Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Computation of DNP coupling factors of a nitroxide radical in toluene: Seamless combination of MD simulations and analytical calculations

Supplementary material

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I. REVISITING THE FFHS MODEL

A. Solving for $g_l(r, r_0; s)$

Here we follow the derivation of Ref. 1. Taking the Laplace transform of the diffusion equation

$$\frac{\partial}{\partial t} P(\mathbf{r}, t|\mathbf{r}_0) = D\nabla^2 P(\mathbf{r}, t|\mathbf{r}_0) \tag{1}$$

and using the initial condition

$$P(\mathbf{r}, 0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{2}$$

results in

$$sP(\mathbf{r}, s|\mathbf{r}_0) - \delta(\mathbf{r} - \mathbf{r}_0) = D\nabla^2 P(\mathbf{r}, s|\mathbf{r}_0), \tag{3}$$

where $P(\mathbf{r}, s|\mathbf{r}_0)$ is the Laplace transform of the transition probability density. Defining

$$\kappa \equiv \sqrt{s/D}, \tag{4}$$

the last equation can be written as

$$(\nabla^2 - \kappa^2) P(\mathbf{r}, s|\mathbf{r}_0) = -\frac{1}{D}\delta(\mathbf{r} - \mathbf{r}_0). \tag{5}$$

Due to the linearity of the Laplace transform, the boundary conditions

$$\left.\frac{\partial P(\mathbf{r}, t|\mathbf{r}_0)}{\partial r}\right|_{r=b} = 0, \quad P(\mathbf{r}, t|\mathbf{r}_0) \underset{r\to\infty}{\to} 0 \tag{6}$$

apply to $P(\mathbf{r}, s|\mathbf{r}_0)$ as well. These boundary conditions are most conveniently imposed in spherical polar coordinates where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} \tag{7}$$

and

$$\delta(\mathbf{r} - \mathbf{r}_0) = \frac{\delta(r - r_0)}{r^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_l^m(\theta, \phi) Y_l^{m*}(\theta_0, \phi_0). \tag{8}$$

We look for a solution of (5) of the form

$$P(\mathbf{r}, s|\mathbf{r}_0) = \sum_{l=0}^{\infty} g_l(r, r_0; s) \sum_{m=-l}^{l} Y_l^m(\theta, \phi) Y_l^{m*}(\theta_0, \phi_0). \tag{9}$$

Substituting (8) and (9) in (5) it is found that $g_l(r, r_0; \kappa)$—now as a function of κ—should satisfy

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial g_l}{\partial r}\right) - [r^2\kappa + l(l+1)] g_l = -\frac{1}{D}\delta(r - r_0) \tag{10}$$

subject to the boundary conditions

$$\left.\frac{\partial g_l(r, r_0; \kappa)}{\partial r}\right|_{r=b} = 0, \quad g_l(r, r_0; \kappa) \underset{r\to\infty}{\to} 0. \tag{11}$$

From (10) we conclude that $g_l(r, r_0; \kappa)$ is a linear combination of the spherical modified Bessel functions $i_l(\kappa r)$ and $k_l(\kappa r)$.

In the interval $r = [b, r_0]$ we impose the hard-wall (reflecting) boundary condition and write g_l to the left as

$$g_l^<(r, r_0; \kappa) = A_l \left[i_l(\kappa r) - \beta_l(\kappa b) k_l(\kappa r)\right], \tag{12}$$

where we have defined

$$\beta_l(x) \equiv \frac{i_l'(x)}{k_l'(x)}. \tag{13}$$

Strictly speaking, the primes in this expression should denote derivatives with respect to r. However, since β_l is the ratio of two such derivatives, the primes can be treated as derivatives with respect to the argument of the function.

In the interval $r = [r_0, \infty)$ we require that g_l vanishes for $r \to \infty$ and write the Green's function to the right as

$$g_l^>(r, r_0; \kappa) = B_l k_l(\kappa r). \tag{14}$$

The continuity of the Green's function at $r = r_0$ implies

$$B_l = A_l \left[\frac{i_l(\kappa r_0)}{k_l(\kappa r_0)} - \beta_l(\kappa b)\right], \tag{15}$$

There is a jump in the first derivative at $r = r_0$. The magnitude of this jump in going from the left to the right is equal to $-1/D$ divided by r_0^2. Thus,

$$A_l \left[i_l'(\kappa r_0) - \beta_l(\kappa b) k_l'(\kappa r_0)\right] - B_l k_l'(\kappa r_0) = \frac{1}{\kappa r_0^2 D}. \tag{16}$$

The κ on the right appears because prime denotes a derivative with respect to the argument, not with respect to r.

