn (21).

In IEF-PCM, the matrices $\mathbf{D}_\varepsilon$ and $\mathbf{\Omega}$ satisfy the following equations according to Ref. A1:

$$\mathbf{D}_\varepsilon = \left(\frac{1}{2} \mathbf{I} - \widetilde{\mathbf{D}} \right)^{-1} \left[\frac{\varepsilon + 1}{2(\varepsilon - 1)} \mathbf{I} - \widetilde{\mathbf{D}} \right] \mathbf{S} \qquad (A9)$$

$$\mathbf{\Omega} = \mathbf{S} \qquad (A10)$$

where $\varepsilon = \varepsilon_0$ or ε_{opt}. The matrices on the right-hand side of these equations do not depend on the dielectric constant, and they are defined in Ref. A1; the matrix $\mathbf{I}$ is the unit matrix. Applying eqn (A9) with $\varepsilon = \varepsilon_0$ and ε_{opt} to the expression in brackets in eqn (A6), one can prove that eqn (21) is also valid within the IEF-PCM formalism.

Equation (21) is also valid within the latest formulation of IEF-PCM (Refs. A2 and A3) where the matrices $\mathbf{D}_\varepsilon$ with $\varepsilon = \varepsilon_0$ or ε_{opt} are defined as

$$\mathbf{D}_\varepsilon = \frac{1}{2} \mathbf{R}_\infty^{-1} \left(\frac{\varepsilon + 1}{\varepsilon - 1} \mathbf{I} - \frac{1}{2\pi} \widetilde{\widetilde{\mathbf{D}}} \mathbf{A} \right) \mathbf{S} + \frac{1}{2} \mathbf{S}^{\mathsf{T}} \left(\frac{\varepsilon + 1}{\varepsilon - 1} \mathbf{I} - \frac{1}{2\pi} \mathbf{A} \widetilde{\mathbf{D}}^{\mathsf{T}} \right) \left(\mathbf{R}_\infty^{-1} \right)^{\mathsf{T}} \qquad (A11)$$

where the superscript "T" denotes the transpose, the matrix $\mathbf{I}$ is the unit matrix, the matrix $\mathbf{S}$ is defined by eqn (19) in Ref. A3, $\mathbf{S}^{\mathrm{T}} = \mathbf{S}$, and $\mathbf{R}_{\infty} = \mathbf{I} - \dfrac{1}{2\pi}\widetilde{\mathbf{D}}\mathbf{A}$. The matrix $\mathbf{A}$ is diagonal, and it contains the values of surface element areas. The matrix $\widetilde{\mathbf{D}}$ is defined by eqn (21) in Ref. A3 where it is called $\mathbf{D}$. The matrix $\widetilde{\mathbf{D}}^{\mathrm{T}}$ is defined by eqn (20) in Ref. A3 where it is called $\mathbf{D}^{*}$.

1.3 The proof of eqn (22)

One can immediately derive eqn (22) using Partition II and eqn (14), eqn (A3), and eqn (A4). Using Partition I and eqn (13), eqn (A1), and eqn (A2), one can obtain the following equation:

$$\overline{\overline{\mathbf{Q}}}^{\mathrm{neq}} = -\mathbf{D}_{\varepsilon_{\mathrm{opt}}}^{-1}\overline{\overline{\mathbf{b}}} - \mathbf{D}_{\varepsilon_{\mathrm{opt}}}^{-1}\left[\frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{\varepsilon_0 - 1}(\mathbf{D}_{\varepsilon_{\mathrm{opt}}} - \mathbf{\Omega})\right]\mathbf{D}_{\varepsilon_0}^{-1}\overline{\mathbf{b}} \tag{A12}$$

Using eqns (A7) and (A8) for CPCM, one can modify the expression in brackets as

$$\frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{\varepsilon_0 - 1}(\mathbf{D}_{\varepsilon_{\mathrm{opt}}} - \mathbf{\Omega}) = \frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{(\varepsilon_0 - 1)(\varepsilon_{\mathrm{opt}} - 1)}\mathbf{\Omega} = \mathbf{D}_{\varepsilon_{\mathrm{opt}}} - \mathbf{D}_{\varepsilon_0} \tag{A13}$$

and then show that eqn (A12) becomes eqn (22).

Using eqns (A9) and (A10) and the IEF-PCM formalism of Ref. A1, one can obtain the following relation for the expression in brackets in eqn (A12):

$$\frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{\varepsilon_0 - 1}(\mathbf{D}_{\varepsilon_{\mathrm{opt}}} - \mathbf{\Omega}) = \frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{(\varepsilon_0 - 1)(\varepsilon_{\mathrm{opt}} - 1)}\left(\frac{1}{2}\mathbf{I} - \widetilde{\mathbf{D}}\right)^{-1}\mathbf{S} = \mathbf{D}_{\varepsilon_{\mathrm{opt}}} - \mathbf{D}_{\varepsilon_0} \tag{A14}$$

