Supplementary Information to
Four-component relativistic range-separated density-functional theory: Short-range exchange local-density approximation

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CONTENTS

Part I
Sums over spin combinations

We give here the expressions of the sums over the “spin” combinations that are needed to calculate the exchange energy per particle of the relativistic homogeneous electron gas for the Coulomb-Breit electron-electron interaction [Eq. (A1) of the main paper]. The notations used here are the same as in the main paper [see in particular Section III A]. We first consider the Coulomb contribution, and then the Breit contribution which contains the $\boldsymbol{\alpha}$ matrices and is thus slightly more complex to calculate.

I. COULOMB CONTRIBUTION

We wish to calculate the expression

$$\sum_{\sigma_1,\sigma_2=\downarrow,\uparrow} \psi^\dagger_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\psi^\dagger_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)\psi_{\mathbf{k}_2,\sigma_1}(\mathbf{r}_2), \tag{1}$$

which means that we have to consider four spin combinations, and contrary to the non-relativistic case none of these combinations is zero.

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a. Calculation of the ↑/↑/↑/↑ and ↓/↓/↓/↓ terms for the Coulomb interaction

We consider the expression of the product of two ↑-spinors

$$\begin{aligned}\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix}\begin{pmatrix} \varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\ &= \left(\varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\right) \\ &= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\left(1+\frac{c^2(\mathbf{k}_1.\mathbf{k}_2+i(\mathbf{k}_1\times\mathbf{k}_2)_z)}{(E_{k_1}+c^2)(E_{k_2}+c^2)}\right)\end{aligned} \tag{2}$$

so that

$$\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\psi^{\dagger}_{\mathbf{k}_2,\uparrow}(\mathbf{r}_2)\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}e^{-i(\mathbf{k}_2-\mathbf{k}_1).(\mathbf{r}_1-\mathbf{r}_2)}\left(\frac{(E_{k_1}+c^2)(E_{k_2}+c^2)}{4E_{k_1}E_{k_2}}+\frac{c^2(\mathbf{k}_1.\mathbf{k}_2)}{2E_{k_1}E_{k_2}}+\frac{c^4((\mathbf{k}_1.\mathbf{k}_2)^2+(\mathbf{k}_1\times\mathbf{k}_2)_z^2)}{4(E_{k_1}+c^2)(E_{k_2}+c^2)E_{k_1}E_{k_2}}\right) \tag{3}$$

with the ↓/↓/↓/↓ term being equal to this one.

b. Calculation of the ↑/↓/↓/↑ and ↓/↑/↑/↓ terms for the Coulomb interaction

We consider the expression of the product of a ↑-spinor and a ↓-spinor

$$\begin{aligned}\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) &= \begin{pmatrix} \varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix}\begin{pmatrix} \varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix} \\ &= (\varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)) \\ &= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\frac{c^2 i((\mathbf{k}_1\times\mathbf{k}_2)_x - i(\mathbf{k}_1\times\mathbf{k}_2)_y)}{(E_{k_1}+c^2)(E_{k_2}+c^2)}\end{aligned} \tag{4}$$

thus giving us

$$\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\psi^{\dagger}_{\mathbf{k}_2,\downarrow}(\mathbf{r}_2)\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}e^{-i(\mathbf{k}_2-\mathbf{k}_1).(\mathbf{r}_1-\mathbf{r}_2)}\left(\frac{c^4((\mathbf{k}_1\times\mathbf{k}_2)_x^2+(\mathbf{k}_1\times\mathbf{k}_2)_y^2)}{4(E_{k_1}+mc^2)(E_{k_2}+mc^2)E_{k_1}E_{k_2}}\right) \tag{5}$$

with the ↓/↑/↑/↓ term being equal to this one.

c. Sum of the four Coulomb spin combinations

The sum of the four spin combinations previously determined is, using the relative variables $\mathbf{k}_{12} = \mathbf{k}_1 - \mathbf{k}_2$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$,

$$\begin{aligned}\sum_{\sigma_1,\sigma_2=\downarrow,\uparrow}\psi^{\dagger}_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\psi^{\dagger}_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)\psi_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_2) &= 2\frac{1}{V^2}e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}\left(\frac{(E_{k_1}+c^2)(E_{k_2}+c^2)}{4E_{k_1}E_{k_2}}+\frac{c^2(\mathbf{k}_1.\mathbf{k}_2)}{2E_{k_1}E_{k_2}}+\frac{c^4((\mathbf{k}_1.\mathbf{k}_2)^2+(\mathbf{k}_1\times\mathbf{k}_2)^2)}{4(E_{k_1}+c^2)(E_{k_2}+c^2)E_{k_1}E_{k_2}}\right) \\ &= \frac{1}{V^2}e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}\frac{E_{k_1}E_{k_2}+(\mathbf{k}_1.\mathbf{k}_2)c^2+c^4}{E_{k_1}E_{k_2}}.\end{aligned} \tag{6}$$

II. BREIT CONTRIBUTION

We wish to calculate the expression

$$\sum_{\sigma_1,\sigma_2=\downarrow,\uparrow}\left(\psi^{\dagger}_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)\boldsymbol{\alpha}_1\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\,.\,\psi^{\dagger}_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)\boldsymbol{\alpha}_2\psi_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_2)+\frac{\psi^{\dagger}_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)(\boldsymbol{\alpha}_1.\mathbf{r}_{12})\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\;\psi^{\dagger}_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)(\boldsymbol{\alpha}_2.\mathbf{r}_{12})\psi_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_2)}{r_{12}^2}\right). \tag{7}$$

We work in two steps: first, we calculate the four spin combinations for the first Gaunt-type part (which we shall simply refer to as Gaunt in the following), and then we calculate the four spin combinations for the Gauge retardation part (which we shall simply refer to as Gauge in the following).

a. Calculation of the ↑/↑/↑/↑ and ↓/↓/↓/↓ terms for the Gaunt part of the Breit interaction:

We consider the expression of the product of two $\uparrow$-spinors

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\alpha}_1\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix}\begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}\begin{pmatrix} \varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\sigma}\varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\sigma}\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\right) \\
&= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\left[\frac{c}{E_{k_1}+c^2}\begin{pmatrix} (k_1)_x - i(k_1)_y \\ i(k_1)_x + (k_1)_y \\ (k_1)_z \end{pmatrix} + \frac{c}{E_{k_2}+c^2}\begin{pmatrix} (k_2)_x + i(k_2)_y \\ -i(k_2)_x + (k_2)_y \\ (k_2)_z \end{pmatrix}\right]
\end{aligned} \tag{8}$$

thus we have

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\alpha}_1\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1).\psi^\dagger_{\mathbf{k}_2,\uparrow}(\mathbf{r}_2)\boldsymbol{\alpha}_2\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{4E_{k_1}E_{k_2}}\Bigg(&\frac{c^2(E_{k_2}+c^2)}{(E_{k_1}+c^2)}(2k_1^2-(k_1)_z^2) + \frac{c^2(E_{k_1}+c^2)}{(E_{k_2}+c^2)}(2k_2^2-(k_2)_z^2) \\
&+2c^2(k_1)_z(k_2)_z\Bigg)
\end{aligned} \tag{9}$$

with the $\downarrow/\downarrow/\downarrow/\downarrow$ term equal to this one.

b. Calculation of the $\uparrow/\downarrow/\downarrow/\uparrow$ and $\downarrow/\uparrow/\uparrow/\downarrow$ terms for the Gaunt part of the Breit interaction

We consider the expression of the product of a $\uparrow$-spinor and a $\downarrow$-spinor

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\alpha}_1\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) &= \begin{pmatrix} \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix}\begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}\begin{pmatrix} \varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\sigma}\varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\sigma}\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\right) \\
&= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\left[\frac{c}{E_{k_1}+c^2}\begin{pmatrix} (k_1)_z \\ -i(k_1)_z \\ -(k_1)_x + i(k_1)_y \end{pmatrix} + \frac{c}{E_{k_2}+c^2}\begin{pmatrix} -(k_2)_z \\ i(k_2)_z \\ (k_2)_x - i(k_2)_y \end{pmatrix}\right]
\end{aligned} \tag{10}$$

so that

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)\boldsymbol{\alpha}_1\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1).\psi^\dagger_{\mathbf{k}_2,\downarrow}(\mathbf{r}_2)\boldsymbol{\alpha}_2\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{4E_{k_1}E_{k_2}}\Bigg(&\frac{c^2(E_{k_1}+c^2)}{(E_{k_1}+c^2)}(k_1^2+(k_1)_z^2) + \frac{c^2(E_{k_1}+c^2)}{(E_{k_2}+c^2)}(k_2^2+(k_2)_z^2) \\
&-2c^2(\mathbf{k}_1.\mathbf{k}_2+(k_1)_z(k_2)_z)\Bigg)
\end{aligned} \tag{11}$$

with the $\downarrow/\uparrow/\uparrow/\downarrow$ term equal to this one.

c. Calculation of the $\uparrow/\uparrow/\uparrow/\uparrow$ and $\downarrow/\downarrow/\downarrow/\downarrow$ term for the Gauge part of the Breit interaction

We consider the expression of the product of two $\uparrow$-spinors

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\alpha}_1.\mathbf{r})\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) &= \begin{pmatrix} \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix}\begin{pmatrix} 0 & \boldsymbol{\sigma}.\mathbf{r} \\ \boldsymbol{\sigma}.\mathbf{r} & 0 \end{pmatrix}\begin{pmatrix} \varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) \end{pmatrix} \\
&= \left(\chi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\sigma}.\mathbf{r})\varphi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1) + \varphi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\sigma}.\mathbf{r})\chi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\right) \\
&= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\left(\frac{c}{E_{k_1}+c^2}\left(\mathbf{k}_1.\mathbf{r}+i(\mathbf{k}_1\times\mathbf{r})_z\right)\right) + \frac{c}{E_{k_2}+c^2}\left(\mathbf{k}_2.\mathbf{r}-i(\mathbf{k}_2\times\mathbf{r})_z\right)\Big)
\end{aligned} \tag{12}$$

so that

$$\begin{aligned}
\psi^\dagger_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\alpha}_1.\mathbf{r})\psi_{\mathbf{k}_2,\uparrow}(\mathbf{r}_1)\psi^\dagger_{\mathbf{k}_2,\uparrow}(\mathbf{r}_2)(\boldsymbol{\alpha}_2.\mathbf{r})\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{4E_{k_1}E_{k_2}}\Bigg(&\frac{c^2(E_{k_2}+c^2)}{(E_{k_1}+c^2)}\left((\mathbf{k}_1.\mathbf{r})^2+(\mathbf{k}_1\times\mathbf{r})_z^2\right) \\
&+\frac{c^2(E_{k_1}+c^2)}{(E_{k_2}+c^2)}\left((\mathbf{k}_2.\mathbf{r})^2+(\mathbf{k}_2\times\mathbf{r})_z^2\right) + 2c^2\left((\mathbf{k}_1.\mathbf{r})(\mathbf{k}_2.\mathbf{r})-(\mathbf{k}_1\times\mathbf{r})_z(\mathbf{k}_2\times\mathbf{r})_z\right)\Bigg)
\end{aligned} \tag{13}$$

with the $\downarrow/\downarrow/\downarrow/\downarrow$ term being equal to this one.