Substituting (15) in (16) we deduce that

$$A_l = \frac{1}{\kappa r_0^2 D}\frac{1}{W(\kappa r_0)} k_l(\kappa r_0) = \frac{\kappa}{D} k_l(\kappa r_0), \qquad (17)$$

where W denotes the Wronskian

$$W(\kappa r_0) = k_l(\kappa r_0) i_l'(\kappa r_0) - i_l(\kappa r_0) k_l'(\kappa r_0) = \frac{1}{\kappa^2 r_0^2} \qquad (18)$$

of the spherical modified Bessel functions $i_l(\kappa r)$ and $k_l(\kappa r)$. Note that the primes here denote derivatives with respect to the argument (κr_0) and not with respect to r_0.

Substitution in (15) yields

$$\begin{aligned} B_l &= \frac{1}{\kappa r_0^2 D}\frac{1}{W(\kappa r_0)}\left[i_l(\kappa r_0) - \beta_l(\kappa b) k_l(\kappa r_0)\right] \\ &= \frac{\kappa}{D}\left[i_l(\kappa r_0) - \beta_l(\kappa b) k_l(\kappa r_0)\right]. \end{aligned} \qquad (19)$$

Putting everything together, we find

$$g_l^<(r, r_0; \kappa) = \frac{\kappa}{D} k_l(\kappa r_0)[i_l(\kappa r) - \beta_l(\kappa b) k_l(\kappa r)],\ b \le r \le r_0 \qquad (20)$$

and

$$g_l^>(r, r_0; \kappa) = \frac{\kappa}{D}[i_l(\kappa r_0) - \beta_l(\kappa b) k_l(\kappa r_0)] k_l(\kappa r),\ r \ge r_0. \qquad (21)$$

B. The FFHS spectral density $J^{\mathrm{ffhs}}(\omega)$

Again, the calculation is based on Ref. 1. To perform the integrals for $G(s)$ and evaluate them for $s = \mathrm{i}\omega$ we will need to use the expressions[1]

$$\int_0^d \mathrm{d}r \frac{i_2(\kappa r)}{r} = \frac{I_{3/2}(\kappa d)}{(\kappa d)^{3/2}},\quad \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} = \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}}, \qquad (22)$$

as well as the relations[1]

$$i_l(z) = z^{-1/2} I_{l+1/2}(z), \quad k_l(z) = z^{-1/2} K_{l+1/2}(z) \qquad (23)$$

between the spherical modified Bessel functions and the modified Bessel functions. Finally,[1]

$$I_{5/2}(z) K_{3/2}(z) + K_{5/2}(z) I_{3/2}(z) = 1/z \qquad (24)$$

is also necessary.

The determined functional form of $g_2(r, r_0; \kappa)$ changes depending on whether r is smaller or larger than r_0. Thus, we split the integral and evaluate

$$\begin{aligned} G^{\mathrm{ffhs}}(s) = &\underbrace{\int_b^\infty \mathrm{d}r \int_r^\infty \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^<(r, r_0; \kappa)}_{r<r_0} \\ &+ \underbrace{\int_b^\infty \mathrm{d}r \int_b^r \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^>(r, r_0; \kappa)}_{r>r_0}. \end{aligned} \qquad (25)$$

The first integral is

$$\begin{aligned} &\frac{\kappa}{D}\left[\int_b^\infty \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_r^\infty \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} \right. \\ &\left. -\beta_2(\kappa b) \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_r^\infty \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0}\right], \end{aligned} \qquad (26)$$

whereas the second integral is

$$\begin{aligned} &\frac{\kappa}{D}\left[\int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} \right. \\ &\left. -\beta_2(\kappa b) \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0}\right]. \end{aligned} \qquad (27)$$

The sum of the two integral is

$$G^{\mathrm{ffhs}}(s) = \frac{\kappa}{D}\left[\int_b^\infty \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_r^\infty \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} + \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} - \beta_2(\kappa b)\left(\int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r}\right)^2\right]. \qquad (28)$$

For the first integral in the square brackets of (28) we find

$$\mathcal{I}_1 \equiv \int_b^\infty \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_r^\infty \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} = \int_b^\infty \mathrm{d}r \frac{i_2(\kappa r)}{r} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} = \int_b^\infty \mathrm{d}r \frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}}, \qquad (29)$$

where (23) was used to write the last equality. For the second integral in the square brackets of (28) we find

$$\begin{aligned} \mathcal{I}_2 \equiv \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} &= \int_b^\infty \mathrm{d}r \frac{k_2(\kappa r)}{r}\left[\frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \\ &= \int_b^\infty \mathrm{d}r \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}} \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}}. \end{aligned} \qquad (30)$$

