

Laue-RISM, ESM-RISM

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1. Laue-RISM

Although Laue-RISM calculates the solute-solvent correlation functions as the same as 3D-RISM, a Laue representation is imposed on the correlation functions, which are periodic on the xy -plane and not periodic along the z -direction. It is possible to apply the Fourier transformation technique on the xy -plane. However, one must deal with the correlation functions in real space along the z -direction. This treatment of the correlation functions allows us to calculate the isolated slab in the solvent system. In addition, we do not need the canonical condition, and the total charge of the solvent system is automatically optimized to screen the electrostatic potential of the solute system. This means that we can obtain the solvent distribution under the grand canonical condition in the solvent system. For example, if the solute slab has a $+1.0e$ charge, the Laue-RISM calculation leads to a solvent distribution whose total charge is $-1.0e$.

1.1. RISM equation

In the Laue-RISM calculation, the Laue representation works to solve the RISM equation. We convert it to the Laue representation to obtain the equation:

$$h_\gamma(\mathbf{g}_\parallel, z) = \sum_\alpha \int_{-\infty}^{\infty} dz' c_\alpha(\mathbf{g}_\parallel, z') \chi_{\alpha\gamma}(\mathbf{g}_\parallel, z' - z). \quad (1)$$

1.2. Solvent susceptibility

In the right-hand side of Eq. 1, $\chi_{\alpha\gamma}(\mathbf{g}_\parallel, z' - z)$ is the Laue-represented solvent susceptibility. It is obtained to apply the Fourier transformation to 1D-RISM's solvent susceptibility $\chi_{\alpha\gamma}(g)$ along g_z , as

$$\begin{aligned} \chi_{\alpha\gamma}(\mathbf{g}_\parallel, z' - z) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dg_z \chi_{\alpha\gamma}(g) e^{ig_z(z' - z)} \\ &= \frac{1}{\pi} \int_0^{\infty} dg_z \chi_{\alpha\gamma}(g) \cos[g_z(z' - z)], \end{aligned} \quad (2)$$

where the integration $\int dg_z$ is performed with the reciprocal space mesh of the 1D-RISM calculation. While $\chi_{\alpha\gamma}(g)$ contains the intra-molecular correlation function $\omega_{\alpha\gamma}(g)$, the delta function of $\omega_{\alpha\gamma}(g)$ causes huge noise when integrating the right-hand side of Eq. 2. To avoid this noise, we introduce Gaussian broadening of $\omega_{\alpha\gamma}(g)$. We also introduce an analytical integration to Eq. 2

$$\begin{aligned} \frac{1}{\pi} \int_0^{\infty} dg_z \omega_{\alpha\gamma}(g) \cos[g_z(z' - z)] \\ = \frac{1}{\sqrt{\pi}\kappa} \exp\left(-\frac{(z' - z)^2}{\kappa^2} - \frac{g_\parallel^2 \kappa^2}{4}\right), \end{aligned} \quad (3)$$

if $\alpha = \gamma$.

1.3. Charge neutrality condition

Deep inside the solvent (far away from the slab surface), $h_\alpha(\mathbf{g}_\parallel, z)$ becomes 0 and $g_\alpha(\mathbf{g}_\parallel, z)$ becomes 1, that is, the solvent distribution is uniform. Because the uniform solvent system is always electrically neutral, the condition about charges q_α and densities ρ_α of all the solvent atomic sites is required as

$$\sum_\alpha q_\alpha \rho_\alpha = 0. \quad (4)$$

The 1D-RISM calculation with the condition of Eq. 4 results in a solvent atomic site (γ) electrostatically screened by the other sites, that is,

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$$\begin{aligned} \sum_{\alpha} q_{\alpha} \rho_{\alpha} h_{\alpha\gamma}(g=0) &= -Q_{\gamma}, \\ \sum_{\alpha} q_{\alpha} \omega_{\alpha\gamma}(g=0) &= Q_{\gamma}, \end{aligned} \quad (5)$$

where Q_{γ} is the total charge of a molecule where the site γ belongs. Eq. 5 provides a condition about solvent susceptibility:

$$\sum_{\alpha} q_{\alpha} \chi_{\alpha\gamma}(g=0) = 0. \quad (6)$$

1.4. Domain of solvent

In Eq. 1, we have to define the domain of total correlation functions $h_{\gamma}(\mathbf{g}_{\parallel}, z)$. Its straightforward definition is $-\infty < z < \infty$. For numerical calculation, the domain is replaced with $-R < z < R$, where R is sufficiently large. It is assumed $h_{\gamma}(\mathbf{g}_{\parallel}, z) = 0$ outside of $-R < z < R$. We call this domain of the solvent “solvent/slab/solvent”.