d. Calculation of the $\uparrow/\downarrow/\downarrow/\uparrow$ and $\downarrow/\uparrow/\uparrow/\downarrow$ term for the Gauge part of the Breit interaction

We consider the expression of the product of a ↑-spinor and a ↓-spinor

$$\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\alpha_1.\mathbf{r})\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) = \begin{pmatrix} \varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) & \chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1) \end{pmatrix} \begin{pmatrix} 0 & \boldsymbol{\sigma}.\mathbf{r} \\ \boldsymbol{\sigma}.\mathbf{r} & 0 \end{pmatrix} \begin{pmatrix} \varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \\ \chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) \end{pmatrix}$$
$$= \left(\chi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\sigma}.\mathbf{r})\varphi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1) + \varphi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\boldsymbol{\sigma}.\mathbf{r})\chi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\right)$$
$$= \frac{1}{V}\sqrt{\frac{E_{k_1}+c^2}{2E_{k_1}}}\sqrt{\frac{E_{k_2}+c^2}{2E_{k_2}}}e^{-i(\mathbf{k}_2-\mathbf{k}_1).\mathbf{r}_1}\Bigg(\frac{c}{E_{k_1}+c^2}\left(i(\mathbf{k}_1\times\mathbf{r})_x + (\mathbf{k}_1\times\mathbf{r})_y\right)$$
$$+ \frac{c}{E_{k_2}+c^2}\left(-i(\mathbf{k}_2\times\mathbf{r})_x - (\mathbf{k}_2\times\mathbf{r})_y\right)\Bigg) \tag{14}$$

so that

$$\psi^{\dagger}_{\mathbf{k}_1,\uparrow}(\mathbf{r}_1)(\alpha_1.\mathbf{r})\psi_{\mathbf{k}_2,\downarrow}(\mathbf{r}_1)\psi^{\dagger}_{\mathbf{k}_2,\downarrow}(\mathbf{r}_2)(\alpha_2.\mathbf{r})\psi_{\mathbf{k}_1,\uparrow}(\mathbf{r}_2) = \frac{1}{V^2}\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{4E_{k_1}E_{k_2}}\Bigg(\frac{c^2(E_{k_2}+c^2)}{(E_{k_1}+c^2)}\left((\mathbf{k}_1\times\mathbf{r})^2_x + (\mathbf{k}_1\times\mathbf{r})^2_y\right)$$
$$+\frac{c^2(E_{k_1}+c^2)}{(E_{k_2}+c^2)}\left((\mathbf{k}_2\times\mathbf{r})^2_x + (\mathbf{k}_2\times\mathbf{r})^2_y\right) - 2c^2\left((\mathbf{k}_1\times\mathbf{r})_x(\mathbf{k}_2\times\mathbf{r})_x + (\mathbf{k}_1\times\mathbf{r})_y(\mathbf{k}_2\times\mathbf{r})_y\right)\Bigg) \tag{15}$$

with the ↓/↑/↑/↓ term equal to this one.

e. Sum of the four Gaunt and four Gauge terms

The sum of the eight spins combinations previously determined is

$$\sum_{\sigma_1,\sigma_2=\downarrow,\uparrow}\left(\psi^{\dagger}_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)\alpha_1\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\,.\,\psi^{\dagger}_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)\alpha_2\psi_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_2) + \frac{\psi^{\dagger}_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_1)(\alpha_1.\mathbf{r}_{12})\psi_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_1)\;\psi^{\dagger}_{\mathbf{k}_2,\sigma_2}(\mathbf{r}_2)(\alpha_2.\mathbf{r}_{12})\psi_{\mathbf{k}_1,\sigma_1}(\mathbf{r}_2)}{r^2_{12}}\right)$$
$$= 2\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{V^2}\frac{c^2}{4E_{k_1}E_{k_2}}\Bigg(\frac{E_{k_2}+c^2}{E_{k_1}+c^2}\Big(3k_1^2 + \frac{(\mathbf{k}_1.\mathbf{r})^2 + (\mathbf{k}_1\times\mathbf{r})^2}{r^2}\Big) + \frac{E_{k_1}+c^2}{E_{k_2}+c^2}\Big(3k_2^2 + \frac{(\mathbf{k}_2.\mathbf{r})^2 + (\mathbf{k}_2\times\mathbf{r})^2}{r^2}\Big)$$
$$+ 2\Big(-\mathbf{k}_1.\mathbf{k}_2 + \frac{(\mathbf{k}_1.\mathbf{r})(\mathbf{k}_2.\mathbf{r})}{r^2} - \frac{(\mathbf{k}_1\times\mathbf{r})(\mathbf{k}_2\times\mathbf{r})}{r^2}\Big)\Bigg)$$
$$= 2\frac{e^{-i\mathbf{k}_{12}.\mathbf{r}_{12}}}{V^2}\frac{c^2}{E_{k_1}E_{k_2}}\left(\frac{E_{k_2}+c^2}{E_{k_1}+c^2}k_1^2 + \frac{E_{k_1}+c^2}{E_{k_2}+c^2}k_2^2\right) \tag{16}$$

where the last expression has been simplified considering that

$$\Big(-\mathbf{k}_1.\mathbf{k}_2 + \frac{(\mathbf{k}_1.\mathbf{r})(\mathbf{k}_2.\mathbf{r})}{r^2} - \frac{(\mathbf{k}_1\times\mathbf{r})(\mathbf{k}_2\times\mathbf{r})}{r^2}\Big) = -2k_1k_2\sin(\theta_1)\sin(\theta_2)\cos(\phi_1-\phi_2) \tag{17}$$

is zero once integrated over ϕ_1 or ϕ_2 on $[0, 2\pi]$, and therefore this term can be removed with the understanding that the expression must always be used in an integral over ϕ_1 or ϕ_2.

Part II

Large-$\tilde{c}$ asymptotic expansion

We explain here the key steps involved in the analytical calculation of the coefficients of the large-$\tilde{c}$ asymptotic expansions of the short-range Coulomb and Breit exchange energies per particle [Eqs. (36) and (41) of the main paper]. The Coulomb and Breit terms being of similar forms, we only explicitly consider the short-range Coulomb exchange energy per particle. We start from its expression in Eq. (35) of the main paper

$$\epsilon_{\mathrm{x}}^{\mathrm{C,sr},\mu} = \frac{3k_{\mathrm{F}}}{4\pi}\int_{\tilde{k}_1=0}^{1}\int_{\tilde{k}_2=0}^{1} d\tilde{k}_1 d\tilde{k}_2\ \tilde{k}_1\tilde{k}_2\Bigg(\frac{1}{\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}}\Big[\tilde{k}_1\tilde{k}_2 + \Big(e^{-\left(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}}\right)^2} - e^{-\left(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}}\right)^2}\Big)\tilde{\mu}^2\Big]$$
$$+ \frac{2\tilde{c}^2+\tilde{k}_1^2+\tilde{k}_2^2+2\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}}{4\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}}\Big[\mathrm{Ei}\Big(-\Big(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}}\Big)^2\Big) - \mathrm{Ei}\Big(-\Big(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}}\Big)^2\Big) + \ln\Big((\tilde{k}_1-\tilde{k}_2)^2\Big) - \ln\Big((\tilde{k}_1+\tilde{k}_2)^2\Big)\Big]\Bigg). \quad (18)$$

From now on, for simplicity, we drop the tilde notation and it will be implicit that k_1, k_2, c, and μ are in units of k_{F}. We want to find the expansion for $c \to \infty$. The expansion of the first part of the integrand is

$$\frac{\frac{1}{c^2}}{\sqrt{1+\frac{k_1^2}{c^2}}\sqrt{1+\frac{k_2^2}{c^2}}} = \frac{1}{c^2} - \left(\frac{k_1^2}{2}+\frac{k_2^2}{2}\right)\frac{1}{c^4} + \left(\frac{3k_1^4}{8}+\frac{k_1^2k_2^2}{4}+\frac{3k_2^4}{8}\right)\frac{1}{c^6} + O\left(\frac{1}{c^8}\right), \quad (19)$$

and the expansion of the second part of the integrand is

$$\frac{2+(k_1^2+k_2^2)\frac{1}{c^2}+2\sqrt{1+\frac{k_1^2}{c^2}}\sqrt{1+\frac{k_2^2}{c^2}}}{4\sqrt{1+\frac{k_1^2}{c^2}}\sqrt{1+\frac{k_2^2}{c^2}}} = 1 + \left(\frac{k_1^4}{16}-\frac{k_1^2k_2^2}{8}+\frac{k_2^4}{16}\right)\frac{1}{c^4} + O\left(\frac{1}{c^6}\right). \quad (20)$$

Permuting the sum and the integrals, we integrate the general term of the large-$\tilde{c}$ expansion. For the first part of the exchange energy, we need to calculate the general term

$$\frac{a_{m,n}}{c^{2m+2n+2}}\int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\Big[k_1k_2 + \Big(e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} - e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2}\Big)\mu^2\Big]dk_2dk_1, \quad (21)$$

and for the second part of the exchange energy, we need to calculate the general term

$$\frac{b_{m,n}}{c^{2m+2n}}\int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\Big[\mathrm{Ei}\Big(-(\frac{k_1+k_2}{2\mu})^2\Big) - \mathrm{Ei}\Big(-(\frac{k_1-k_2}{2\mu})^2\Big) + \ln\Big((k_1-k_2)^2\Big) - \ln\Big((k_1+k_2)^2\Big)\Big]dk_2dk_1, \quad (22)$$

with m and n positive integers, $a_{m,n}$ and $b_{m,n}$ being expressed using the coefficients of Eqs. (19) and (20) and are determined uniquely by the pair $\{m, n\}$. We observe a symmetry in m and n, so that only half the terms needs to be calculated.

These integrals are analytically calculated in the following pages because, although they can be calculated using the program Wolfram Mathematica [1] for a given value of $2m + 2n$, the general term for an unspecified value of $2m + 2n$ cannot be directly integrated by the program. It is convenient to have the analytical expression of the general term in order to calculate the expansion for large orders. The final complete expressions of the large-c expansions and their associated Padé approximants are explicitly given up to an arbitrary order in the accompanying Mathematica notebook.