Again, we used (23) to write the last equality. The sum of these two results is

$$\mathcal{I}_1 + \mathcal{I}_2 = \int_b^\infty \mathrm{d}r \left[\frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} + \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}}\right] - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}} \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}}. \qquad (31)$$

Using (24),

$$\int_b^\infty \mathrm{d}r \left[\frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} + \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} \right] = \int_b^\infty \mathrm{d}r \frac{1}{r(\kappa r)^3} = \frac{1}{3} \frac{1}{(\kappa b)^3}. \tag{32}$$

Finally, the third integral in the square brackets of (28) is

$$\mathcal{I}_3 \equiv \left[\int_b^\infty \mathrm{d}r \frac{k_l(\kappa r)}{r} \right]^2 = \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} \right]^2. \tag{33}$$

Putting all these results together,

$$G^{\mathrm{ffhs}}(s) = \frac{\kappa}{D}(\mathcal{I}_1 + \mathcal{I}_2 - \beta_2(\kappa b)\mathcal{I}_3) = \frac{\kappa}{D} \frac{1}{(\kappa b)^3} \left[\frac{1}{3} - I_{3/2}(\kappa b) K_{3/2}(\kappa b) - \beta_2(\kappa b) K_{3/2}^2(\kappa b) \right].$$

This expression has to be evaluated for $s = \mathrm{i}\omega$, i.e., $\kappa = \sqrt{\mathrm{i}\omega/D}$. With

$$x \equiv b\sqrt{\mathrm{i}\omega/D} \tag{34}$$

we find

$$\boxed{G^{\mathrm{ffhs}}(\mathrm{i}\omega) = \frac{1}{Db} \frac{1}{x^2} \left[\frac{1}{3} - I_{3/2}(x) K_{3/2}(x) - \beta_2(x) K_{3/2}^2(x) \right].} \tag{35}$$

This is the expression given in the main text. It is the well-known result of Refs. 1 and 2.

C. The long range-long range FFHS spectral density $J_{\mathrm{ll}}^{\mathrm{ffhs}}(\omega)$

In this case we need to evaluate

$$G_{\mathrm{ll}}^{\mathrm{ffhs}}(s) = \int_d^\infty \mathrm{d}r \int_r^\infty \mathrm{d}r_0 \frac{1}{r} \frac{1}{r_0} g_2^<(r, r_0; \kappa) + \int_d^\infty \mathrm{d}r \int_d^r \mathrm{d}r_0 \frac{1}{r} \frac{1}{r_0} g_2^>(r, r_0; \kappa). \tag{36}$$

Clearly, the calculation is identical to the one above with d replacing b in the limits of integration. Hence, with

$$y \equiv d\sqrt{\mathrm{i}\omega/D}, \tag{37}$$

$$\boxed{G_{\mathrm{ll}}^{\mathrm{ffhs}}(\mathrm{i}\omega) = \frac{1}{Dd} \frac{1}{y^2} \left[\frac{1}{3} - I_{3/2}(y) K_{3/2}(y) - \beta_2(x) K_{3/2}^2(y) \right].} \tag{38}$$

This expression first appeared in the supplementary material of Ref. 3.

D. The short range-short range FFHS spectral density $J_{\mathrm{ss}}^{\mathrm{ffhs}}(\omega)$

The calculation runs as before, the only difference being that now the limits of integration do not go to infinity but are restricted to the finite domain $r < d$:

$$G_{\mathrm{ss}}^{\mathrm{ffhs}}(s) = \int_b^d \mathrm{d}r \int_r^d \mathrm{d}r_0 \frac{1}{r} \frac{1}{r_0} g_2^<(r, r_0; \kappa) + \int_b^d \mathrm{d}r \int_b^r \mathrm{d}r_0 \frac{1}{r} \frac{1}{r_0} g_2^>(r, r_0; \kappa). \tag{39}$$

To perform the integrals in this case we use

$$\int_b^d \mathrm{d}r \frac{i_2(\kappa r)}{r} = \frac{I_{3/2}(\kappa d)}{(\kappa d)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}, \qquad \int_b^d \mathrm{d}r \frac{k_2(\kappa r)}{r} = \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}} \tag{40}$$

for $b < d$, which follow from (22).