Again, eqn (A12) becomes equivalent to eqn (22). The validity of eqn (22) can also be proven by using eqns (A10) and (A11) within the most recent IEF-PCM formalism [see eqns (23–25) and eqns (34), (35) in Ref. A3] through the following sequence of equations:

$$\mathbf{D}_{\varepsilon_{\mathrm{opt}}} = -\frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{\varepsilon_{\mathrm{opt}} - 1}\mathbf{\Omega} - \frac{\varepsilon_0 - 1}{\varepsilon_{\mathrm{opt}} - 1}\mathbf{D}_{\varepsilon_0} \tag{A15}$$

$$\mathbf{S} = -\frac{\varepsilon_0 - \varepsilon_{\mathrm{opt}}}{\varepsilon_{\mathrm{opt}} - 1}\mathbf{S} + \frac{\varepsilon_0 - 1}{\varepsilon_{\mathrm{opt}} - 1}\mathbf{S} \tag{A16}$$

1.4 The proof of eqn (31)

Starting with Partition II's definition of $\overline{\overline{G}}_{\mathrm{P}}$ [see eqns (28–30) in the main text], one can express ω as follows

$$\omega = \langle \overline{\overline{\Psi}} | H_0 | \overline{\overline{\Psi}} \rangle - \langle \overline{\Psi} | H_0 | \overline{\Psi} \rangle + \frac{1}{2}\sum_m \overline{\overline{V}}_m \overline{\overline{Q}}_m^{\,\mathrm{dyn}} + \sum_m \left(\overline{\overline{V}}_m - \frac{1}{2}\overline{V}_m \right) \overline{Q}_m^{\,\mathrm{in}} - \frac{1}{2}\sum_m \overline{V}_m \overline{Q}_m$$

$$= \langle \overline{\overline{\Psi}} | H_0 | \overline{\overline{\Psi}} \rangle - \langle \overline{\Psi} | H_0 | \overline{\Psi} \rangle + \frac{1}{2}\sum_m \Delta V_m \Delta Q_m^{\,\mathrm{dyn}} + \frac{1}{2}\sum_m \Delta V_m \overline{Q}_m^{\,\mathrm{dyn}} + \frac{1}{2}\sum_m \overline{V}_m \Delta Q_m^{\,\mathrm{dyn}} + \sum_m \Delta V_m \overline{Q}_m^{\,\mathrm{in}}$$

$$= \overline{\overline{E}}_0 - \overline{E}_0 + \sum_m \Delta V_m \overline{Q}_m + \frac{1}{2}\sum_m \Delta V_m \Delta Q_m^{\,\mathrm{dyn}} \tag{A17}$$

where we used the following notations:

$$\Delta V_m = \overline{\overline{V}}_m - \overline{V}_m \tag{A18}$$

$$\Delta Q_m^{\,\mathrm{dyn}} = \overline{\overline{Q}}_m^{\,\mathrm{dyn}} - \overline{Q}_m^{\,\mathrm{dyn}} \tag{A19}$$

$$\overline{Q}_m = \overline{Q}_m^{\,\mathrm{dyn}} + \overline{Q}_m^{\,\mathrm{in}} \tag{A20}$$

$$\sum_m \overline{V}_m \Delta Q_m^{\,\mathrm{dyn}} = \sum_m \Delta V_m \overline{Q}_m^{\,\mathrm{dyn}} \tag{A21}$$

Note that eqn (A21) is exact within the CPCM formalism and also within the latest IEF-PCM formalism (Refs. A2 and A3), whereas it is approximate for the previous versions of IEF-PCM. This equation can be expressed in matrix form as follows

$$\mathbf{V}^{\mathsf{T}}\mathbf{\Delta Q}^{\mathrm{dyn}} = \mathbf{V}^{\mathsf{T}}\overline{\overline{\mathbf{Q}}}^{\mathrm{dyn}} - \mathbf{V}^{\mathsf{T}}\overline{\mathbf{Q}}^{\mathrm{dyn}} = -\mathbf{V}^{\mathsf{T}}\mathbf{D}_{\varepsilon_{\mathrm{opt}}}^{-1}\overline{\overline{\mathbf{V}}} + \mathbf{V}^{\mathsf{T}}\mathbf{D}_{\varepsilon_{\mathrm{opt}}}^{-1}\overline{\mathbf{V}}$$

$$= -(\mathbf{D}_{\varepsilon_{\mathrm{opt}}}^{-1}\overline{\mathbf{V}})^{\mathsf{T}}(\overline{\overline{\mathbf{V}}} - \overline{\mathbf{V}}) = \mathbf{\Delta V}^{\mathsf{T}}\overline{\mathbf{Q}}^{\mathrm{dyn}} \tag{A22}$$

1.5 The proof of eqns (32–36)

To obtain the GB expressions for reaction fields and polarization energy components, we use the following relations

$$\sum_m \frac{\overline{Q}_m}{|\mathbf{r} - \mathbf{r}_m|} = -\frac{\varepsilon_0 - 1}{\varepsilon_0} \sum_{n'} \gamma_{nn'} \overline{q}_{n'} \tag{A23}$$

$$\sum_m \frac{\overline{\overline{Q}}_m}{|\mathbf{r} - \mathbf{r}_m|} = -\frac{\varepsilon_0 - 1}{\varepsilon_0} \sum_{n'} \gamma_{nn'} \overline{\overline{q}}_{n'} \tag{A24}$$

$$\sum_m \overline{V}_m \overline{Q}_m = -\frac{\varepsilon_0 - 1}{\varepsilon_0} \sum_{n,n'} \overline{q}_n \gamma_{nn'} \overline{q}_{n'} \tag{A25}$$

$$\sum_m \overline{\overline{V}}_m \overline{\overline{Q}}_m = -\frac{\varepsilon_0 - 1}{\varepsilon_0} \sum_{n,n'} \overline{\overline{q}}_n \gamma_{nn'} \overline{\overline{q}}_{n'} \tag{A26}$$

$$\sum_m \overline{\overline{V}}_m \overline{Q}_m = -\frac{\varepsilon_0 - 1}{\varepsilon_0} \sum_{n,n'} \overline{\overline{q}}_n \gamma_{nn'} \overline{q}_{n'} \tag{A27}$$