I. FIRST PART OF THE EXCHANGE ENERGY (I)

$$I = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\Big[k_1k_2 + \Big(e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} - e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2}\Big)\mu^2\Big]dk_2dk_1. \quad (23)$$

A. First integral of the first part (I_1)

The first integral of the first part gives

$$I_1 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{2+2m}k_2^{2+2n}dk_2dk_1 = \frac{1}{9+6m+6n+4mn}. \quad (24)$$

B. Second integral of the first part (I_2)

The second integral of the first part is

$$I_2 = \int_{k_1=0}^{1} \int_{k_2=0}^{1} k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} dk_2 dk_1, \tag{25}$$

which can be calculated using changes of variables, binomial expansions, and integrations by parts. It will be more or less the same procedure for all the following integral calculations, we shall do it once in full.

We start with a change of variable, $k_2 = 2\mu k - k_1$, so that we have

$$I_2 = 2\mu \int_{k_1=0}^{1} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k_1^{1+2m} (2\mu k - k_1)^{1+2n} e^{-k^2} dk dk_1, \tag{26}$$

then we use a binomial expansion to express our integral as

$$I_2 = \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^{1} k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk \right) dk_1. \tag{27}$$

We now consider the two last integrals successively, first the one over k and then the one over k_1.

1. Integration over k in I_2

We calculate the integral over k with repeated integrations by parts using at each step

$$\frac{d}{dk} k^{i-1} = (i-1) k^{i-2} \quad \text{and} \quad \int^{k} x\, e^{-x^2} dx = -\frac{1}{2} e^{-k^2}. \tag{28}$$

For the first step of the integration by parts, we have

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^{i-1} k\, e^{-k^2} dk = -\frac{1}{2} \left[\left(\frac{1+k_1}{2\mu}\right)^{i-1} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] + \frac{i-1}{2} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^{i-3} k\, e^{-k^2} dk. \tag{29}$$

The repeated integrations by parts lead to two different cases for the last integral, depending on the parity of the integer i.

If i is even, the final integral obtained is

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} e^{-k^2} dk = \frac{\sqrt{\pi}}{2} \left[\mathrm{erf}\left(\frac{1+k_1}{2\mu}\right) - \mathrm{erf}\left(\frac{k_1}{2\mu}\right) \right] \tag{30}$$

so that we have

$$\begin{aligned} \int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk = &- \sum_{l_p=0}^{\frac{i}{2}-1} \frac{1}{2^{l_p+1}} \frac{(i-1)!!}{(i-1-2l_p)!!} \left[\left(\frac{1+k_1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_p} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\ &+ \frac{(i-1)!!}{2^{\frac{i}{2}}} \frac{\sqrt{\pi}}{2} \left[\mathrm{erf}\left(\frac{1+k_1}{2\mu}\right) - \mathrm{erf}\left(\frac{k_1}{2\mu}\right) \right]. \end{aligned} \tag{31}$$

If i is odd, the final integral obtained is

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k e^{-k^2} dk = \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \tag{32}$$

so that we have

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk = -\sum_{l_\mathrm{i}=0}^{\frac{i-1}{2}-1} \frac{1}{2^{l_\mathrm{i}+1}} \frac{(i-1)!!}{(i-1-2l_\mathrm{i})!!} \left[\left(\frac{1+k_1}{2\mu}\right)^{i-1-2l_\mathrm{i}} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - \left(\frac{k_1}{2\mu}\right)^{i-1-2l_\mathrm{i}} e^{-\left(\frac{k_1}{2\mu}\right)^2}\right] + \frac{(i-1)!!}{2^{\frac{i-1}{2}}} \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2}\right]. \quad (33)$$

2. Integration over k_1 in I_2

We calculate the remaining integral as the sum of two sums over two different indices, i_p and i_i with $i = 2i_\mathrm{p}$ if i is even and $i = 2i_\mathrm{i} + 1$ if i is odd, which both run between 0 and n so that we have indeed $2 + 2n$ terms

$$\begin{aligned}
I_2 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1-i} (2\mu)^{1+i} \int_{k_1=0}^{1} k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2} dk\right) dk_1 \\
&= -\sum_{i_\mathrm{p}=0}^{n} \binom{1+2n}{2i_\mathrm{p}} (2\mu)^{1+2i_\mathrm{p}} \int_{k_1=0}^{1} k_1^{2+2(m+n)-2i_\mathrm{p}} \Bigg(\frac{(2i_\mathrm{p}-1)!!}{2^{i_\mathrm{p}}} \frac{\sqrt{\pi}}{2} \left[\mathrm{erf}\left(\frac{1+k_1}{2\mu}\right) - \mathrm{erf}\left(\frac{k_1}{2\mu}\right)\right] \\
&\qquad - \sum_{l_\mathrm{p}=0}^{i_\mathrm{p}-1} \frac{1}{2^{l_\mathrm{p}+1}} \frac{(2i_\mathrm{p}-1)!!}{(2i_\mathrm{p}-1-2l_\mathrm{p})!!} \frac{1}{(2\mu)^{2i_\mathrm{p}-1-2l_\mathrm{p}}} \left[(1+k_1)^{2i_\mathrm{p}-1-2l_\mathrm{p}} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - k_1^{2i_\mathrm{p}-1-2l_\mathrm{p}} e^{-\left(\frac{k_1}{2\mu}\right)^2}\right] \Bigg) dk_1 \\
&\quad + \sum_{i_\mathrm{i}=0}^{n} \binom{1+2n}{2i_\mathrm{i}+1} (2\mu)^{2+2i_\mathrm{i}} \int_{k_1=0}^{1} k_1^{1+2(m+n)-2i_\mathrm{i}} \Bigg(\frac{(2i_\mathrm{i})!!}{2^{i_\mathrm{i}}} \frac{-1}{2} \left[e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2}\right] \\
&\qquad - \sum_{l_\mathrm{i}=0}^{i_\mathrm{i}-1} \frac{1}{2^{l_\mathrm{i}+1}} \frac{(2i_\mathrm{i})!!}{(2i_\mathrm{i}-2l_\mathrm{i})!!} \frac{1}{(2\mu)^{2i_\mathrm{i}-2l_\mathrm{i}}} \left[(1+k_1)^{2i_\mathrm{i}-2l_\mathrm{i}} e^{-\left(\frac{1+k_1}{2\mu}\right)^2} - k_1^{2i_\mathrm{i}-2l_\mathrm{p}} e^{-\left(\frac{k_1}{2\mu}\right)^2}\right] \Bigg) dk_1 \quad (34)
\end{aligned}$$

a. Sum over i_p

There are four sub-integrals in the sum over i_p.

First sub-integral

$$\begin{aligned}
&-\frac{\sqrt{\pi}}{2} \int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})} \mathrm{erf}\left(\frac{k_1}{2\mu}\right) dk_1 \\
&= -\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})} \int_{t=0}^{\frac{k_1}{2\mu}} e^{-t^2} dt dk_1 \\
&= -\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})} \int_{k=0}^{k_1} e^{-\left(\frac{k}{2\mu}\right)^2} \frac{1}{2\mu} dk dk_1 \\
&= \frac{1}{3+2(m+n-i_\mathrm{p})} \left(-\frac{\sqrt{\pi}}{2} \mathrm{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} \int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})} k_1 e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 \right) \\
&= \frac{1}{3+2(m+n-i_\mathrm{p})} \Bigg(-\frac{\sqrt{\pi}}{2} \mathrm{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} \Bigg((2\mu^2)^{1+m+n-i_\mathrm{p}} (2+2(m+n-i_\mathrm{p}))!! \, (-2\mu^2) \left[e^{-\left(\frac{1}{2\mu}\right)^2} - 1\right] \\
&\qquad - \sum_{\lambda_\mathrm{i}=0}^{m+n-i_\mathrm{p}} (2\mu^2)^{\lambda_\mathrm{i}+1} \frac{(2+2(m+n-i_\mathrm{p}))!!}{(2+2(m+n-i_\mathrm{p})-2\lambda_\mathrm{i})!!} e^{-\left(\frac{1}{2\mu}\right)^2} \Bigg) \Bigg) \\
&= \frac{1}{3+2(m+n-i_\mathrm{p})} \left(-\frac{\sqrt{\pi}}{2} \mathrm{erf}\left(\frac{1}{2\mu}\right) + \frac{1}{2\mu} S_\mathrm{i}[1+m+n-i_\mathrm{p}] \right) \quad (35)
\end{aligned}$$

where we used first the change of variable $t = \frac{k}{2\mu}$, then an integration by parts with

$$\frac{d}{dk_1}\frac{\sqrt{\pi}}{2}\mathrm{erf}\Big(\frac{k_1}{2\mu}\Big) = \frac{d}{dk_1}\int_{k=0}^{k_1} e^{-\left(\frac{k}{2\mu}\right)^2}\frac{1}{2\mu}\,dk = \frac{e^{-\left(\frac{k_1}{2\mu}\right)^2}}{2\mu} \quad\text{and}\quad \int^{k_1} x^{2+2(m+n-i_\mathrm{p})}dx = \frac{k_1^{3+2(m+n-i_\mathrm{p})}}{3+2(m+n-i_\mathrm{p})}, \tag{36}$$

to get rid of the error function. We then used repeated integrations by parts with the first step being

$$\frac{d}{dk}k^{2+2(m+n-i_\mathrm{p})} = (2+2(m+n-i_\mathrm{p}))k^{1+2(m+n-i_\mathrm{p})} \quad\text{and}\quad \int^{k_1} xe^{-\left(\frac{x}{2\mu}\right)^2}dx = -2\mu^2 e^{-\left(\frac{k_1}{2\mu}\right)^2} \tag{37}$$

and the final step is

$$\int_{k_1=0}^{1} k_1 e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = (-2\mu^2)\left[e^{-\left(\frac{1}{2\mu}\right)^2} - 1\right]. \tag{38}$$

We also define a convenient notation for the result of the repeated integrations by parts over k_1 as

$$\int_{k_1=0}^{1} k_1^{2N} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = S_\mathrm{p}[N] \quad\text{and}\quad \int_{k_1=0}^{1} k_1^{2N+1} e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = S_\mathrm{i}[N]. \tag{39}$$