As before,

$$G_{\rm ss}^{\rm ffhs}(\kappa) = \frac{\kappa}{D}\left[\int_b^d {\rm d}r \frac{i_2(\kappa r)}{r}\int_r^d {\rm d}r_0 \frac{k_2(\kappa r_0)}{r_0} + \int_b^d {\rm d}r \frac{k_2(\kappa r)}{r}\int_b^r {\rm d}r_0 \frac{i_2(\kappa r_0)}{r_0} - \beta_2(\kappa b)\left(\int_b^d {\rm d}r \frac{k_2(\kappa r)}{r}\right)^2\right]. \tag{41}$$

For the first integral in the square brackets of (41) we find

$$\begin{aligned}\mathcal{I}_1 \equiv \int_b^d {\rm d}r \frac{i_2(\kappa r)}{r}\int_r^d {\rm d}r_0 \frac{k_2(\kappa r_0)}{r_0} &= \int_b^d {\rm d}r \frac{i_2(\kappa r)}{r}\left[\frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right] \\ &= \int_b^d {\rm d}r \frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}}\frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \left[\frac{I_{3/2}(\kappa d)}{(\kappa d)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right]\frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}.\end{aligned} \tag{42}$$

For the second integral in the square brackets of (41) we find

$$\begin{aligned}\mathcal{I}_2 \equiv \int_b^d {\rm d}r \frac{k_2(\kappa r)}{r}\int_b^r {\rm d}r_0 \frac{i_2(\kappa r_0)}{r_0} &= \int_b^d {\rm d}r \frac{k_2(\kappa r)}{r}\left[\frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \\ &= \int_b^d {\rm d}r \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}}\frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right].\end{aligned} \tag{43}$$

Finally, the third integral in the square brackets of (41) is

$$\mathcal{I}_3 \equiv \left[\int_b^d {\rm d}r \frac{k_l(\kappa r)}{r}\right]^2 = \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right]^2. \tag{44}$$

Using

$$\int_b^d {\rm d}r\left[\frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}}\frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} + \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}}\frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}}\right] = \frac{1}{3}\left[\frac{1}{(\kappa b)^3} - \frac{1}{(\kappa d)^3}\right], \tag{45}$$

we can evaluate the sum in the square brackets of (41) as

$$\begin{aligned}\mathcal{I}_1 + \mathcal{I}_2 - \beta_2(\kappa b)\mathcal{I}_3 = {} & \frac{1}{3}\left[\frac{1}{(\kappa b)^3} - \frac{1}{(\kappa d)^3}\right] - \left[\frac{I_{3/2}(\kappa d)}{(\kappa d)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right]\frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}} \\ & - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right] - \beta_2(\kappa b)\left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right]^2.\end{aligned} \tag{46}$$

Thus, when evaluated at $s = {\rm i}\omega$, $G_{\rm ss}^{\rm ffhs}$ becomes

$$\boxed{\begin{aligned}G_{\rm ss}^{\rm ffhs}({\rm i}\omega) = \frac{1}{Db}\frac{1}{x^2}\Big\{ & \frac{1}{3}\left[1-(b/d)^3\right] - \left[(b/d)^{3/2}I_{3/2}(y) - I_{3/2}(x)\right](b/d)^{3/2}K_{3/2}(y) \\ & - I_{3/2}(x)\left[K_{3/2}(x) - (b/d)^{3/2}K_{3/2}(y)\right] - \beta_2(x)\left[K_{3/2}(x) - (b/d)^{3/2}K_{3/2}(y)\right]^2\Big\}.\end{aligned}} \tag{47}$$

E. The short range-long range FFHS spectral density $J_{\rm sl}^{\rm ffhs}(\omega)$

In this case $r_0 \in [b, d]$ and $r \in [d, \infty)$, thus r_0 is always smaller than r. Therefore,

$$G_{\rm sl}^{\rm ffhs}(s) = \int_d^\infty {\rm d}r \int_b^d {\rm d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^{>}(r, r_0; \kappa) = \frac{\kappa}{D}\int_d^\infty {\rm d}r \frac{k_2(\kappa r)}{r}\int_b^d {\rm d}r_0 \frac{i_2(\kappa r_0) - \beta_2(\kappa b)k_2(\kappa r_0)}{r_0}. \tag{48}$$

Performing the integration we find

$$G_{\rm sl}^{\rm ffhs}(s) = \frac{\kappa}{D}\frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\left\{\left[\frac{I_{3/2}(\kappa d)}{(\kappa d)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] - \beta_2(\kappa b)\left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa d)}{(\kappa d)^{3/2}}\right]\right\}. \tag{49}$$