If the solute is a slab system, we can define the domain of the solvent only on the right-hand side of the slab. Thus, $h_{\gamma}(\mathbf{g}_{\parallel}, z)$ is defined in $a \leq z < \infty$ (Fig. 1), which we call “vacuum/slab/solvent”. Although z is restricted in the right-hand side of the slab, the integration of Eq. 1 is performed still in $-\infty < z' < \infty$. However, $c_{\alpha}(\mathbf{g}_{\parallel}, z')$ is not defined in $-\infty < z' < a$. To perform the integration, we have to extrapolate $c_{\alpha}(\mathbf{g}_{\parallel}, z')$ outside the domain of the solvent. While $c_{\alpha}(\mathbf{g}_{\parallel}, z')$ is uniform in the xy -plane inside the slab, we consider only to extrapolate $c_{\alpha}(\mathbf{g}_{\parallel} = 0, z')$. The asymptotic behavior at the left vacuum region of $c_{\alpha}(\mathbf{g}_{\parallel} = 0, z')$ needs to have the following form: $c_{\alpha}(\mathbf{g}_{\parallel} = 0, z')$ is defined with the slope of the electrostatic potential b , as

$$\begin{aligned} c_{\alpha}(\mathbf{g}_{\parallel} = 0, z') &= c_{\alpha}(\mathbf{g}_{\parallel} = 0, a) \\ &\quad - \beta q_{\alpha} b (z' - a), \end{aligned} \quad (7)$$

where $-\infty < z' < a$ (see Fig. 2) and b is the gradient of the electrostatic potential of the “solute”. Owing to Eq. 7, the solvent system completely screens the solute electrostatic potential and the total charge of the solvent system becomes opposite to that of the solute system. Also, summation of the electrostatic potentials of the

solvent system and the solute system converges to a finite value when $z \rightarrow \pm\infty$. It is worth mentioning that since $h_{\gamma}(\mathbf{g}_{\parallel}, z)$ needs to be -1 (and $g_{\gamma}(\mathbf{g}_{\parallel}, z) = 0$) deep inside the slab and the left vacuum region, we can derive a sum rule for the direct correlation function at this region. At $z = a$, we can easily show the sum rule as

$$\sum_{\alpha} c_{\alpha}(\mathbf{g}_{\parallel} = 0, a) \chi_{\alpha\gamma}(g=0) = -1. \quad (8)$$

1.5. Solvation free energy

The definitions of the solvent free energy are available not only for 3D-RISM but also for Laue-RISM. However, in the present work, we implemented only the GF model using Laue representation as

$$\begin{aligned} \Delta\mu_{solv} &= \frac{S}{\beta} \sum_{\alpha} \rho_{\alpha} \int dz \left[-c_{\alpha}(\mathbf{g}_{\parallel} = 0, z) \right. \\ &\quad \left. - \frac{1}{2} \sum_{\mathbf{g}_{\parallel}} h_{\alpha}(\mathbf{g}_{\parallel}, z) c_{\alpha}^{*}(\mathbf{g}_{\parallel}, z) \right], \end{aligned} \quad (9)$$

where S is the area of the xy -plane. Integration in the right-hand side of Eq. 9 is performed through the domain of the solvent.

1.6. Solvent charge density

Although the solvent charge density ρ_{RISM} has to be calculated, we approximate it as

$$\rho_{solv}(\mathbf{g}_{\parallel}, z) = \sum_{\alpha} q_{\alpha} \rho_{\alpha} h_{\alpha}(\mathbf{g}_{\parallel}, z). \quad (10)$$

Because $g_{\alpha}(\mathbf{r}) = h_{\alpha}(\mathbf{r}) + 1$, when the Laue-RISM calculation is converged. Additionally, we consider the charge neutrality condition.

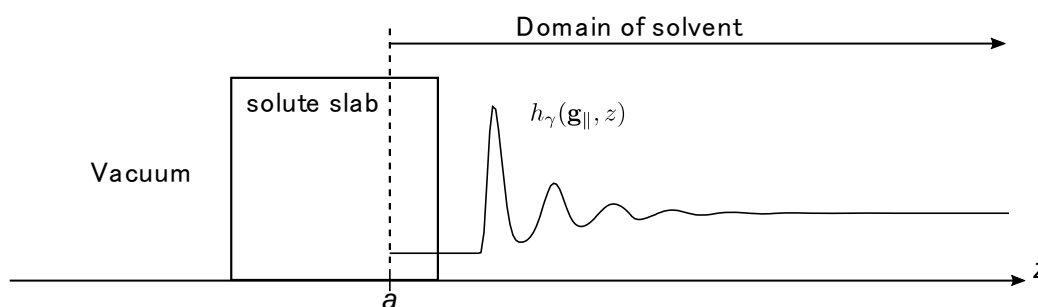


FIG. 1: Domain of the solvent defined on the right-hand side of a slab.