In the equations above, the index m runs over all surface elements situated at the corresponding position $\mathbf{r}_m$, the index n or n' runs over all nuclei situated at $\mathbf{r}_n$ or $\mathbf{r}_{n'}$, $\gamma_{nn'}$ is the Coulomb integral, q_n or $q_{n'}$ is a partial atomic charge, and ε_0 is the static dielectric constant. The physical meaning of $\overline{\overline{Q}}_m$ in the context of nonequilibrium solvation will be specified later.

Equation (32) can be obtained immediately from eqn (5) with $Q_m = \overline{Q}_m$ and eqn (12), respectively. Equation (34) can be obtained from eqn (5) with $Q_m = \overline{\overline{Q}}_m^{\text{neq}}$ defined by eqn (22) as follows

$$\begin{aligned} \overline{\overline{\mathbf{Q}}}^{\text{neq}} &= -\mathbf{D}_{\varepsilon_{\text{opt}}}^{-1} \overline{\overline{\mathbf{b}}} - (\mathbf{D}_{\varepsilon_0}^{-1} - \mathbf{D}_{\varepsilon_{\text{opt}}}^{-1}) \overline{\mathbf{b}} = \mathbf{D}_{\varepsilon_{\text{opt}}}^{-1} \mathbf{D}_{\varepsilon_0} \overline{\overline{\mathbf{Q}}} + (\mathbf{D}_{\varepsilon_0}^{-1} - \mathbf{D}_{\varepsilon_{\text{opt}}}^{-1}) \mathbf{D}_{\varepsilon_0} \overline{\mathbf{Q}} \\ &= \overline{\mathbf{Q}} + \mathbf{D}_{\varepsilon_{\text{opt}}}^{-1} \mathbf{D}_{\varepsilon_0} (\overline{\overline{\mathbf{Q}}} - \overline{\mathbf{Q}}) = \overline{\mathbf{Q}} + \frac{\varepsilon_{\text{opt}} - 1}{\varepsilon_{\text{opt}}} \frac{\varepsilon_0}{\varepsilon_0 - 1} (\overline{\overline{\mathbf{Q}}} - \overline{\mathbf{Q}}) \end{aligned} \tag{A28}$$

where we use eqns (A7) and (A8) and the following equations:

$$\mathbf{D}_{\varepsilon_0}\overline{\mathbf{Q}} = -\overline{\mathbf{b}} \tag{A29}$$

$$\mathbf{D}_{\varepsilon_0}\overline{\overline{\mathbf{Q}}} = -\overline{\overline{\mathbf{b}}} \tag{A30}$$

Then, eqn (5) with $Q_m = \overline{\overline{Q}}_m^{\text{neq}}$ can be expressed as

$$
\begin{aligned}
\overline{\overline{\Phi}}(\mathbf{r}_n) &= \overline{\Phi}(\mathbf{r}_n) + \Delta\Phi(\mathbf{r}_n) = -\frac{\varepsilon_0-1}{\varepsilon_0}\sum_{n'}\gamma_{nn'}\overline{q}_{n'} - \frac{\varepsilon_{\text{opt}}-1}{\varepsilon_{\text{opt}}}\sum_{n'}\gamma_{nn'}(\overline{\overline{q}}_{n'}-\overline{q}_{n'}) \\
&= -\frac{\varepsilon_{\text{opt}}-1}{\varepsilon_{\text{opt}}}\sum_{n'}\gamma_{nn'}\overline{\overline{q}}_{n'} - \left(\frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_0}\right)\sum_{n'}\gamma_{nn'}\overline{q}_{n'}
\end{aligned}
\tag{A31}
$$

To prove eqn (35), we begin with eqns (28–30), and with the use of eqns (A3), (A4), (A7), (A8), (A29), and (A30) we obtain the following relation:

$$
\begin{aligned}
\overline{\overline{G}}_{\text{P}} &= \frac{1}{2}\sum_m \overline{\overline{V}}_m\overline{\overline{Q}}_m^{\text{dyn}} + \sum_m\left(\overline{\overline{V}}_m - \frac{1}{2}\overline{V}_m\right)\overline{Q}_m^{\text{in}} \\
&= \frac{1}{2}\frac{\varepsilon_{\text{opt}}-1}{\varepsilon_{\text{opt}}}\frac{\varepsilon_0}{\varepsilon_0-1}\sum_m\overline{V}_m\overline{\overline{Q}}_m + \frac{\varepsilon_0-\varepsilon_{\text{opt}}}{\varepsilon_{\text{opt}}(\varepsilon_0-1)}\sum_m\left(\overline{\overline{V}}_m - \frac{1}{2}\overline{V}_m\right)\overline{Q}_m
\end{aligned}
\tag{A32}
$$

Equation (35) can be obtained from eqn (A32) using eqns (A25–A27).