For $s = \mathrm{i}\omega$ this becomes

$$\boxed{G_{\rm sl}^{\rm ffhs}(\mathrm{i}\omega) = \frac{1}{Db}\frac{1}{x^2}(b/d)^{3/2}K_{3/2}(y)\left\{\left[(b/d)^{3/2}I_{3/2}(y) - I_{3/2}(x)\right] - \beta_2(x)\left[K_{3/2}(x) - (b/d)^{3/2}K_{3/2}(y)\right]\right\}.} \tag{50}$$

One can calculate $G_{\rm ls}^{\rm ffhs}$ in a similar manner and observe that it is identical to $G_{\rm sl}^{\rm ffhs}$, as evident by the symmetry of the problem under exchange of r_0 and r.

II. FFHS MODEL WITH ABSORBING OUTER BOUNDARY CONDITION

In this case, the boundary conditions are

$$\left.\frac{\partial P(\mathbf{r},t|\mathbf{r}_0)}{\partial r}\right|_{r=b} = 0, \quad P(\mathbf{r},t|\mathbf{r}_0)|_{r=a} = 0. \tag{51}$$

For $g_l(r,r_0;\kappa)$ these imply

$$\left.\frac{\partial g_l(r,r_0;\kappa)}{\partial r}\right|_{r=b} = 0, \quad g_l(r,r_0;\kappa)|_{r=a} = 0. \tag{52}$$

As in the previous section, in the interval $r = [b, r_0]$ we impose the hard sphere inner boundary condition and write g_l to the left as

$$g_l^<(r,r_0;\kappa) = A_l\left[i_l(\kappa r) - \beta_l(\kappa b)k_l(\kappa r)\right], \tag{53}$$

where $\beta_l(x)$ was defined in (13). In the interval $r = [r_0, a]$ we impose the absorbing boundary condition and write g_l to the right as

$$g_l^>(r,r_0;\kappa) = B_l\left[i_l(\kappa r) - \alpha_l(\kappa a)k_l(\kappa r)\right], \tag{54}$$

where

$$\alpha_l(z) \equiv \frac{i_l(z)}{k_l(z)}. \tag{55}$$

The continuity of g_l at $r = r_0$ implies

$$B_l = A_l\frac{i_l(\kappa r_0) - \beta_l(\kappa b)k_l(\kappa r_0)}{i_l(\kappa r_0) - \alpha_l(\kappa a)k_l(\kappa r_0)}. \tag{56}$$

The jump in the first derivative of g_l at $r = r_0$ yields

$$A_l\left[i_l'(\kappa r_0) - \beta_l(\kappa b)k_l'(\kappa r_0)\right] - B_l\left[i_l'(\kappa r_0) - \alpha_l(\kappa a)k_l'(\kappa r_0)\right] = \frac{1}{\kappa r_0^2 D}. \tag{57}$$

As before, the κ on the right appears because prime denotes a derivative with respect to the argument, not with respect to r. Using the expression for the Wronskian (18) we find

$$A_l = \frac{\kappa}{D}\frac{i_l(\kappa r_0) - \alpha_l(\kappa a)k_l(\kappa r_0)}{\beta_l(\kappa b) - \alpha_l(\kappa a)}, \qquad B_l = \frac{\kappa}{D}\frac{i_l(\kappa r_0) - \beta_l(\kappa b)k_l(\kappa r_0)}{\beta_l(\kappa b) - \alpha_l(\kappa a)}. \tag{58}$$

Thus, limiting our interest to $l = 2$ only, for $b \le r \le r_0$ we have

$$g_2^<(r,r_0;\kappa) = \frac{\kappa}{D}\frac{i_2(\kappa r)i_2(\kappa r_0) + \alpha_2(\kappa a)\beta_2(\kappa b)k_2(\kappa r)k_2(\kappa r_0) - \alpha_2(\kappa a)i_2(\kappa r)k_2(\kappa r_0) - \beta_2(\kappa b)k_2(\kappa r)i_2(\kappa r_0)}{\beta_2(\kappa b) - \alpha_2(\kappa a)}, \tag{59}$$

whereas for $b \le r_0 \le r \le a$,

$$g_2^>(r,r_0;\kappa) = \frac{\kappa}{D}\frac{i_2(\kappa r)i_2(\kappa r_0) + \alpha_2(\kappa a)\beta_2(\kappa b)k_2(\kappa r)k_2(\kappa r_0) - \alpha_2(\kappa a)k_2(\kappa r)i_2(\kappa r_0) - \beta_2(\kappa b)i_2(\kappa r)k_2(\kappa r_0)}{\beta_2(\kappa b) - \alpha_2(\kappa a)}. \tag{60}$$