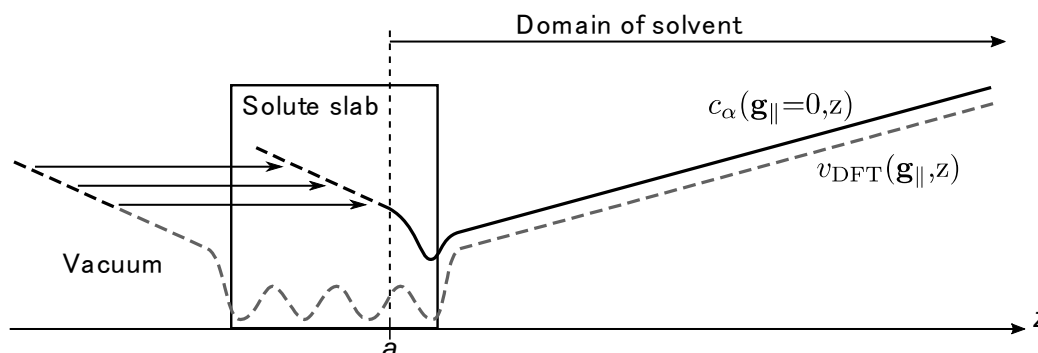


FIG. 2: Extrapolation of the direct correlation function (black line) outside the domain of the solvent, using the electrostatic potential (red line) of the solute slab.

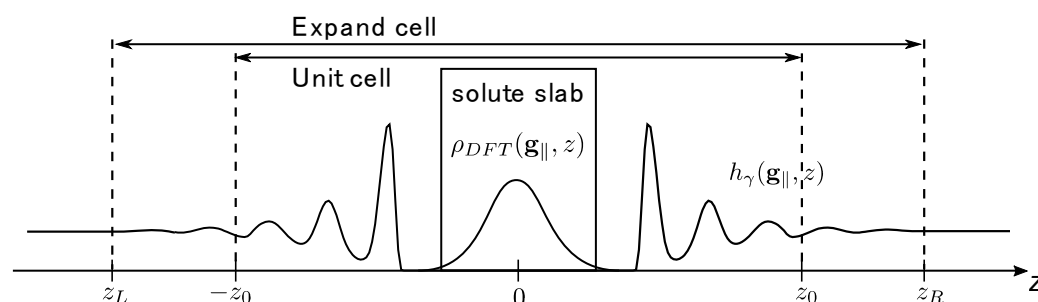


FIG. 3: The unit cell and expanded cell along the z-axis.

2. ESM-RISM

Laue-RISM calculation requires an electrostatic potential of solute in the Laue representation, that is, it is necessary to replace the electrostatic potential obtained under the mixed boundary condition (MBC) instead of under 3D PBC; where MBC means 2D PBC along the surface lateral direction and the open boundary condition (OBC) along the surface normal direction. Here, we apply the ESM method with OBC (vacuum/slab/vacuum), which deals with an isolated slab system. We put the domains of the solvent on the right-hand side and/or the left-hand side of the vacuum regions beside the slab. Finally, the models become solvent/slab/solvent and

vacuum/slab/solvent. The electronic structure is optimized with the Laue-RISM calculation as an analogy of 3D-RISM-SCF. We call this calculation combining the ESM and Laue-RISM methods “ESM-RISM”.

2.1. Expanded cell

The ESM method defines a unit cell as $[-z_0, z_0]$, and it requires the solute slab to be located around $z = 0$ (Fig. 3). It is assumed that the electronic wave function and charge density are localized inside the unit cell, and both of the functions must be zero at $z = \pm z_0$. However, although $h_\gamma(\mathbf{g}_\parallel, z)$ of the Laue-RISM calculation becomes zero a constant value (0 or -1) when $z \rightarrow \pm\infty$,

it converges more slowly than the electronic wave function. Then, we introduced an expanded cell, where the Laue-RISM calculation is performed (Fig. 3). The expanded cell is defined as $[z_L, z_R]$, where $z_L \leq -z_0$ and $z_0 \leq z_R$. If the boundary condition is vacuum/slab/solvent, $z_L = -z_0$. DFT calculation is still performed in the unit cell $[-z_0, z_0]$.