Equation (36) can be obtained from eqn (31) using the following relation:

$$\overline{\overline{\mathbf{Q}}}^{\text{dyn}} - \overline{\mathbf{Q}}^{\text{dyn}} = \overline{\overline{\mathbf{Q}}}^{\text{neq}} - \overline{\mathbf{Q}} = \frac{\varepsilon_{\text{opt}}-1}{\varepsilon_{\text{opt}}}\frac{\varepsilon_0}{\varepsilon_0-1}(\overline{\overline{\mathbf{Q}}}-\overline{\mathbf{Q}}) \tag{A33}$$

1.6 The proof of eqn (48)

Omitting the superscript (k), we can express eqn (48) as follows

$$\omega_{\text{VEM}} = \omega_{\text{VEM}}^* - \frac{1}{2}\sum_m (\overline{\overline{V}}_m - \overline{V}_m)(\overline{\overline{Q}}_m^{\text{dyn}} - \overline{Q}_m^{\text{dyn}}) = \omega_{\text{VEM}}^* - \frac{1}{2}\langle \overline{\overline{\Psi}} | \Delta\Phi | \overline{\overline{\Psi}}\rangle + \frac{1}{2}\langle \overline{\Psi} | \Delta\Phi | \overline{\Psi}\rangle$$

$$= \langle \overline{\overline{\Psi}} | H_0 | \overline{\overline{\Psi}}\rangle - \langle \overline{\Psi} | H_0 | \overline{\Psi}\rangle + \langle \overline{\overline{\Psi}} | \Phi | \overline{\overline{\Psi}}\rangle - \langle \overline{\Psi} | \Phi | \overline{\Psi}\rangle$$

$$+ \langle \overline{\overline{\Psi}} | \Delta\Phi | \overline{\overline{\Psi}}\rangle - \langle \overline{\Psi} | \Delta\Phi | \overline{\Psi}\rangle - \frac{1}{2}\langle \overline{\overline{\Psi}} | \Delta\Phi | \overline{\overline{\Psi}}\rangle + \frac{1}{2}\langle \overline{\Psi} | \Delta\Phi | \overline{\Psi}\rangle$$

$$= \langle \overline{\overline{\Psi}} | H_0 | \overline{\overline{\Psi}}\rangle - \langle \overline{\Psi} | H_0 | \overline{\Psi}\rangle + \langle \overline{\overline{\Psi}} | \Phi | \overline{\overline{\Psi}}\rangle - \langle \overline{\Psi} | \Phi | \overline{\Psi}\rangle + \frac{1}{2}\langle \overline{\overline{\Psi}} | \Delta\Phi | \overline{\overline{\Psi}}\rangle - \frac{1}{2}\langle \overline{\Psi} | \Delta\Phi | \overline{\Psi}\rangle$$

$$= \overline{\overline{E}}_0 - \overline{E}_0 + \frac{1}{2}\sum_m (\overline{\overline{V}}_m - \overline{V}_m)\overline{Q}_m + \frac{1}{2}\sum_m (\overline{\overline{V}}_m - \overline{V}_m)(\overline{\overline{Q}}_m^{\text{dyn}} - \overline{Q}_m^{\text{dyn}}) \tag{A34}$$

which is equivalent to eqn (31).

1.7 The PCM formalism in more detail

We have shown that eqn (22) remains valid within both partitions (Partition I and Partition II) when one uses the CPCM or IEF-PCM models. Here we show that Partition I and Partition II yield identical total reaction fields when one uses the original dielectric formulation of PCM (see Refs. A4 and A5).

The excited-state electronic polarization charge $\overline{\overline{Q}}_m^{\text{el}}$ on the mth surface element used by Partition I satisfies the following equation

$$\overline{\overline{Q}}_m^{\text{el}} = -\frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}}\Delta S_m \overline{\overline{E}}_n(\mathbf{r}_m; \overline{\overline{\Psi}}, \overline{\overline{\mathbf{Q}}}^{\text{neq}}) - \frac{\varepsilon_{\text{opt}} - 1}{\varepsilon_{\text{opt}}}\overline{Q}_m^{\text{or}} \tag{A35}$$

where ΔS_m is the area of the mth surface element situated at $\mathbf{r}_m$, and $\overline{\overline{E}}_n(\mathbf{r}_m)$ is the normal component of the total electric field due to the solute's charge density $\rho(\mathbf{r}; \overline{\overline{\Psi}})$ and the solvent's total polarization charges defined by the column vector $\overline{\overline{\mathbf{Q}}}^{\text{neq}}$; $\overline{\overline{E}}_n(\mathbf{r}_m)$ is taken at $\mathbf{r}_m$ on the internal side of the solute's cavity, i.e., *in vacuo* from the point of view of the dielectric. The orientational polarization charge $\overline{Q}_m^{\text{or}}$ is expressed as

$$\overline{Q}_m^{\text{or}} = \frac{\varepsilon_0 - \varepsilon_{\text{opt}}}{\varepsilon_0 - 1} \overline{Q}_m \tag{A36}$$

where $\overline{Q}_m$ is the total ground-state equilibrium polarization charge computed independently of