A. The finite-size (fs) FFHS spectral density $J^{\mathrm{abs}}(\omega)$

As before, the determined functional form of $g_2(r, r_0; \kappa)$ changes depending on whether r is smaller or larger than r_0. Thus, we split the integral and evaluate

$$G^{\mathrm{abs}}(s) = \underbrace{\int_b^a \mathrm{d}r \int_r^a \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^{<}(r, r_0; \kappa)}_{r<r_0} + \underbrace{\int_b^a \mathrm{d}r \int_b^r \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^{>}(r, r_0; \kappa)}_{r>r_0}. \tag{61}$$

Looking at the form of $g_l(r, r_0; \kappa)$ it is clear that $G^{\mathrm{abs}}(s)$ will have the form

$$G^{\mathrm{abs}}(s) = \frac{\kappa}{D} \frac{J^1 + \alpha_2(\kappa a)\beta_2(\kappa b)J^2 - \alpha_2(\kappa a)J^3 - \beta_2(\kappa b)J^4}{\beta_2(\kappa b) - \alpha_2(\kappa a)}, \tag{62}$$

where the J^i's need to be determined by performing the integrations.

We immediately see that

$$J^1 = \int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_b^a \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} = \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right]^2 \tag{63}$$

and

$$J^2 = \int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^a \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} = \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right]^2. \tag{64}$$

The other two integrals are

$$J^3 = \int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_r^a \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} + \int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} \tag{65}$$

and

$$J^4 = \int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_r^a \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} + \int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0}. \tag{66}$$

For the first integral of J^3 we find

$$\begin{aligned}\int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_r^a \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} &= \int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \left[\frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right] \\ &= \int_b^a \mathrm{d}r \frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}},\end{aligned} \tag{67}$$

where (23) was used to write the last integral. For the second integral of J^3 we find

$$\begin{aligned}\int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} &= \int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \left[\frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \\ &= \int_b^a \mathrm{d}r \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}} - \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right] \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}.\end{aligned} \tag{68}$$

Adding (67) and (68), and using (24) to deduce that

$$\int_b^a \mathrm{d}r \left[\frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}} + \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}}\right] = \int_b^a \mathrm{d}r \frac{1}{\kappa^3 r^4} = \frac{1}{3}\left[\frac{1}{(\kappa b)^3} - \frac{1}{(\kappa a)^3}\right]$$

yields

$$J^3 = \frac{1}{3}\left[\frac{1}{(\kappa b)^3} - \frac{1}{(\kappa a)^3}\right] - \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right] \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}. \tag{69}$$

For the first integral of J^4 we find

$$\begin{aligned}\int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_r^a \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0} &= \int_b^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}}\right] \\ &= \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right] \frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \int_b^a \mathrm{d}r \frac{K_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{I_{3/2}(\kappa r)}{(\kappa r)^{3/2}}.\end{aligned} \tag{70}$$

For the second integral of J^4 we find

$$\begin{aligned}\int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_b^r \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0} &= \int_b^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}}\right] \\ &= \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \int_b^a \mathrm{d}r \frac{I_{5/2}(\kappa r)}{r(\kappa r)^{1/2}} \frac{K_{3/2}(\kappa r)}{(\kappa r)^{3/2}}.\end{aligned} \tag{71}$$

Adding (70) and (71)yields

$$J^4 = \frac{1}{3}\left[\frac{1}{(\kappa a)^3} - \frac{1}{(\kappa b)^3}\right] + \left[\frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}} - \frac{K_{3/2}(\kappa a)}{(\kappa a)^{3/2}}\right] \frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} + \left[\frac{I_{3/2}(\kappa a)}{(\kappa a)^{3/2}} - \frac{I_{3/2}(\kappa b)}{(\kappa b)^{3/2}}\right] \frac{K_{3/2}(\kappa b)}{(\kappa b)^{3/2}}. \tag{72}$$