Second sub-integral

$$\begin{aligned}
&\frac{\sqrt{\pi}}{2}\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\mathrm{erf}\Big(\frac{1+k_1}{2\mu}\Big)dk_1\\
&= \int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\int_{t=0}^{\frac{1+k_1}{2\mu}} e^{-t^2}dtdk_1\\
&= \int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\int_{k=0}^{k_1} e^{-\left(\frac{1+k}{2\mu}\right)^2}\frac{1}{2\mu}\,dkdk_1\\
&= \frac{1}{3+2(m+n-i_\mathrm{p})}\left(\frac{\sqrt{\pi}}{2}\mathrm{erf}\Big(\frac{1}{\mu}\Big) - \frac{1}{2\mu}\int_{k_1=0}^{1} k_1^{3+2(m+n-i_\mathrm{p})}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\right)\\
&= \frac{1}{3+2(m+n-i_\mathrm{p})}\left(\frac{\sqrt{\pi}}{2}\mathrm{erf}\Big(\frac{1}{\mu}\Big) - \frac{1}{2\mu}\sum_{j=0}^{3+2(m+n-i_\mathrm{p})}\binom{3+2(m+n-i_\mathrm{p})}{j}(-1)^{3-j}\int_{k_1=0}^{1}(1+k_1)^j e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\right)\\
&= \frac{1}{3+2(m+n-i_\mathrm{p})}\left(\frac{\sqrt{\pi}}{2}\mathrm{erf}\Big(\frac{1}{\mu}\Big) + \frac{1}{2\mu}\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}\left[(2\mu^2)^{j_\mathrm{p}}(2j_\mathrm{p}-1)!!\,2\mu\frac{\sqrt{\pi}}{2}\left[\mathrm{erf}\Big(\frac{1}{\mu}\Big) - \mathrm{erf}\Big(\frac{1}{2\mu}\Big)\right]\right.\right.\\
&\qquad\left. - \sum_{\lambda_\mathrm{p}=0}^{j_\mathrm{p}-1}[(2\mu^2)^{\lambda_\mathrm{p}+1}\frac{(2j_\mathrm{p}-1)!!}{(2j_\mathrm{p}-1-2\lambda_\mathrm{p})!!}\left[2^{2j_\mathrm{p}-1-2\lambda_\mathrm{p}}e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2}\right]\right]\\
&\qquad - \frac{1}{2\mu}\sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}\left[(2\mu^2)^{j_\mathrm{i}}(2j_\mathrm{i})!!\,(-2\mu^2)\left[e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2}\right]\right.\\
&\qquad\left.\left. - \sum_{\lambda_\mathrm{i}=0}^{j_\mathrm{i}-1}[(2\mu^2)^{\lambda_\mathrm{i}+1}\frac{(2j_\mathrm{i})!!}{(2j_\mathrm{i}-2\lambda_\mathrm{i})!!}\left[2^{2j_\mathrm{i}-2\lambda_\mathrm{i}}e^{-\left(\frac{1}{\mu}\right)^2} - e^{-\left(\frac{1}{2\mu}\right)^2}\right]\right]\right)\\
&= \frac{1}{3+2(m+n-i_\mathrm{p})}\left(\frac{\sqrt{\pi}}{2}\mathrm{erf}\Big(\frac{1}{\mu}\Big) + \frac{1}{2\mu}\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S_\mathrm{p}^{+}[j_\mathrm{p}] - \frac{1}{2\mu}\sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}S_\mathrm{i}^{+}[j_\mathrm{i}]\right)
\end{aligned} \tag{40}$$

where we used the binomial expansion

$$k_1^{3+2(m+n-i_\mathrm{p})} = \sum_{j=0}^{3+2(m+n-i_\mathrm{p})}\binom{3+2(m+n-i_\mathrm{p})}{j}(-1)^{3-j}\,(1+k_1)^j \tag{41}$$

and split the sum over j into two sums over $j_{\rm p}$ and $j_{\rm i}$. We also introduced the definitions

$$\int_{k_1=0}^{1}(1+k_1)^{2N}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}\,dk_1 = S^+_{\rm p}[N] \;\text{ and }\; \int_{k_1=0}^{1}(1+k_1)^{2N+1}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}\,dk_1 = S^+_{\rm i}[N]. \tag{42}$$

Third sub-integral

$$-\int_{k_1=0}^{1}k_1^{1+2(m+n-l_{\rm p})}e^{-\left(\frac{k_1}{2\mu}\right)^2}dk_1 = -S_{\rm i}[m+n-l_{\rm p}] \tag{43}$$

Fourth sub-integral

$$\begin{aligned}
&\int_{k_1=0}^{1}k_1^{2+2(m+n-i_{\rm p})}(1+k_1)^{2i_{\rm p}-1-2l_{\rm p}}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\\
&=\sum_{j=0}^{2+2(m+n-i_{\rm p})}\binom{2+2(m+n-i_{\rm p})}{j}(-1)^j\int_{k_1=0}^{1}(1+k_1)^{j+2(i_{\rm p}-l_{\rm p})-1}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\\
&=\sum_{j_{\rm p}=0}^{1+m+n-i_{\rm p}}\binom{2+2(m+n-i_{\rm p})}{2j_{\rm p}}\int_{k_1=0}^{1}(1+k_1)^{2(j_{\rm p}+i_{\rm p}-l_{\rm p})-1}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1-\sum_{j_{\rm i}=0}^{m+n-i_{\rm p}}\binom{2+2(m+n-i_{\rm p})}{2j_{\rm i}+1}\int_{k_1=0}^{1}(1+k_1)^{2(j_{\rm i}+i_{\rm p}-l_{\rm p})}e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\\
&=\sum_{j_{\rm p}=0}^{1+m+n-i_{\rm p}}\binom{2+2(m+n-i_{\rm p})}{2j_{\rm p}}S^+_{\rm i}[j_{\rm p}+i_{\rm p}-l_{\rm p}-1]\;-\sum_{j_{\rm i}=0}^{m+n-i_{\rm p}}\binom{2+2(m+n-i_{\rm p})}{2j_{\rm i}+1}S^+_{\rm p}[j_{\rm i}+i_{\rm p}-l_{\rm p}]
\end{aligned} \tag{44}$$

b. Sum over i_i

There are also four sub-integrals in the sum over $i_{\rm i}$.

First sub-integral

$$-\int_{k_1=0}^{1}k_1^{1+2(m+n-i_{\rm i})}\,e^{-\left(\frac{k_1}{2\mu}\right)^2}dk_1 = -S_{\rm i}[m+n+i_{\rm i}] \tag{45}$$

Second sub-integral

$$\begin{aligned}
\int_{k_1=0}^{1}k_1^{1+2(m+n-i_{\rm i})}\,e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1 &= \sum_{j=0}^{1+2(m+n-i_{\rm i})}\binom{1+2(m+n-i_{\rm i})}{j}(-1)^{1-j}\int_{k_1=0}^{1}(1+k_1)^j\,e^{-\left(\frac{1+k_1}{2\mu}\right)^2}dk_1\\
&= -\sum_{j_{\rm p}=0}^{m+n-i_{\rm i}}\binom{1+2(m+n-i_{\rm i})}{2j_{\rm p}}S^+_{\rm p}[j_{\rm p}]\;+\sum_{j_{\rm i}=0}^{m+n-i_{\rm i}}\binom{1+2(m+n-i_{\rm i})}{2j_{\rm i}+1}S^+_{\rm i}[j_{\rm i}]
\end{aligned} \tag{46}$$

Third sub-integral

$$-\int_{k_1=0}^{1}k_1^{1+2(m+n-l_{\rm i})}\,e^{-\left(\frac{k_1}{2\mu}\right)^2}dk_1 = -S_{\rm i}[m+n-l_{\rm i}] \tag{47}$$

Fourth sub-integral

$$
\begin{aligned}
&\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\,(1+k_1)^{2(i_\mathrm{i}-l_\mathrm{i})}\,e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_\mathrm{i})} \binom{1+2(m+n-i_\mathrm{i})}{j} (-1)^{1-j} \int_{k_1=0}^{1} (1+k_1)^j\, e^{-\left(\frac{1+k_1}{2\mu}\right)^2} dk_1 \\
&= -\sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}} S_\mathrm{p}^+[j_\mathrm{p}+i_\mathrm{i}-l_\mathrm{i}] \;+\; \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1} S_\mathrm{i}^+[j_\mathrm{i}+i_\mathrm{i}-l_\mathrm{i}]
\end{aligned}
\tag{48}
$$

3. Expression of integral I_2

We have found each sub-integral of the second integral I_2 of the first part of the exchange energy. The expression of I_2 is thus

$$
\begin{aligned}
I_2 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1+k_2}{2\mu}\right)^2} dk_2 dk_1 \\
&= -\sum_{i_\mathrm{p}=0}^{n} \binom{1+2n}{2i_\mathrm{p}} (2\mu)^{1+2i_\mathrm{p}} \Bigg\{ \frac{(2i_\mathrm{p}-1)!!}{2^{i_\mathrm{p}}} \frac{1}{3+2(m+n-i_\mathrm{p})} \Bigg(\frac{\sqrt{\pi}}{2}\Big[\mathrm{erf}\Big(\frac{1}{\mu}\Big)-\mathrm{erf}\Big(\frac{1}{2\mu}\Big)\Big] \\
&\qquad + \frac{1}{2\mu}\Big[S_\mathrm{i}[1+m+n-i_\mathrm{p}] + \sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}} \binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}} S_\mathrm{p}^+[j_\mathrm{p}] - \sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}} \binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1} S_\mathrm{i}^+[j_\mathrm{i}] \Big] \Bigg) \\
&\qquad - \sum_{l_\mathrm{p}=0}^{i_\mathrm{p}-1} \frac{1}{2^{l_\mathrm{p}+1}} \frac{(2i_\mathrm{p}-1)!!}{(2i_\mathrm{p}-1-2l_\mathrm{p})!!} \frac{1}{(2\mu)^{2i_\mathrm{p}-1-2l_\mathrm{p}}} \Bigg(-S_\mathrm{i}[m+n-l_\mathrm{p}] \\
&\qquad\quad + \sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}} \binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}} S_\mathrm{i}^+[j_\mathrm{p}+i_\mathrm{p}-l_\mathrm{p}-1] \;-\; \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}} \binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1} S_\mathrm{p}^+[j_\mathrm{i}+i_\mathrm{p}-l_\mathrm{p}] \Bigg) \Bigg\} \\
&\quad + \sum_{i_\mathrm{i}=0}^{n} \binom{1+2n}{2i_\mathrm{i}+1} (2\mu)^{2+2i_\mathrm{i}} \Bigg\{ \frac{(2i_\mathrm{i})!!}{2^{i_\mathrm{i}}} \frac{-1}{2} \Bigg(-S_\mathrm{i}[m+n-i_\mathrm{i}] \\
&\qquad - \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}} S_\mathrm{p}^+[j_\mathrm{p}] \;+\; \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1} S_\mathrm{i}^+[j_\mathrm{i}] \Bigg) \\
&\qquad - \sum_{l_\mathrm{i}=0}^{i_\mathrm{i}-1} \frac{1}{2^{l_\mathrm{i}+1}} \frac{(2i_\mathrm{i})!!}{(2i_\mathrm{i}-2l_\mathrm{i})!!} \frac{1}{(2\mu)^{2i_\mathrm{i}-2l_\mathrm{i}}} \Bigg(-S_\mathrm{i}[m+n-l_\mathrm{i}] \\
&\qquad\quad + \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}} S_\mathrm{p}^+[j_\mathrm{p}+i_\mathrm{i}-l_\mathrm{i}] \;-\; \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1} S_\mathrm{i}^+[j_\mathrm{i}+i_\mathrm{i}-l_\mathrm{i}] \Bigg) \Bigg\}.
\end{aligned}
\tag{49}
$$

Most of the following calculations use exactly the same steps. They are written now with less details.