$\rho(\mathbf{r}; \overline{\overline{\Psi}})$ and $\overline{\overline{\mathbf{Q}}}^{\text{neq}}$. The total polarization charge $\overline{Q}_m$ satisfies the following equation:

$$\overline{Q}_m = -\frac{\varepsilon_0 - 1}{4\pi\varepsilon_0} \Delta S_m \overline{E}_{\text{n}}(\mathbf{r}_m; \overline{\Psi}, \overline{\mathbf{Q}}) \tag{A37}$$

where $\overline{E}_{\text{n}}(\mathbf{r}_m)$ is the normal component of the total electric field (taken inside the solute's cavity)

due to the solute's charge density $\rho(\mathbf{r}; \overline{\Psi})$ and the solvent's total polarization charges defined by

the column vector $\overline{\mathbf{Q}}$. The total nonequilibrium polarization charge in Partition I is

$$\overline{\overline{Q}}_m^{\text{neq}} = \overline{\overline{Q}}_m^{\text{el}} + \overline{Q}_m^{\text{or}} = -\frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}} \Delta S_m \overline{\overline{E}}_{\text{n}}(\mathbf{r}_m; \overline{\overline{\Psi}}, \overline{\overline{\mathbf{Q}}}^{\text{neq}}) + \frac{1}{\varepsilon_{\text{opt}}} \overline{Q}_m^{\text{or}} =$$

$$= -\frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}} \Delta S_m \overline{\overline{E}}_{\text{n}}(\mathbf{r}_m; \overline{\overline{\Psi}}, \overline{\overline{\mathbf{Q}}}^{\text{neq}}) + \frac{\varepsilon_0 - \varepsilon_{\text{opt}}}{\varepsilon_{\text{opt}}(\varepsilon_0 - 1)} \overline{Q}_m \tag{A38}$$

The excited-state dynamic polarization charge $\overline{\overline{Q}}_m^{\text{dyn}}$ used by Partition II satisfies the

following equation

$$\overline{\overline{Q}}_m^{\text{dyn}} = -\frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}} \Delta S_m \overline{\overline{E}}_{\text{n}}(\mathbf{r}_m; \overline{\overline{\Psi}}, \overline{\overline{\mathbf{Q}}}^{\text{neq}}) \tag{A39}$$

The corresponding inertial charge $\overline{Q}_m^{\text{in}}$ is expressed as

$$\overline{Q}_m^{\text{in}} = \overline{Q}_m - \overline{Q}_m^{\text{dyn}} = \overline{Q}_m + \frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}} \Delta S_m \overline{E}_{\text{n}}(\mathbf{r}_m; \overline{\Psi}, \overline{\mathbf{Q}}) = \frac{\varepsilon_0 - \varepsilon_{\text{opt}}}{\varepsilon_{\text{opt}}(\varepsilon_0 - 1)} \overline{Q}_m \tag{A40}$$

The total nonequilibrium polarization charge in Partition II is

$$\overline{\overline{Q}}_m^{\text{neq}} = \overline{\overline{Q}}_m^{\text{dyn}} + \overline{Q}_m^{\text{in}} = -\frac{\varepsilon_{\text{opt}} - 1}{4\pi\varepsilon_{\text{opt}}} \Delta S_m \overline{\overline{E}}_{\text{n}}(\mathbf{r}_m; \overline{\Psi}, \overline{\overline{\mathbf{Q}}}^{\text{neq}}) + \overline{Q}_m^{\text{in}} =$$

$$= -\frac{\varepsilon_{opt}-1}{4\pi\varepsilon_{opt}}\Delta S_m \overline{\overline{E}}_n(\mathbf{r}_m;\overline{\overline{\Psi}},\overline{\overline{\mathbf{Q}}}^{neq}) + \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_{opt}(\varepsilon_0 -1)}\overline{Q}_m \qquad (A41)$$

Keeping the slow polarization charges ($\overline{\mathbf{Q}}^{or}$ or $\overline{\mathbf{Q}}^{in}$) fixed at the their values defined by the column vector $\overline{\mathbf{Q}}$ calculated earlier, we compute the column vectors of fast polarization charges ($\overline{\overline{\mathbf{Q}}}^{el}$ or $\overline{\overline{\mathbf{Q}}}^{dyn}$) iteratively using the corresponding equations. At the first iteration, we approximate $\overline{\overline{E}}_n(\mathbf{r}_m;\overline{\overline{\Psi}},\overline{\overline{\mathbf{Q}}}^{neq})$ with $\overline{\overline{E}}_n(\mathbf{r}_m;\overline{\overline{\Psi}},\overline{\mathbf{Q}})$. The latter is determined using the reaction field $\Phi(\overline{\mathbf{Q}})$ induced by the ground-state polarization charges defined by the column vector $\overline{\mathbf{Q}}$ and the solute's charge density $\rho(\mathbf{r};\overline{\overline{\Psi}})$ corresponding to the excited-state wave function $\overline{\overline{\Psi}}$ evaluated using $\Phi = \Phi(\overline{\mathbf{Q}})$. Since the definition of $\overline{\overline{E}}_n(\mathbf{r}_m;\overline{\overline{\Psi}},\overline{\mathbf{Q}})$ does not involve partitioning, the quantity $\overline{\overline{E}}_n(\mathbf{r}_m)$ remains the same in eqn (A35) and eqn (A39). This leads to the same set of total charges $\overline{\overline{\mathbf{Q}}}^{neq}$ in Partition I and Partition II because the right-hand side of eqns (A38) and (A41) is the same when $\overline{\overline{E}}_n(\mathbf{r}_m)$ is identical. Using the new total reaction field $\Phi(\overline{\overline{\mathbf{Q}}}^{neq})$, we evaluate $\overline{\overline{\Psi}}$, $\rho(\mathbf{r};\overline{\overline{\Psi}})$, and $\overline{\overline{E}}_n(\mathbf{r}_m;\overline{\overline{\Psi}},\overline{\overline{\mathbf{Q}}}^{neq})$ again. The latter quantity retains the same value in both partitions because $\Phi(\overline{\overline{\mathbf{Q}}}^{neq})$ is partition-independent. We repeat the procedure until it converges self-consistently with respect to $\overline{\overline{\mathbf{Q}}}^{neq}$.