To obtain the spectral density, $G^{\mathrm{abs}}(s)$ has to be evaluated for $s = \mathrm{i}\omega$, i.e., $\kappa = \sqrt{\mathrm{i}\omega/D}$. With

$$z \equiv a\sqrt{\mathrm{i}\omega/D} \tag{73}$$

we find

$$\boxed{G^{\mathrm{abs}}(\mathrm{i}\omega) = \frac{x}{Db} \frac{J^1 + \alpha_2(z)\beta_2(x)J^2 - \alpha_2(z)J^3 - \beta_2(x)J^4}{\beta_2(x) - \alpha_2(z)},} \tag{74}$$

where

$$\boxed{\begin{aligned} J^1 &= \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right]^2, \qquad J^2 = \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right]^2, \\ J^3 &= \frac{1}{3}\left[\frac{1}{x^3} - \frac{1}{z^3}\right] - \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right] \frac{K_{3/2}(z)}{z^{3/2}} - \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right] \frac{I_{3/2}(x)}{x^{3/2}}, \\ J^4 &= \frac{1}{3}\left[\frac{1}{z^3} - \frac{1}{x^3}\right] + \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right] \frac{I_{3/2}(z)}{z^{3/2}} + \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right] \frac{K_{3/2}(x)}{x^{3/2}}. \end{aligned}} \tag{75}$$

B. The long range-long range fs-FFHS spectral density $J_{\mathrm{ll}}^{\mathrm{abs}}(\omega)$

Similarly to the situation without absorbing boundary, $G_{\mathrm{ll}}^{\mathrm{abs}}$ follows directly from G^{abs} after replacing b with d (and x with y) in the limits of integration (but not in the argument of β). Hence,

$$\boxed{G_{\mathrm{ll}}^{\mathrm{abs}}(\mathrm{i}\omega) = \frac{x}{Db} \frac{J_{\mathrm{ll}}^1 + \alpha_2(z)\beta_2(x)J_{\mathrm{ll}}^2 - \alpha_2(z)J_{\mathrm{ll}}^3 - \beta_2(x)J_{\mathrm{ll}}^4}{\beta_2(x) - \alpha_2(z)},} \tag{76}$$

with

$$\boxed{\begin{aligned} J_{\mathrm{ll}}^1 &= \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(y)}{y^{3/2}}\right]^2, \qquad J_{\mathrm{ll}}^2 = \left[\frac{K_{3/2}(y)}{y^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right]^2, \\ J_{\mathrm{ll}}^3 &= \frac{1}{3}\left[\frac{1}{y^3} - \frac{1}{z^3}\right] - \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(y)}{y^{3/2}}\right] \frac{K_{3/2}(z)}{z^{3/2}} - \left[\frac{K_{3/2}(y)}{y^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right] \frac{I_{3/2}(y)}{y^{3/2}}, \\ J_{\mathrm{ll}}^4 &= \frac{1}{3}\left[\frac{1}{z^3} - \frac{1}{y^3}\right] + \left[\frac{K_{3/2}(y)}{y^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right] \frac{I_{3/2}(z)}{z^{3/2}} + \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(y)}{y^{3/2}}\right] \frac{K_{3/2}(y)}{y^{3/2}}. \end{aligned}} \tag{77}$$

C. The short range-short range fs-FFHS spectral density $J^{\rm abs}_{\rm ss}(\omega)$

In this case we need to evaluate

$$G^{\rm abs}_{\rm ss}(s) = \int_b^d \mathrm{d}r \int_r^d \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^<(r, r_0; \kappa) + \int_b^d \mathrm{d}r \int_b^r \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^>(r, r_0; \kappa). \tag{78}$$

We immediately see that the evaluation of the integrals is identical to the one carried out above for $G_{\rm abs}$, with the only difference that the upper limit is now d instead of a. Hence, we have

$$\boxed{G^{\rm abs}_{\rm ss}(\mathrm{i}\omega) = \frac{x}{Db} \frac{J^1_{\rm ss} + \alpha_2(z)\beta_2(x)J^2_{\rm ss} - \alpha_2(z)J^3_{\rm ss} - \beta_2(x)J^4_{\rm ss}}{\beta_2(x) - \alpha_2(z)},} \tag{79}$$

where

$$\boxed{\begin{aligned} J^1_{\rm ss} &= \left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right]^2, \qquad J^2_{\rm ss} = \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right]^2, \\ J^3_{\rm ss} &= \frac{1}{3}\left[\frac{1}{x^3} - \frac{1}{y^3}\right] - \left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right]\frac{K_{3/2}(y)}{y^{3/2}} - \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(y)}{z^{3/2}}\right]\frac{I_{3/2}(x)}{x^{3/2}}, \\ J^4_{\rm ss} &= \frac{1}{3}\left[\frac{1}{y^3} - \frac{1}{x^3}\right] + \left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right]\frac{I_{3/2}(y)}{y^{3/2}} + \left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right]\frac{K_{3/2}(x)}{x^{3/2}}. \end{aligned}} \tag{80}$$