C. Third integral of the first part (I_3)

$$
I_3 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m} k_2^{1+2n} e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2} dk_2 dk_1 = \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^{1} k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk \right) dk_1. \tag{50}
$$

where we used the change of variable $k_2 = 2\mu k + k_1$.

1. Integration over k in I_3

Once again, we can calculate the integral over k with repeated integrations by parts, with two different cases depending on the parity of i. If i is even we have

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk$$
$$= -\sum_{l_{\mathrm{p}}=0}^{\frac{i}{2}-1} \frac{1}{2^{l_{\mathrm{p}}+1}} \frac{(i-1)!!}{(i-1-2l_{\mathrm{p}})!!} \left[\Big(\frac{k_1-1}{2\mu}\Big)^{i-1-2l_{\mathrm{p}}} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - \Big(\frac{k_1}{2\mu}\Big)^{i-1-2l_{\mathrm{p}}} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] + \frac{(i-1)!!}{2^{\frac{i}{2}}} \frac{\sqrt{\pi}}{2} \left[\mathrm{erf}\Big(\frac{k_1-1}{2\mu}\Big) - \mathrm{erf}\Big(\frac{k_1}{2\mu}\Big) \right], \quad (51)$$

while if i is odd we have

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1+1}{2\mu}} k^i e^{-k^2} dk$$
$$= -\sum_{l_{\mathrm{i}}=0}^{\frac{i-1}{2}-1} \frac{1}{2^{l_{\mathrm{i}}+1}} \frac{(i-1)!!}{(i-1-2l_{\mathrm{i}})!!} \left[\Big(\frac{k_1-1}{2\mu}\Big)^{i-1-2l_{\mathrm{i}}} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - \Big(\frac{k_1}{2\mu}\Big)^{i-1-2l_{\mathrm{i}}} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] + \frac{(i-1)!!}{2^{\frac{i-1}{2}}} \frac{-1}{2} \left[e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right]. \quad (52)$$

2. Integration over k_1 in I_3

We write the integral I_3 as the sum of two sums over two indices, i_{p} and i_{i} with $i = 2i_{\mathrm{p}}$ if i is even and $i = 2i_{\mathrm{i}} + 1$ if i is odd, which both run between 0 and n so that we have indeed $2 + 2n$ terms. We have

$$\begin{aligned}
I_3 = \sum_{i=0}^{1+2n} \binom{1+2n}{i} & (-1)^{1+i} (2\mu)^{1+i} \int_{k_1=0}^{1} k_1^{2+2(m+n)-i} \left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}} k^i e^{-k^2} dk \right) dk_1 \\
&= -\sum_{i_{\mathrm{p}}=0}^{n} \binom{1+2n}{2i_{\mathrm{p}}} (2\mu)^{1+2i_{\mathrm{p}}} \int_{k_1=0}^{1} k_1^{2+2(m+n)-2i_{\mathrm{p}}} \Bigg(\frac{(2i_{\mathrm{p}}-1)!!}{2^{i_{\mathrm{p}}}} \frac{\sqrt{\pi}}{2} \left[\mathrm{erf}\Big(\frac{k_1-1}{2\mu}\Big) - \mathrm{erf}\Big(\frac{k_1}{2\mu}\Big) \right] \\
&\qquad - \sum_{l_{\mathrm{p}}=0}^{i_{\mathrm{p}}-1} \frac{1}{2^{l_{\mathrm{p}}+1}} \frac{(2i_{\mathrm{p}}-1)!!}{(2i_{\mathrm{p}}-1-2l_{\mathrm{p}})!!} \frac{1}{(2\mu)^{2i_{\mathrm{p}}-1-2l_{\mathrm{p}}}} \left[(k_1-1)^{2i_{\mathrm{p}}-1-2l_{\mathrm{p}}} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - k_1^{2i_{\mathrm{p}}-1-2l_{\mathrm{p}}} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \Bigg) dk_1 \\
&+ \sum_{i_{\mathrm{i}}=0}^{n} \binom{1+2n}{2i_{\mathrm{i}}+1} (2\mu)^{2+2i_{\mathrm{i}}} \int_{k_1=0}^{1} k_1^{1+2(m+n)-2i_{\mathrm{i}}} \Bigg(\frac{(2i_{\mathrm{i}})!!}{2^{i_{\mathrm{i}}}} \frac{-1}{2} \left[e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \\
&\qquad - \sum_{l_{\mathrm{i}}=0}^{i_{\mathrm{i}}-1} \frac{1}{2^{l_{\mathrm{i}}+1}} \frac{(2i_{\mathrm{i}})!!}{(2i_{\mathrm{i}}-2l_{\mathrm{i}})!!} \frac{1}{(2\mu)^{2i_{\mathrm{i}}-2l_{\mathrm{i}}}} \left[(k_1-1)^{2i_{\mathrm{i}}-2l_{\mathrm{i}}} e^{-\left(\frac{k_1-1}{2\mu}\right)^2} - k_1^{2i_{\mathrm{i}}-2l_{\mathrm{p}}} e^{-\left(\frac{k_1}{2\mu}\right)^2} \right] \Bigg) dk_1. \quad (53)
\end{aligned}$$

a. Sum over i_p

There are four sub-integrals in the sum over i_{p}.

First sub-integral

$$-\frac{\sqrt{\pi}}{2} \int_{k_1=0}^{1} k_1^{2+2(m+n-i_{\mathrm{p}})} \mathrm{erf}\Big(\frac{k_1}{2\mu}\Big) dk_1 = \frac{1}{3+2(m+n-i_{\mathrm{p}})} \left(-\frac{\sqrt{\pi}}{2} \mathrm{erf}\Big(\frac{1}{2\mu}\Big) + \frac{1}{2\mu} S_{\mathrm{i}}[1+m+n-i_{\mathrm{p}}] \right) \quad (54)$$

Second sub-integral

$$
\begin{aligned}
&\frac{\sqrt{\pi}}{2}\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\mathrm{erf}\Big(\frac{k_1-1}{2\mu}\Big)dk_1\\
&=\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\int_{t=0}^{\frac{k_1-1}{2\mu}} e^{-t^2}dt dk_1\\
&=\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\int_{k=0}^{k_1} e^{-\left(\frac{k-1}{2\mu}\right)^2}\frac{1}{2\mu}\,dk dk_1\\
&=\frac{1}{3+2(m+n-i_\mathrm{p})}\Bigg(0-\frac{1}{2\mu}\int_{k_1=0}^{1} k_1^{3+2(m+n-i_\mathrm{p})}e^{-\left(\frac{k_1-1}{2\mu}\right)^2}\,dk_1\Bigg)\\
&=\frac{1}{3+2(m+n-i_\mathrm{p})}\Bigg(0-\frac{1}{2\mu}\sum_{j=0}^{3+2(m+n-i_\mathrm{p})}\binom{3+2(m+n-i_\mathrm{p})}{j}\int_{k_1=0}^{1}(k_1-1)^j e^{-\left(\frac{k_1-1}{2\mu}\right)^2}\,dk_1\Bigg)\\
&=\frac{1}{3+2(m+n-i_\mathrm{p})}\frac{-1}{2\mu}\Bigg(\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}\Bigg[(2\mu^2)^{j_\mathrm{p}}(2j_\mathrm{p}-1)!!\,2\mu\frac{\sqrt{\pi}}{2}\Big[0-\mathrm{erf}\Big(\frac{-1}{2\mu}\Big)\Big]\\
&\qquad\qquad-\sum_{\lambda_\mathrm{p}=0}^{j_\mathrm{p}-1}[(2\mu^2)^{\lambda_\mathrm{p}+1}\frac{(2j_\mathrm{p}-1)!!}{(2j_\mathrm{p}-1-2\lambda_\mathrm{p})!!}\Big[0-(-1)^{2j_\mathrm{p}-1-2\lambda_\mathrm{p}}e^{-\left(\frac{-1}{2\mu}\right)^2}\Big]\Bigg]\\
&\qquad\qquad+\sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}\Bigg[(2\mu^2)^{j_\mathrm{i}}(2j_\mathrm{i})!!\,(-2\mu^2)\Big[1-e^{-\left(\frac{-1}{2\mu}\right)^2}\Big]\\
&\qquad\qquad\qquad-\sum_{\lambda_\mathrm{i}=0}^{j_\mathrm{i}-1}[(2\mu^2)^{\lambda_\mathrm{i}+1}\frac{(2j_\mathrm{i})!!}{(2j_\mathrm{i}-2\lambda_\mathrm{i})!!}\Big[0-(-1)^{2j_\mathrm{i}-2\lambda_\mathrm{i}}e^{-\left(\frac{-1}{2\mu}\right)^2}\Big]\Bigg]\Bigg)\\
&=\frac{1}{3+2(m+n-i_\mathrm{p})}\frac{-1}{2\mu}\Bigg(\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S_\mathrm{p}^{-}[j_\mathrm{p}]+\sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}S_\mathrm{i}^{-}[j_\mathrm{i}]\Bigg)
\end{aligned}\tag{55}
$$

where we used the binomial expansion

$$
k_1^{3+2(m+n-i_\mathrm{p})}=\sum_{j=0}^{3+2(m+n-i_\mathrm{p})}\binom{3+2(m+n-i_\mathrm{p})}{j}(k_1-1)^j \tag{56}
$$

and split the sum over j into two sums over j_p and j_i. We also introduced the notations

$$
\int_{k_1=0}^{1}(k_1-1)^{2N}e^{-\left(\frac{k_1-1}{2\mu}\right)^2}\,dk_1=S_\mathrm{p}^{-}[N]\ \text{ and }\ \int_{k_1=0}^{1}(k_1-1)^{2N+1}e^{-\left(\frac{k_1-1}{2\mu}\right)^2}\,dk_1=S_\mathrm{i}^{-}[N]. \tag{57}
$$

Third sub-integral

$$
-\int_{k_1=0}^{1}k_1^{1+2(m+n-l_\mathrm{p})}e^{-\left(\frac{k_1}{2\mu}\right)^2}dk_1=-S_\mathrm{i}[m+n-l_\mathrm{p}] \tag{58}
$$

Fourth sub-integral

$$
\begin{aligned}
&\int_{k_1=0}^{1}k_1^{2+2(m+n-i_\mathrm{p})}(k_1-1)^{2i_\mathrm{p}-1-2l_\mathrm{p}}e^{-\left(\frac{k_1-1}{2\mu}\right)^2}dk_1\\
&=\sum_{j=0}^{2+2(m+n-i_\mathrm{p})}\binom{2+2(m+n-i_\mathrm{p})}{j}\int_{k_1=0}^{1}(k_1-1)^{j+2(i_\mathrm{p}-l_\mathrm{p})-1}e^{-\left(\frac{k_1-1}{2\mu}\right)^2}dk_1\\
&=\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S_\mathrm{i}^{-}[j_\mathrm{p}+i_\mathrm{p}-l_\mathrm{p}-1]\ +\sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}S_\mathrm{p}^{-}[j_\mathrm{i}+i_\mathrm{p}-l_\mathrm{p}]
\end{aligned}\tag{59}
$$

b. Sum over i_i

There are four sub-integrals in the sum over i_i.