Equations (A38) and (A41) can be rewritten in the matrix form as

$$\overline{\overline{\mathbf{Q}}}^{neq} = \frac{\varepsilon_{opt}-1}{\varepsilon_{opt}}\frac{\varepsilon_0}{\varepsilon_0 -1}\overline{\overline{\mathbf{Q}}} + \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_{opt}(\varepsilon_0 -1)}\overline{\mathbf{Q}} \qquad (A42)$$

where the components of the column vector $\overline{\overline{\mathbf{Q}}}$ satisfy the following condition

$$\bar{\bar{Q}}_m = -\frac{\varepsilon_0 - 1}{4\pi\varepsilon_0} \Delta S_m \bar{\bar{E}}_n (\mathbf{r}_m; \bar{\bar{\Psi}}, \bar{\bar{\mathbf{Q}}}^{neq}) \tag{A43}$$

In the case of excited-state equilibrium solvation ($\varepsilon_{opt} = \varepsilon_0$), the quantity $\bar{\bar{Q}}_m$ simply means the

total equilibrium ("eq") excited-state electronic polarization charge, $\bar{\bar{Q}}_m^{eq}$. However, in the case of

excited-state nonequilibrium solvation ($\varepsilon_{opt} \neq \varepsilon_0$), the quantity $\bar{\bar{Q}}_m$ defined by eqn (A43) is not

the same as $\bar{\bar{Q}}_m^{eq}$ or $\bar{\bar{Q}}_m^{neq}$. Note that for the ground state we have $\bar{\mathbf{Q}} = \bar{\mathbf{Q}}^{eq} = \bar{\mathbf{Q}}^{neq}$ where the

quantity $\bar{\mathbf{Q}}$ satisfies eqn (A29). We can express eqns (A35) and (A39) as

$$\bar{\bar{\mathbf{Q}}}^{el} = \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \left(\frac{\varepsilon_0}{\varepsilon_0 - 1} \bar{\bar{\mathbf{Q}}} - \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1} \bar{\mathbf{Q}} \right) \tag{A44}$$

$$\bar{\bar{\mathbf{Q}}}^{dyn} = \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \frac{\varepsilon_0}{\varepsilon_0 - 1} \bar{\bar{\mathbf{Q}}} \tag{A45}$$

Using eqn (A42), we can express the partition-independent PCM total excited-state

reaction field as

$$\bar{\bar{\Phi}}(\mathbf{r}) = \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \frac{\varepsilon_0}{\varepsilon_0 - 1} \sum_m \frac{\bar{\bar{Q}}_m}{|\mathbf{r} - \mathbf{r}_m|} + \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_{opt}(\varepsilon_0 - 1)} \sum_m \frac{\bar{Q}_m}{|\mathbf{r} - \mathbf{r}_m|} \tag{A46}$$

and we can rewrite the equations for individual components of the polarization free energy $\bar{\bar{G}}_P$

for Partition I as

$$\bar{\bar{G}}_{P,el} = \frac{1}{2} \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \frac{\varepsilon_0}{\varepsilon_0 - 1} \sum_m \bar{\bar{V}}_m \bar{\bar{Q}}_m - \frac{1}{2} \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1} \sum_m \bar{\bar{V}}_m \bar{Q}_m \tag{A47}$$

$$\bar{\bar{G}}_{P,or} = \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1} \sum_m \left(\bar{\bar{V}}_m - \frac{1}{2} \bar{V}_m \right) \bar{Q}_m \tag{A48}$$

$$\bar{\bar{G}}_{P,el\text{-}or} = \frac{1}{2} \frac{\varepsilon_{opt} - 1}{\varepsilon_{opt}} \frac{\varepsilon_0 - \varepsilon_{opt}}{\varepsilon_0 - 1} \frac{\varepsilon_0}{\varepsilon_0 - 1} \sum_{m,m'} \frac{(\bar{\bar{Q}}_{m'} - \bar{Q}_{m'})}{|\mathbf{r}_m - \mathbf{r}_{m'}|} \bar{Q}_m \tag{A49}$$

and for Partition II as

$$\overline{\overline{G}}_{\mathrm{P,dyn}} = \frac{1}{2}\frac{\varepsilon_{\mathrm{opt}}-1}{\varepsilon_{\mathrm{opt}}}\frac{\varepsilon_0}{\varepsilon_0-1}\sum_m \overline{\overline{V}}_m \overline{\overline{Q}}_m \tag{A50}$$

$$\overline{\overline{G}}_{\mathrm{P,in}} = \frac{\varepsilon_0-\varepsilon_{\mathrm{opt}}}{\varepsilon_{\mathrm{opt}}(\varepsilon_0-1)}\sum_m \left(\overline{\overline{V}}_m - \frac{1}{2}\overline{V}_m\right)\overline{\overline{Q}}_m \tag{A51}$$