D. The short range-long range fs-FFHS spectral density $J^{\rm abs}_{\rm sl}(\omega)$

For the present case r_0 can only be smaller than r, so we need to evaluate

$$G^{\rm abs}_{\rm sl}(s) = \int_d^a \mathrm{d}r \int_b^d \mathrm{d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^>(r, r_0; \kappa). \tag{81}$$

Again it is of the form

$$G^{\rm abs}_{\rm sl}(s) = \frac{\kappa}{D} \frac{J^1_{\rm sl} + \alpha_2(\kappa a)\beta_2(\kappa b)J^2_{\rm sl} - \alpha_2(\kappa a)J^3_{\rm sl} - \beta_2(\kappa b)J^4_{\rm sl}}{\beta_2(\kappa b) - \alpha_2(\kappa a)}, \tag{82}$$

where now

$$\begin{aligned} J^1_{\rm sl} &= \int_d^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_b^d \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0}, \quad J^2_{\rm sl} = \int_d^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^d \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0}, \\ J^3_{\rm sl} &= \int_d^a \mathrm{d}r \frac{k_2(\kappa r)}{r} \int_b^d \mathrm{d}r_0 \frac{i_2(\kappa r_0)}{r_0}, \quad J^4_{\rm sl} = \int_d^a \mathrm{d}r \frac{i_2(\kappa r)}{r} \int_b^d \mathrm{d}r_0 \frac{k_2(\kappa r_0)}{r_0}. \end{aligned} \tag{83}$$

Evaluating for $s = \mathrm{i}\omega$ leads to

$$\boxed{G^{\rm abs}_{\rm sl}(\mathrm{i}\omega) = \frac{x}{Db} \frac{J^1_{\rm sl} + \alpha_2(z)\beta_2(x)J^2_{\rm sl} - \alpha_2(z)J^3_{\rm sl} - \beta_2(x)J^4_{\rm sl}}{\beta_2(x) - \alpha_2(z)},} \tag{84}$$

with

$$\boxed{\begin{aligned} J^1_{\rm sl} &= \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(y)}{y^{3/2}}\right]\left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right], \quad J^2_{\rm sl} = \left[\frac{K_{3/2}(y)}{y^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right]\left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right], \\ J^3_{\rm sl} &= \left[\frac{K_{3/2}(y)}{y^{3/2}} - \frac{K_{3/2}(z)}{z^{3/2}}\right]\left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(x)}{x^{3/2}}\right], \quad J^4_{\rm sl} = \left[\frac{I_{3/2}(z)}{z^{3/2}} - \frac{I_{3/2}(y)}{y^{3/2}}\right]\left[\frac{K_{3/2}(x)}{x^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right]. \end{aligned}} \tag{85}$$

E. The restricted short range-long range fs-FFHS spectral density $J_{\rm rl}^{\rm abs}(\omega)$

In this case, we need to calculate

$$G_{\rm rl}^{\rm abs}(s) = \int_d^a {\rm d}r \int_{b'}^{d'} {\rm d}r_0 \frac{1}{r}\frac{1}{r_0} g_2^{>}(r, r_0; \kappa). \tag{86}$$

The result is of the same form as the other $G^{\rm abs}({\rm i}\omega)$'s with

$$\boxed{\begin{aligned} J_{\rm rl}^1 &= \left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(z)}{z^{3/2}}\right]\left[\frac{I_{3/2}(y')}{(y')^{3/2}} - \frac{I_{3/2}(x')}{(x')^{3/2}}\right], \quad J_{\rm rl}^2 = \left[\frac{K_{3/2}(z)}{z^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right]\left[\frac{K_{3/2}(x')}{(x')^{3/2}} - \frac{K_{3/2}(y')}{(y')^{3/2}}\right], \\ J_{\rm rl}^3 &= \left[\frac{I_{3/2}(y)}{y^{3/2}} - \frac{I_{3/2}(z)}{z^{3/2}}\right]\left[\frac{K_{3/2}(x')}{(x')^{3/2}} - \frac{K_{3/2}(y')}{(y')^{3/2}}\right], \quad J_{\rm rl}^4 = \left[\frac{K_{3/2}(z)}{z^{3/2}} - \frac{K_{3/2}(y)}{y^{3/2}}\right]\left[\frac{I_{3/2}(y')}{(y')^{3/2}} - \frac{I_{3/2}(x')}{(x')^{3/2}}\right], \end{aligned}} \tag{87}$$

where

$$x' \equiv b'\sqrt{{\rm i}\omega/D} \qquad \text{and} \qquad y' \equiv d'\sqrt{{\rm i}\omega/D}. \tag{88}$$

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