2.2. Electrostatic potential of ESM method

The ESM method requires the Laue-represented Green's function about the Poisson equation:

$$G(\mathbf{g}_{\parallel}, z - z') = \frac{4\pi}{2g_{\parallel}} e^{-g_{\parallel}|z-z'|}. \quad (11)$$

If $\mathbf{g}_{\parallel} = 0$, Eq. 11 becomes

$$G(\mathbf{g}_{\parallel} = 0, z - z') = \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} - 2\pi|z - z'|. \quad (12)$$

Multiplying the Green's function and charge density and with convolution, yields the electrostatic potential.

2.3. Diverging term of electrostatic potential

If the solute slab is charged, the long-range electrostatic potential contains a diverging term, that is, the first term of the right-hand side of Eq. S46. Taking the diverging term into account at $\mathbf{g}_{\parallel} = 0$, long-range part of solute potential becomes

$$u_{\alpha}^L(\mathbf{g}_{\parallel} = 0, z) = -q_{\alpha} v^L(\mathbf{g}_{\parallel} = 0, z) + \frac{q_{\alpha} q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\}, \quad (13)$$

where q_{DFT} is the total charge of the solute slab and $v^L(\mathbf{g}_{\parallel} = 0, z)$ does not have a diverging term. Substituting Eq. S62 for RISM equation causes

$$\begin{aligned} & -\beta \sum_{\alpha} \int_{-\infty}^{\infty} dz' u_{\alpha}^L(\mathbf{g}_{\parallel}, z') \chi_{\alpha\gamma}(\mathbf{g}_{\parallel}, z' - z) \\ & = -\beta \sum_{\alpha} \int_{-\infty}^{\infty} dz' \left[-q_{\alpha} v^L(\mathbf{g}_{\parallel} = 0, z') \right. \\ & \quad \left. + \frac{q_{\alpha} q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \chi_{\alpha\gamma}(\mathbf{g}_{\parallel}, z' - z) \end{aligned} \quad (14)$$

$$\begin{aligned} & = -\beta \sum_{\alpha} \int_{-\infty}^{\infty} dz' [-q_{\alpha} v^L(\mathbf{g}_{\parallel} = 0, z')] \chi_{\alpha\gamma}(\mathbf{g}_{\parallel}, z' \\ & - z) \\ & - \beta \sum_{\alpha} \int_{-\infty}^{\infty} dz' \left[\frac{q_{\alpha} q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \chi_{\alpha\gamma}(\mathbf{g}_{\parallel}, z' \\ & - z) \\ & = -\beta \sum_{\alpha} \int_{-\infty}^{\infty} dz' [-q_{\alpha} v^L(\mathbf{g}_{\parallel} = 0, z')] \chi_{\alpha\gamma}(\mathbf{g}_{\parallel}, z' \\ & - z) - \beta \left[\frac{q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \sum_{\alpha} q_{\alpha} \chi_{\alpha\gamma}(g = 0). \end{aligned}$$

The second term of the right-hand side of Eq. 14 becomes zero, because of the charge neutrality condition. Thus, we can neglect the diverging term to solve the RISM equation.

2.4. Total energy

Energy of the solute slab calculated by DFT with ESM method is

$$\begin{aligned} E_{DFT} & = E_{kin} + E_{XC} \\ & + \frac{S}{2} \sum_{\mathbf{g}_{\parallel}} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel}, z) G(\mathbf{g}_{\parallel}, z \\ & - z') \rho_{DFT}^*(\mathbf{g}_{\parallel}, z'), \end{aligned} \quad (15)$$

where E_{kin} and E_{XC} are the electronic kinetic energy and exchange correlation energy, respectively. ρ_{DFT} is the charge density of the solute system, which contains the densities of the electrons and ion cores. The third term of the right-hand side of Eq. 15 is the electrostatic energy, and it is expanded as

$$\begin{aligned} & \frac{S}{2} \sum_{\mathbf{g}_{\parallel}} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel}, z) G(\mathbf{g}_{\parallel}, z \\ & - z') \rho_{DFT}^*(\mathbf{g}_{\parallel}, z') \\ & = \frac{S}{2} \sum_{\mathbf{g}_{\parallel} \neq 0} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel}, z) G(\mathbf{g}_{\parallel}, z \\ & - z') \rho_{DFT}^*(\mathbf{g}_{\parallel}, z') \\ & + \frac{S}{2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel} \\ & = 0, z) \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \rho_{DFT}^*(\mathbf{g}_{\parallel} \\ & = 0, z') \end{aligned} \quad (16)$$