First sub-integral

$$-\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\, e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = -S_\mathrm{i}[m+n+i_\mathrm{i}] \tag{60}$$

Second sub-integral

$$\begin{aligned}
&\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\, e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_\mathrm{i})} \binom{1+2(m+n-i_\mathrm{i})}{j} \int_{k_1=0}^{1} (k_1-1)^j\, e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}} S_\mathrm{p}^-[j_\mathrm{p}] \;+ \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1} S_\mathrm{i}^-[j_\mathrm{i}]
\end{aligned} \tag{61}$$

Third sub-integral

$$-\int_{k_1=0}^{1} k_1^{1+2(m+n-l_\mathrm{i})}\, e^{-\left(\frac{k_1}{2\mu}\right)^2} dk_1 = -S_\mathrm{i}[m+n-l_\mathrm{i}] \tag{62}$$

Fourth sub-integral

$$\begin{aligned}
&\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\,(k_1-1)^{2(i_\mathrm{i}-l_\mathrm{i})}\, e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j=0}^{1+2(m+n-i_\mathrm{i})} \binom{1+2(m+n-i_\mathrm{i})}{j} \int_{k_1=0}^{1} (k_1-1)^j\, e^{-\left(\frac{k_1-1}{2\mu}\right)^2} dk_1 \\
&= \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}} S_\mathrm{p}^-[j_\mathrm{p}+i_\mathrm{i}-l_\mathrm{i}] \;+ \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}} \binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1} S_\mathrm{i}^-[j_\mathrm{i}+i_\mathrm{i}-l_\mathrm{i}]
\end{aligned} \tag{63}$$

3. Expression of integral I_3

We have found each sub-integral of the third integral I_3 of the first part of the exchange energy. The expression of I_3 is thus

$$
\begin{aligned}
I_3 = & \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}e^{-\left(\frac{k_1-k_2}{2\mu}\right)^2}dk_2dk_1 \\
= & -\sum_{i_\mathrm{p}=0}^{n}\binom{1+2n}{2i_\mathrm{p}}(2\mu)^{1+2i_\mathrm{p}}\Bigg\{\frac{(2i_\mathrm{p}-1)!!}{2^{i_\mathrm{p}}}\frac{1}{3+2(m+n-i_\mathrm{p})}\Bigg(\frac{\sqrt{\pi}}{2}\Big[0-\mathrm{erf}\Big(\frac{1}{2\mu}\Big)\Big] \\
& + \frac{1}{2\mu}\Bigg[S_\mathrm{i}[1+m+n-i_\mathrm{p}]-\sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S^-_\mathrm{p}[j_\mathrm{p}]-\sum_{j_\mathrm{i}=0}^{1+m+n-i_\mathrm{p}}\binom{3+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}S^-_\mathrm{i}[j_\mathrm{i}]\Bigg]\Bigg) \\
& -\sum_{l_\mathrm{p}=0}^{i_\mathrm{p}-1}\frac{1}{2^{l_\mathrm{p}+1}}\frac{(2i_\mathrm{p}-1)!!}{(2i_\mathrm{p}-1-2l_\mathrm{p})!!}\frac{1}{(2\mu)^{2i_\mathrm{p}-1-2l_\mathrm{p}}}\Bigg(-S_\mathrm{i}[m+n-l_\mathrm{p}] \\
& + \sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S^-_\mathrm{i}[j_\mathrm{p}+i_\mathrm{p}-l_\mathrm{p}-1] + \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}S^-_\mathrm{p}[j_\mathrm{i}+i_\mathrm{p}-l_\mathrm{p}]\Bigg)\Bigg\} \\
& + \sum_{i_\mathrm{i}=0}^{n}\binom{1+2n}{2i_\mathrm{i}+1}(2\mu)^{2+2i_\mathrm{i}}\Bigg\{\frac{(2i_\mathrm{i})!!}{2^{i_\mathrm{i}}}\frac{-1}{2}\Bigg(-S_\mathrm{i}[m+n-i_\mathrm{i}] \\
& + \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}}S^-_\mathrm{p}[j_\mathrm{p}] + \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}S^-_\mathrm{i}[j_\mathrm{i}]\Bigg) \\
& -\sum_{l_\mathrm{i}=0}^{i_\mathrm{i}-1}\frac{1}{2^{l_\mathrm{i}+1}}\frac{(2i_\mathrm{i})!!}{(2i_\mathrm{i}-2l_\mathrm{i})!!}\frac{1}{(2\mu)^{2i_\mathrm{i}-2l_\mathrm{i}}}\Bigg(-S_\mathrm{i}[m+n-l_\mathrm{i}] \\
& + \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}S^-_\mathrm{p}[j_\mathrm{p}+i_\mathrm{i}-l_\mathrm{i}] + \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}S^-_\mathrm{i}[j_\mathrm{i}+i_\mathrm{i}-l_\mathrm{i}]\Bigg)\Bigg\}.
\end{aligned}
\tag{64}
$$

This expression has to be subtracted from the one of the second integral I_2, many terms in fact cancel each other.

II. SECOND PART OF THE EXCHANGE ENERGY (II)

$$
II = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\Big[\mathrm{Ei}\Big(-\Big(\frac{k_1+k_2}{2\mu}\Big)^2\Big)-\mathrm{Ei}\Big(-\Big(\frac{k_1-k_2}{2\mu}\Big)^2\Big)+\ln\big((k_1-k_2)^2\big)-\ln\big((k_1+k_2)^2\big)\Big]dk_2dk_1 \tag{65}
$$

A. First integral of the second part (II_1)

$$
II_1 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\ln\big((k_1+k_2)^2\big)dk_2dk_1 = \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1-i}\int_{k_1=0}^{1}k_1^{1+2(m+n)-i}\Big(\int_{k=k_1}^{1+k_1}k^i\,2\ln(k)\,dk\Big)dk_1 \tag{66}
$$

where we used the change of variable $k_2 = k - k_1$.

1. Integration over k in II_1

$$\int_{k=k_1}^{1+k_1} k^i\, 2\ln(k)\, dk = 2\,\frac{1}{(1+i)^2}\Big(k_1^{1+i} \;-\; (1+k_1)^{1+i} \;-\; (1+i)k_1^{1+i}\ln(k_1) \;+\; (1+i)(1+k_1)^{1+i}\ln(1+k_1)\Big) \tag{67}$$

2. Integration over k_1 in II_1

$$\begin{aligned} II_1 &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1-i}\int_{k_1=0}^{1} k_1^{1+2(m+n)-i}\Big(\int_{k=k_1}^{1+k_1} k^i\, 2\ln(k)\, dk\Big)dk_1 \\ &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}\frac{2\,(-1)^{1-i}}{(1+i)^2}\int_{k_1=0}^{1} k_1^{1+2(m+n)-i}\Big(k_1^{1+i} \;-\; (1+k_1)^{1+i} \;-\; (1+i)k_1^{1+i}\ln(k_1) \;+\; (1+i)(1+k_1)^{1+i}\ln(1+k_1)\Big)dk_1, \end{aligned} \tag{68}$$

which we will integrate term by term over k_1.

First sub-integral

$$\int_{k_1=0}^{1} k_1^{2+2(m+n)+1} dk_1 = \frac{1}{4+2(m+n)} \tag{69}$$

Second sub-integral

$$\begin{aligned} -\int_{k_1=0}^{1} k_1^{2+2(m+n)-i}\,(1+k_1)^{i+1} dk_1 &= -\sum_{j=0}^{1+i}\binom{1+i}{j}\int_{k_1=0}^{1} k_1^{2+2(m+n)-i+j} dk_1 \\ &= -\sum_{j=0}^{1+i}\binom{1+i}{j}\frac{1}{3+2(m+n)-i+j} \end{aligned} \tag{70}$$

Third sub-integral

$$-(1+i)\int_{k_1=0}^{1} k_1^{2+2(m+n)+1}\ln(k_1)\, dk_1 = (1+i)\frac{1}{4(2+m+n)^2} \tag{71}$$

Fourth sub-integral

$$\begin{aligned} &(1+i)\int_{k_1=0}^{1} k_1^{2+2(m+n)-i}\,(1+k_1)^{i+1}\,\ln(1+k_1)\, dk_1 \\ &= (1+i)\sum_{j=0}^{2+2(m+n)-i}\binom{2+2(m+n)-i}{j}(-1)^{-i-j}\int_{k_1=0}^{1}(1+k_1)^{1+i+j}\ln(1+k_1)\, dk_1 \\ &= (1+i)\sum_{j=0}^{2+2(m+n)-i}\binom{2+2(m+n)-i}{j}\frac{(-1)^{-i-j}}{(2+i+j)^2}\Big(1+2^{2+i+j}\big(-1+(i+j)\ln(2)+\ln(4)\big)\Big) \end{aligned} \tag{72}$$

where we used the binomial relation in Eq. (41).

3. Expression of integral II_1

We have found each sub-integral of the first integral II_1 of the second part of the exchange energy. The expression of II_1 is thus

$$
\begin{aligned}
II_1 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m} k_2^{1+2n} \ln\left((k_1+k_2)^2\right) dk_2 dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2(-1)^{1-i}}{(1+i)^2} \Bigg\{ \frac{1}{4+2(m+n)} - \sum_{j=0}^{1+i} \binom{1+i}{j} \frac{1}{3+2(m+n)-i+j} + (1+i)\frac{1}{4(2+m+n)^2} \\
&\qquad + (1+i) \sum_{j=0}^{2+2(m+n)-i} \binom{2+2(m+n)-i}{j} \frac{(-1)^{-i-j}}{(2+i+j)^2} \left(1 + 2^{2+i+j}\Big(-1+(i+j)\ln(2)+\ln(4)\Big)\right)\Bigg\}. \qquad (73)
\end{aligned}
$$

B. Second integral of the second part (II_2)

$$
II_2 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m} k_2^{1+2n} \ln\left((k_1-k_2)^2\right) dk_2 dk_1 = \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} \int_{k_1=0}^{1} k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{k_1-1} k^i\, 2\ln(k)\, dk \right) dk_1 \qquad (74)
$$

where we used the change of variable $k_2 = k_1 - k$ and a binomial expansion.