The polarization free energy $\overline{\overline{G}}_{\mathrm{P}}$ in Partition I differs from the one derived in Partition II according to the following equation

$$\overline{\overline{G}}_{\mathrm{P}}(\mathrm{I}) - \overline{\overline{G}}_{\mathrm{P}}(\mathrm{II}) = \frac{1}{2}\frac{\varepsilon_{\mathrm{opt}}-1}{\varepsilon_{\mathrm{opt}}}\frac{\varepsilon_0-\varepsilon_{\mathrm{opt}}}{\varepsilon_0-1}\sum_m (\overline{\overline{V}}_m - \overline{V}_m)\overline{\overline{Q}}_m + \overline{\overline{G}}_{\mathrm{P,el-or}} \tag{A52}$$

Although the magnitude of the difference is likely to depend on a particular PCM model and the solute's molecular cavity, one can reasonably expect that it approaches zero. Using eqns (6) and (8) from Ref. A1 for CPCM, we can make the following approximation for $\overline{\overline{V}}_m$ and $\overline{V}_m$

$$V_m = -\frac{\varepsilon_0}{\varepsilon_0-1}\sum_{m'}\frac{Q_{m'}}{|\mathbf{r}_m - \mathbf{r}_{m'}|} \tag{A53}$$

When applied to eqn (A52), eqn (A53) leads to $\overline{\overline{G}}_{\mathrm{P}}(\mathrm{I}) - \overline{\overline{G}}_{\mathrm{P}}(\mathrm{II}) = 0$.

Note that in the most recent IEF-PCM formulation (see Refs. A2 and A3) defines the reaction field by eqns (8) and (9) in the main text. In this case, eqn (A46) is replaced by

$$\overline{\overline{\Phi}}(\mathbf{r}) = \frac{\varepsilon_{\mathrm{opt}}-1}{\varepsilon_{\mathrm{opt}}}\frac{\varepsilon_0}{\varepsilon_0-1}\sum_m \left[\int_C d\mathbf{r}'\frac{\phi_m(\mathbf{r}'-\mathbf{r}_m)}{|\mathbf{r}-\mathbf{r}'|}\right]\overline{\overline{Q}}_m + \frac{\varepsilon_0-\varepsilon_{\mathrm{opt}}}{\varepsilon_{\mathrm{opt}}(\varepsilon_0-1)}\sum_m \left[\int_C d\mathbf{r}'\frac{\phi_m(\mathbf{r}'-\mathbf{r}_m)}{|\mathbf{r}-\mathbf{r}'|}\right]\overline{Q}_m \tag{A54}$$

where the integral in brackets is taken over the cavity C, and the quantity ϕ_m is defined in Refs. A2 and A3. Equation (A49) is replaced by

$$\overline{\overline{G}}_{\mathrm{P,el-or}} = \frac{1}{2}\frac{\varepsilon_{\mathrm{opt}}-1}{\varepsilon_{\mathrm{opt}}}\frac{\varepsilon_0-\varepsilon_{\mathrm{opt}}}{\varepsilon_0-1}\frac{\varepsilon_0}{\varepsilon_0-1}\sum_{m,m'}\overline{Q}_m S_{mm'}(\overline{\overline{Q}}_{m'} - \overline{Q}_{m'}) \tag{A55}$$

where the matrix $\mathbf{S}$ is defined in Ref. A2. Equation (53) is replaced by

$$V_m = -\frac{\varepsilon_0}{\varepsilon_0 - 1} \sum_{m'} \left[\int_C d\mathbf{r}' \frac{\phi_m(\mathbf{r}' - \mathbf{r}_m)}{|\mathbf{r} - \mathbf{r}'|} \right] Q_{m'} \tag{A56}$$

When applied to eqn (A52), eqn (A56) also leads to $\overline{\overline{G}}_P(\text{I}) - \overline{\overline{G}}_P(\text{II}) = 0$.

The GB expressions of Partition I's and Partition II's individual components of the nonequilibrium excited-state polarization free energy given by eqns (A47–A51) can be readily obtained using eqns (A25–A27) and eqn (A53). The latter equation is used to convert eqn (A49), thereby leading to $\overline{\overline{G}}_P(\text{I}) - \overline{\overline{G}}_P(\text{II}) = 0$.

2. Description of the VEM(d,RD)/GB method

Within the VEM(d) approach, we consider only the diagonal (d) elements of the $\Delta\Phi^{(k)}$ state-specific reaction field operator in eqn (46). In this case, eqn (46) is replaced by

$$H_{ia,jb}^{\text{VEM}(k)} = \delta_{ij}\delta_{ab}\left[\varepsilon_a + \Delta\varepsilon_a - \varepsilon_i - \Delta\varepsilon_i\right] - (ja \,\|\, ib) \tag{A57}$$

where the quantity $\Delta\varepsilon_p$ ($p = a$ or i) is defined as

$$\Delta\varepsilon_p = \langle\psi_p \,|\, \Delta\Phi^{(k)} \,|\, \psi_p\rangle = \langle\psi_p \,|\, \overline{\overline{\Phi}}^{(k)} \,|\, \psi_p\rangle - \langle\psi_p \,|\, \overline{\Phi} \,|\, \psi_p\rangle \tag{A58}$$

using notations adopted in the main text. The quantities ε_p and ψ_p ($p = a$ or i) are obtained from an equilibrium ground-state SCRF calculation, and they do not depend on k. The VEM excitation energy at the kth iteration is calculated by eqn (48) which can be expressed as

$$\begin{aligned}
\omega_{\text{VEM}}^{(k)} &= \langle\overline{\overline{\Psi}}^{(k)} \,|\, H_0 + \overline{\Phi} \,|\, \overline{\overline{\Psi}}^{(k)}\rangle - \langle\overline{\Psi} \,|\, H_0 + \overline{\Phi} \,|\, \overline{\Psi}\rangle \\
&\quad + \frac{1}{2}\langle\overline{\overline{\Psi}}^{(k)} \,|\, \Delta\Phi^{(k)} \,|\, \overline{\overline{\Psi}}^{(k)}\rangle - \frac{1}{2}\langle\overline{\Psi} \,|\, \Delta\Phi^{(k)} \,|\, \overline{\Psi}\rangle
\end{aligned} \tag{A59}$$