$$\begin{aligned}
& -\frac{S}{2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel} \\
& \quad = 0, z) \{2\pi|z - z'|\} \rho_{DFT}^*(\mathbf{g}_{\parallel} \\
& \quad = 0, z'),
\end{aligned}$$

where the first and third term of the right-hand side can be calculated easily. The matter is the second term, which includes the divergence of $4\pi/2g_{\parallel}$. And it becomes

$$\begin{aligned}
& \frac{S}{2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \rho_{DFT}(\mathbf{g}_{\parallel} \\
& \quad = 0, z) \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \rho_{DFT}^*(\mathbf{g}_{\parallel} \\
& \quad = 0, z') = \frac{q_{DFT}^2}{2S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\}.
\end{aligned} \quad (17)$$

If the solute slab is neutral ($q_{DFT} = 0$), Eq. 17 becomes zero and one can define E_{DFT} as a finite number. However, if the solute slab is charged ($q_{DFT} \neq 0$), Eq. S66 is diverging and one cannot obtain E_{DFT} with the open boundary condition (OBC).

However, the free energy of ESM-RISM method is defined as

$$A = E_{DFT} + \Delta\mu_{solv}, \quad (18)$$

where $\Delta\mu_{solv}$ is the solvation free energy defined as Eq. 9. Although direct correlation contributes to calculate $\Delta\mu_{solv}$, its long-range part has a diverging term. To evaluate the diverging term in $\Delta\mu_{solv}$, $c_{\alpha}(\mathbf{g}_{\parallel}, z)$ is replaced for $-\beta u_{\alpha}^L(\mathbf{g}_{\parallel}, z)$ as

$$\begin{aligned}
& \frac{S}{\beta} \sum_{\alpha} \rho_{\alpha} \int dz \left[\beta u_{\alpha}^L(\mathbf{g}_{\parallel} = 0, z) \right. \\
& \quad \left. + \frac{1}{2} \sum_{\mathbf{g}_{\parallel}} h_{\alpha}(\mathbf{g}_{\parallel}, z) \beta u_{\alpha}^{L*}(\mathbf{g}_{\parallel}, z) \right]
\end{aligned} \quad (19)$$

$$\begin{aligned}
& = S \sum_{\alpha} \rho_{\alpha} q_{\alpha} \int dz \left[-v^L(\mathbf{g}_{\parallel} = 0, z) \right. \\
& \quad \left. + \frac{q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \\
& \quad + \frac{S}{2} \sum_{\alpha} \rho_{\alpha} q_{\alpha} \int dz h_{\alpha}(\mathbf{g}_{\parallel} \\
& \quad = 0, z) [-v^L(\mathbf{g}_{\parallel} = 0, z)] \\
& \quad + \frac{S}{2} \sum_{\alpha} \rho_{\alpha} q_{\alpha} \int dz h_{\alpha}(\mathbf{g}_{\parallel} \\
& \quad = 0, z) \left[\frac{q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \\
& \quad + \frac{S}{2} \sum_{\alpha} \rho_{\alpha} \int dz \left[\sum_{\mathbf{g}_{\parallel} \neq 0} h_{\alpha}(\mathbf{g}_{\parallel}, z) u_{\alpha}^{L*}(\mathbf{g}_{\parallel}, z) \right],
\end{aligned}$$

where the charge neutrality condition lets the first term of the right-hand side become zero. The second term and fourth term of the right-hand side are able to be calculated easily. The third term is diverging and it becomes

$$\begin{aligned}
& \frac{S}{2} \sum_{\alpha} \rho_{\alpha} q_{\alpha} \int dz h_{\alpha}(\mathbf{g}_{\parallel} \\
& \quad = 0, z) \left[\frac{q_{DFT}}{S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \\
& \quad = \int dz \rho_{sol}(\mathbf{g}_{\parallel} = 0, z) \left[\frac{q_{DFT}}{2} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\} \right] \\
& \quad = \frac{q_{solv} q_{DFT}}{2S} \left\{ \lim_{g_{\parallel} \rightarrow 0} \frac{4\pi}{2g_{\parallel}} \right\},
\end{aligned} \quad (20)$$

where the definition of the solvent charge density is applied for the first equality. q_{solv} is the total charge of solvent system. In the Laue-RISM calculation, the charge density of the solvent system screens the charged solute slab completely, and one can mention that

$$q_{solv} = -q_{DFT}. \quad (21)$$

Thus, the divergence of the solvent free energy cancels out that of the energy of the DFT. The free energy A is always calculated as a finite number even if the solute slab is charged in OBC, although one cannot define E_{DFT} or $\Delta\mu_{solv}$ by itself.

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