1. Integration over k in II_2

$$
\int_{k=k_1}^{k_1-1} k^i\, 2\ln(k)\, dk_1 = 2\,\frac{1}{(1+i)^2}\left(k_1^{1+i} - (k_1-1)^{1+i} - (1+i)k_1^{1+i}\ln(k_1) + (1+i)(k_1-1)^{1+i}\ln(k_1-1)\right) \qquad (75)
$$

2. Integration over k_1 in II_2

$$
\begin{aligned}
II_2 &= \sum_{i=0}^{1+2n} \binom{1+2n}{i} (-1)^{1+i} \int_{k_1=0}^{1} k_1^{1+2(m+n)-i} \left(\int_{k=k_1}^{k_1-1} k^i\, 2\ln(k)\, dk \right) dk_1 \\
&= \sum_{i=0}^{1+2n} \binom{1+2n}{i} \frac{2\,(-1)^{1-i}}{(1+i)^2} \int_{k_1=0}^{1} k_1^{1+2(m+n)-i} \left(k_1^{1+i} - (k_1-1)^{1+i} - (1+i)k_1^{1+i}\ln(k_1) + (1+i)(k_1-1)^{1+i}\ln(1-k_1)\right) dk_1, \qquad (76)
\end{aligned}
$$

which we integrate term by term over k_1.

First sub-integral

$$
\int_{k_1=0}^{1} k_1^{2+2(m+n)+1} dk_1 = \frac{1}{4+2(m+n)} \qquad (77)
$$

Second sub-integral

$$
\begin{aligned}
-\int_{k_1=0}^{1} k_1^{2+2(m+n)-i} (k_1-1)^{i+1} dk_1 &= -\sum_{j=0}^{1+i} \binom{1+i}{j} (-1)^{1+i-j} \int_{k_1=0}^{1} k_1^{2+2(m+n)-i+j} dk_1 \\
&= -\sum_{j=0}^{1+i} \binom{1+i}{j} (-1)^{1+i-j} \frac{1}{3+2(m+n)-i+j} \qquad (78)
\end{aligned}
$$

Third sub-integral

$$-(1+i)\int_{k_1=0}^{1} k_1^{2+2(m+n)+1}\ln(k_1)\,dk_1 = (1+i)\frac{1}{4(2+m+n)^2} \tag{79}$$

Fourth sub-integral

$$\begin{aligned}(1+i)\int_{k_1=0}^{1} k_1^{2+2(m+n)-i}\,(k_1-1)^{i+1}\ln(1-k_1)\,dk_1 &= (1+i)\sum_{j=0}^{2+2(m+n)-i}\binom{2+2(m+n)-i}{j}\int_{k_1=0}^{1}(k_1-1)^{1+i+j}\ln(1-k_1)\,dk_1\\ &= (1+i)\sum_{j=0}^{2+2(m+n)-i}\binom{2+2(m+n)-i}{j}\frac{(-1)^{i+j}}{(2+i+j)^2}\end{aligned} \tag{80}$$

where we used the binomial relation in Eq. (56).

3. *Expression of integral II_2*

We have found each sub-integral of the second integral II_2 of the second part of the exchange energy. The expression of II_2 is thus

$$\begin{aligned}II_2 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\ln\left((k_1-k_2)^2\right)dk_2dk_1\\ &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}\frac{2(-1)^{1-i}}{(1+i)^2}\Bigg\{\frac{1}{4+2(m+n)} - \sum_{j=0}^{1+i}\binom{1+i}{j}(-1)^{1+i-j}\frac{1}{3+2(m+n)-i+j}\\ &\qquad + (1+i)\frac{1}{4(2+m+n)^2} + (1+i)\sum_{j=0}^{2+2(m+n)-i}\binom{2+2(m+n)-i}{j}\frac{(-1)^{i+j}}{(2+i+j)^2}\Bigg\}.\end{aligned} \tag{81}$$

C. Third integral of the second part (II_3)

$$\begin{aligned}II_3 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\mathrm{Ei}\left(-\left(\frac{k_1+k_2}{2\mu}\right)^2\right)dk_1dk_2\\ &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\left(-\int_{\left(\frac{k_1+k_2}{2\mu}\right)^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk_1dk_2\\ &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1-i}(2\mu)^{1+i}\int_{k_1=0}^{1}k_1^{2+2(m+n)-i}\left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}}k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk\right)dk_1\end{aligned} \tag{82}$$

where we used the change of variable $k_2 = 2\mu k - k_1$.

1. *Integration over k in II_3*

We calculate the integral over k with an integration by parts using

$$\frac{d}{dk}\mathrm{Ei}\left(-k^2\right) = \frac{2\,e^{-k^2}}{k} \quad\text{and}\quad \int^{k} x^i dx = \frac{k^{i+1}}{i+1} \tag{83}$$

so that we have

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk=\frac{1}{i+1}\frac{1}{\left(2\mu\right)^{i+1}}\left[(1+k_1)^{i+1}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)-(k_1)^{i+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right]-\frac{2}{i+1}\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2}dk. \quad (84)$$

We can observe that the integral over k is now exactly the integral that has been calculated for the second integral of the first part of the exchange energy but for a $-2/(1+i)$ factor. We introduce the notation

$$\binom{1+2n}{i}(-1)^{1-i}(2\mu)^{1+i}\int_{k_1=0}^{1} k_1^{2+2(m+n)-i}\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i e^{-k^2}dk\,dk_1=\{I_{2,i}\} \quad (85)$$

for the following calculations.

2. *Integration over k_1 in II_3*

We now can split the sum over i_p and i_i

$$\begin{aligned}
II_3 &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1-i}(2\mu)^{1+i}\int_{k_1=0}^{1} k_1^{2+2(m+n)-i}\left(\int_{k=\frac{k_1}{2\mu}}^{\frac{1+k_1}{2\mu}} k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk\right)dk_1\\
&= \sum_{i_\mathrm{p}=0}^{n}\left(\frac{-2}{2i_\mathrm{p}+1}\{I_{2,2i_\mathrm{p}}\}-\binom{1+2n}{2i_\mathrm{p}}\int_{k_1=0}^{1}\frac{k_1^{2+2(m+n)-2i_\mathrm{p}}}{2i_\mathrm{p}+1}\left[(1+k_1)^{2i_\mathrm{p}+1}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)-(k_1)^{2i_\mathrm{p}+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right]dk_1\right)\\
&\quad+\sum_{i_\mathrm{i}=0}^{n}\left(\frac{-2}{2i_\mathrm{i}+2}\{I_{2,2i_\mathrm{i}+1}\}+\binom{1+2n}{2i_\mathrm{i}+1}\int_{k_1=0}^{1}\frac{k_1^{1+2(m+n)-2i_\mathrm{i}}}{2i_\mathrm{i}+2}\left[(1+k_1)^{2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)-(k_1)^{2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right]dk_1\right). \quad (86)
\end{aligned}$$

a. *Sum over i_p*

There are two sub-integrals in the sum over i_p.

First sub-integral

We calculate this integral over k_1 with an integration by parts using

$$\frac{d}{dk}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)=\frac{2\,e^{-\left(\frac{k_1}{2\mu}\right)^2}}{k_1}\quad\text{and}\quad\int^k x^{3+2(m+n)}dx=\frac{k^{4+2(m+n)}}{4+2(m+n)} \quad (87)$$

so that we have

$$\begin{aligned}
-\int_{k_1=0}^{1} k_1^{2+2(m+n)+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)dk_1 &= -\frac{\mathrm{Ei}\left(-(\frac{1}{2\mu})^2\right)}{4+2(m+n)}+\frac{2}{4+2(m+n)}\int_{k_1=0}^{1} k_1^{3+2(m+n)}e^{-\left(\frac{k_1}{2\mu}\right)^2}dk_1\\
&= -\frac{\mathrm{Ei}\left(-(\frac{1}{2\mu})^2\right)}{4+2(m+n)}+\frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1]. \quad (88)
\end{aligned}$$

Second sub-integral

$$\int_{k_1=0}^{1} k_1^{2+2(m+n-i_\mathrm{p})}\,(1+k_1)^{2i_\mathrm{p}+1}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)dk_1 = \sum_{j=0}^{2+2(m+n-i_\mathrm{p})}\binom{2+2(m+n-i_\mathrm{p})}{j}(-1)^{-j}\int_{k_1=0}^{1}(1+k_1)^{j+2i_\mathrm{p}+1}\mathrm{Ei}\left(-(\frac{1+k_1}{2\mu})^2\right)dk_1$$

$$= \sum_{j=0}^{2+2(m+n-i_\mathrm{p})}\binom{2+2(m+n-i_\mathrm{p})}{j}\frac{(-1)^{-j}}{j+2i_\mathrm{p}+2}\left[2^{j+2i_\mathrm{p}+2}\mathrm{Ei}\left(-\left(\frac{1}{\mu}\right)^2\right) - \mathrm{Ei}\left(-(\frac{1}{2\mu})^2\right)\right]$$

$$- \sum_{j_\mathrm{p}=0}^{1+m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{p}+2}S_\mathrm{i}^+[j_\mathrm{p}+i_\mathrm{p}]$$

$$+ \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{p}+3}S_\mathrm{p}^+[j_\mathrm{i}+i_\mathrm{p}+1] \tag{89}$$

where we used a binomial expansion, the same integration by parts as before, and then split the sum over j.

b. *Sum over i_i*

There are two sub-integrals in the sum over i_i.

First sub-integral

$$-\int_{k_1=0}^{1} k_1^{2+2(m+n)+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)dk_1 = -\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)} + \frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1] \tag{90}$$

Second sub-integral

$$\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\,(1+k_1)^{2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)dk_1 = \sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}(-1)^{-j}\int_{k_1=0}^{1}(1+k_1)^{j+2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{1+k_1}{2\mu}\right)^2\right)dk_1$$

$$= \sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}\frac{(-1)^{1-j}}{j+2i_\mathrm{i}+3}\left[2^{j+2i_\mathrm{i}+3}\mathrm{Ei}\left(-\left(\frac{1}{\mu}\right)^2\right) - \mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)\right]$$

$$+ \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{i}+3}S_\mathrm{p}^+[j_\mathrm{p}+i_\mathrm{i}+1]$$

$$- \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{i}+4}S_\mathrm{i}^+[j_\mathrm{i}+i_\mathrm{i}+1] \tag{91}$$