Within the VEM(d) protocol, the VEM excitation energy can be calculated simply as the corresponding eigenvalue of the CIS matrix defined by the following equation

$$H_{ia,jb}^{\text{VEM(d)}(k)} = \delta_{ij}\delta_{ab}\left[\varepsilon_a + \frac{1}{2}\Delta\varepsilon_a - \varepsilon_i - \frac{1}{2}\Delta\varepsilon_i\right] - (ja \,\|\, ib) \tag{A60}$$

where the quantity $\Delta\varepsilon_p$ ($p = a$ or i) is defined by eqn (A58).

Within the VEM(d,RD)/GB protocol, the quantity $\overline{\Phi}$ is calculated by eqn (32), and the quantity $\overline{\overline{\Phi}}^{(k)}$ is calculated by eqn (34) using a set of excited-state partial atomic charges $\overline{\overline{q}}^{(k-1)}$ computed at the previous VEM iteration based on the relaxed density (RD) approach.

3. Excitation energies of acetone, acrolein, methanal, and pyridine in water and the corresponding gas–water solvatochromic shifts (in cm^{-1}) computed using the hydrogen-bonding contribution correction ($\Delta\omega_H$)

3.1 The GBSD/CIS/INDO/S2 method

protocol	ω_{water}	$\omega_{gas} - \omega_{water}$	ω_{water}	$\omega_{gas} - \omega_{water}$
	acetone, n $\to \pi^*$ ($^1A_2$)		acrolein, n $\to \pi^*$ ($^1A''$)	
GSRF	35673	−2618	33462	−3076
cGSRF	35314	−2259	33008	−2622
VEM(f,UD)	35303	−2248	32963	−2577
IBSF	37271	−4216	35319	−4933
IESRF	35266	−2211	32859	−2473
reference	37760	−1785	31746	−1984
	methanal, n $\to \pi^*$ ($^1A_2$)		pyridine, n $\to \pi^*$ ($^1B_1$)	
GSRF	35402	−2057	37243	−2415
cGSRF	35140	−1794	36980	−2152
VEM(f,UD)	35131	−1786	36959	−2132
IBSF	36445	−3100	38010	−3183
IESRF	35108	−1763	36893	−2066
reference	33079	−1785	39813	−2490

3.2 The GBAD/TDDFT/M06/MG3S method

protocol	ω_{water}	$\omega_{gas} - \omega_{water}$	ω_{water}	$\omega_{gas} - \omega_{water}$
	acetone, n $\to \pi^*$ ($^1A_2$)		acrolein, n $\to \pi^*$ ($^1A''$)	
GSRF	38671	−2604	32934	−3317
VEM(d,RD)	38247	−2180	32057	−2440
IBSF	40529	−4462	34272	−4655
IESRF	38408	−2341	32289	−2672
reference	37760	−1785	31746	−1984
	methanal, n $\to \pi^*$ ($^1A_2$)		pyridine, n $\to \pi^*$ ($^1B_1$)	
GSRF	33833	−1881	40277	−2421
VEM(d,RD)	33585	−1633	39758	−1902
IBSF	35030	−3078	41074	−3218
IESRF	33524	−1572	39782	−1926
reference	33079	−1785	39813	−2490

3.2 The PCM/TDDFT/M06/MG3S method

protocol	ω_{water}	$\omega_{gas} - \omega_{water}$	ω_{water}	$\omega_{gas} - \omega_{water}$
	acetone, n → π* ($^1A_2$)		acrolein, n → π* ($^1A''$)	
GSRF	39289	−3222	33097	−3480
cGSRF	39061	−2994	32644	−3027
VEM(f,RD)	38637	−2570	31493	−1876
VEM(d,RD)	38625	−2558	31373	−1756
VEM(d,UD)	38530	−2463	31108	−1491
LR	39224	−3157	33040	−3423
cLR	38936	−2869	32310	−2693
IBSF	41020	−4953	34278	−4661
IBSF [a]	39229	−3162	32865	−3248
reference	37760	−1785	31746	−1984
	methanal, n → π* ($^1A_2$)		pyridine, n → π* ($^1B_1$)	
GSRF	34598	−2646	41221	−3365
cGSRF	34281	−2329	40880	−3024
VEM(f,RD)	33910	−1958	39993	−2137
VEM(d,RD)	33915	−1963	39994	−2138
VEM(d,UD)	33832	−1880	39795	−1939
LR	34481	−2529	41146	−3290
cLR	34191	−2239	40613	−2757
IBSF	35360	−3408	41798	−3942
IBSF [a]	34491	−2539	41441	−3585
reference	33079	−1785	39813	−2490

[a] This calculation was carried out using the UFF Coulomb radii scaled by the factor of 1.1; all the other PCM calculations were carried out using the SMD radii.