3. Expression of integral II_3

We have found each sub-integral of the third integral II_3 of the second part of the exchange energy. The expression of II_3 is thus

$$\begin{aligned}
II_3 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\mathrm{Ei}\left(-\left(\frac{k_1+k_2}{2\mu}\right)^2\right)dk_2dk_1 \\
&= \sum_{i_\mathrm{p}=0}^{n}\Bigg\{\frac{-2}{2i_\mathrm{p}+1}\{I_{2,2i_\mathrm{p}}\} - \frac{1}{2i_\mathrm{p}+1}\binom{1+2n}{2i_\mathrm{p}}\Bigg[-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)} + \frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1] \\
&\quad + \sum_{j=0}^{2+2(m+n-i_\mathrm{p})}\binom{2+2(m+n-i_\mathrm{p})}{j}\frac{(-1)^{-j}}{j+2i_\mathrm{p}+2}\left[2^{j+2i_\mathrm{p}+2}\mathrm{Ei}\left(-\left(\frac{1}{\mu}\right)^2\right) - \mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)\right] \\
&\quad + \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{p}+1}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{p}+2}S_\mathrm{i}^{+}[j_\mathrm{p}+i_\mathrm{p}] \\
&\quad - \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{p}+3}S_\mathrm{p}^{+}[j_\mathrm{i}+i_\mathrm{p}+1]\Bigg]\Bigg\} \\
&\quad + \sum_{i_\mathrm{i}=0}^{n}\Bigg\{\frac{-2}{2i_\mathrm{i}+2}\{I_{2,2i_\mathrm{i}+1}\} - \frac{1}{2i_\mathrm{i}+2}\binom{1+2n}{2i_\mathrm{i}+1}\Bigg[-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)} + \frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1] \\
&\quad + \sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}\frac{(-1)^{1-j}}{j+2i_\mathrm{i}+3}\left[2^{j+2i_\mathrm{i}+3}\mathrm{Ei}\left(-\left(\frac{1}{\mu}\right)^2\right) - \mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)\right] \\
&\quad + \sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{i}+3}S_\mathrm{p}^{+}[j_\mathrm{p}+i_\mathrm{i}+1] \\
&\quad - \sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{i}+4}S_\mathrm{i}^{+}[j_\mathrm{i}+i_\mathrm{i}+1]\Bigg]\Bigg\}.
\end{aligned} \tag{92}$$

D. Fourth integral of the second part (II_4)

$$\begin{aligned}
II_4 &= \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\mathrm{Ei}\left(-\left(\frac{k_1-k_2}{2\mu}\right)^2\right)dk_2dk_1 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\left(-\int_{\left(\frac{k_1-k_2}{2\mu}\right)^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk_2dk_1 \\
&= \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1+i}(2\mu)^{1+i}\int_{k_1=0}^{1}k_1^{2+2(m+n)-i}\left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}}k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk\right)dk_1
\end{aligned} \tag{93}$$

where we used the change of variable $k_2 = -2\mu k + k_1$.

1. Integration over k in II_4

We calculate the integral over k using the usual integration by parts

$$\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}}k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk = \frac{1}{i+1}\frac{1}{(2\mu)^{i+1}}\left[(k_1-1)^{i+1}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right) - (k_1)^{i+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right] - \frac{2}{i+1}\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}}k^ie^{-k^2}dk. \tag{94}$$

We observe that the integral on k is now exactly the integral that has been calculated for the third integral of the first part of the exchange energy but for a $-2/(1+i)$ factor. We introduce the notation

$$\binom{1+2n}{i}(-1)^{1-i}(2\mu)^{1+i}\int_{k_1=0}^{1}k_1^{2+2(m+n)-i}\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}}k^i e^{-k^2}dkdk_1=\{I_{3,i}\} \tag{95}$$

for the following calculations.

2. Integration over k_1 in II_4

We split the sum over i_{p} and i_{i}

$$\begin{aligned}II_4 &= \sum_{i=0}^{1+2n}\binom{1+2n}{i}(-1)^{1+i}(2\mu)^{1+i}\int_{k_1=0}^{1}k_1^{2+2(m+n)-i}\left(\int_{k=\frac{k_1}{2\mu}}^{\frac{k_1-1}{2\mu}}k^i\left(-\int_{k^2}^{\infty}\frac{e^{-t}}{t}dt\right)dk\right)dk_1\\ &= \sum_{i_{\mathrm{p}}=0}^{n}\left(\frac{-2}{2i_{\mathrm{p}}+1}\{I_{3,2i_{\mathrm{p}}}\}-\binom{1+2n}{2i_{\mathrm{p}}}\int_{k_1=0}^{1}\frac{k_1^{2+2(m+n)-2i_{\mathrm{p}}}}{2i_{\mathrm{p}}+1}\left[(k_1-1)^{2i_{\mathrm{p}}+1}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)-(k_1)^{2i_{\mathrm{p}}+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right]dk_1\right)\\ &+\sum_{i_{\mathrm{i}}=0}^{n}\left(\frac{-2}{2i_{\mathrm{i}}+2}\{I_{3,2i_{\mathrm{i}}+1}\}+\binom{1+2n}{2i_{\mathrm{i}}+1}\int_{k_1=0}^{1}\frac{k_1^{1+2(m+n)-2i_{\mathrm{i}}}}{2i_{\mathrm{i}}+2}\left[(k_1-1)^{2i_{\mathrm{i}}+2}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)-(k_1)^{2i_{\mathrm{i}}+2}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)\right]dk_1\right).\end{aligned} \tag{96}$$

a. Sum over i_p

There are two sub-integrals in the sum over i_{p}.

First sub-integral

$$-\int_{k_1=0}^{1}k_1^{2+2(m+n)+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)dk_1=-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)}+\frac{2}{4+2(m+n)}S_{\mathrm{i}}[m+n+1] \tag{97}$$

Second sub-integral

$$\begin{aligned}\int_{k_1=0}^{1}k_1^{2+2(m+n-i_{\mathrm{p}})}(k_1-1)^{2i_{\mathrm{p}}+1}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)dk_1 &= \sum_{j=0}^{2+2(m+n-i_{\mathrm{p}})}\binom{2+2(m+n-i_{\mathrm{p}})}{j}\int_{k_1=0}^{1}(k_1-1)^{j+2i_{\mathrm{p}}+1}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)dk_1\\ &= \sum_{j=0}^{2+2(m+n-i_{\mathrm{p}})}\binom{2+2(m+n-i_{\mathrm{p}})}{j}\frac{1}{j+2i_{\mathrm{p}}+2}\left[0-(-1)^{j+2i_{\mathrm{p}}+2}\,\mathrm{Ei}\left(-\left(\frac{-1}{2\mu}\right)^2\right)\right]\\ &-\sum_{j_{\mathrm{p}}=0}^{1+m+n-i_{\mathrm{p}}}\binom{2+2(m+n-i_{\mathrm{p}})}{2j_{\mathrm{p}}}\frac{1}{2j_{\mathrm{p}}+2i_{\mathrm{p}}+2}S_{\mathrm{i}}^{-}[j_{\mathrm{p}}+i_{\mathrm{p}}]\\ &-\sum_{j_{\mathrm{i}}=0}^{m+n-i_{\mathrm{p}}}\binom{2+2(m+n-i_{\mathrm{p}})}{2j_{\mathrm{i}}+1}\frac{1}{2j_{\mathrm{i}}+2i_{\mathrm{p}}+3}S_{\mathrm{p}}^{-}[j_{\mathrm{i}}+i_{\mathrm{p}}+1].\end{aligned} \tag{98}$$

b. Sum over i_i

There are two sub-integrals in the sum over i_{i}.

First sub-integral

$$-\int_{k_1=0}^{1}k_1^{2+2(m+n)+1}\mathrm{Ei}\left(-\left(\frac{k_1}{2\mu}\right)^2\right)dk_1=-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)}+\frac{2}{4+2(m+n)}S_{\mathrm{i}}[m+n+1] \tag{99}$$

Second sub-integral

$$\int_{k_1=0}^{1} k_1^{1+2(m+n-i_\mathrm{i})}\,(k_1-1)^{2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)dk_1 = \sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}\int_{k_1=0}^{1}(k_1-1)^{j+2i_\mathrm{i}+2}\mathrm{Ei}\left(-\left(\frac{k_1-1}{2\mu}\right)^2\right)dk_1$$
$$= \sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}\frac{1}{j+2i_\mathrm{i}+3}\left[0\;-\;(-1)^{j+i_\mathrm{i}+3}\mathrm{Ei}\left(-\left(\frac{-1}{2\mu}\right)^2\right)\right]$$
$$-\sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{i}+3}S_\mathrm{p}^{+}[j_\mathrm{p}+i_\mathrm{i}+1]$$
$$-\sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{i}+4}S_\mathrm{i}^{+}[j_\mathrm{i}+i_\mathrm{i}+1] \qquad (100)$$

3. Expression of integral II_4

We have found each sub-integral of the fourth integral II_4 of the second part of the exchange energy. The expression of II_4 is thus

$$II_4 = \int_{k_1=0}^{1}\int_{k_2=0}^{1} k_1^{1+2m}k_2^{1+2n}\mathrm{Ei}\left(-\left(\frac{k_1-k_2}{2\mu}\right)^2\right)dk_2dk_1$$
$$= \sum_{i_\mathrm{p}=0}^{n}\Bigg\{\frac{-2}{2i_\mathrm{p}+1}\{I_{3,2i_\mathrm{p}}\}\;-\;\frac{1}{2i_\mathrm{p}+1}\binom{1+2n}{2i_\mathrm{p}}\Bigg[-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)}\;+\;\frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1]$$
$$+\sum_{j=0}^{2+2(m+n-i_\mathrm{p})}\binom{2+2(m+n-i_\mathrm{p})}{j}\frac{1}{j+2i_\mathrm{p}+2}\left[0\;-\;\mathrm{Ei}\left(-\left(\frac{-1}{2\mu}\right)^2\right)\right]$$
$$-\sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{p}+1}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{p}+2}S_\mathrm{i}^{-}[j_\mathrm{p}+i_\mathrm{p}]$$
$$-\sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{p}}\binom{2+2(m+n-i_\mathrm{p})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{p}+3}S_\mathrm{p}^{-}[j_\mathrm{i}+i_\mathrm{p}+1]\Bigg]\Bigg\}$$
$$+\sum_{i_\mathrm{i}=0}^{n}\Bigg\{\frac{-2}{2i_\mathrm{i}+2}\{I_{3,2i_\mathrm{i}+1}\}\;-\;\frac{1}{2i_\mathrm{i}+2}\binom{1+2n}{2i_\mathrm{i}+1}\Bigg[-\frac{\mathrm{Ei}\left(-\left(\frac{1}{2\mu}\right)^2\right)}{4+2(m+n)}\;+\;\frac{2}{4+2(m+n)}S_\mathrm{i}[m+n+1]$$
$$+\sum_{j=0}^{1+2(m+n-i_\mathrm{i})}\binom{1+2(m+n-i_\mathrm{i})}{j}\frac{1}{j+2i_\mathrm{i}+3}\left[0\;-\;\mathrm{Ei}\left(-\left(\frac{-1}{2\mu}\right)^2\right)\right]$$
$$+\sum_{j_\mathrm{p}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{p}}\frac{1}{2j_\mathrm{p}+2i_\mathrm{i}+3}S_\mathrm{p}^{-}[j_\mathrm{p}+i_\mathrm{i}+1]$$
$$-\sum_{j_\mathrm{i}=0}^{m+n-i_\mathrm{i}}\binom{1+2(m+n-i_\mathrm{i})}{2j_\mathrm{i}+1}\frac{1}{2j_\mathrm{i}+2i_\mathrm{i}+4}S_\mathrm{i}^{-}[j_\mathrm{i}+i_\mathrm{i}+1]\Bigg]\Bigg\}. \qquad (101)$$

[1] Wolfram Research, Inc., Mathematica, Version 11.1, Champaign, IL (2017).