A new form of transcorrelated Hamiltonian inspired by range-separated DFT: II

Emmanuel Giner[a)]

I. THE GENERAL SCOPE

According to Eq. (2) of Ref. 1, the similarity transformed Hamiltonian can be written as

$$e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}} = H + [H,\hat{\tau}] + \frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big] \tag{1}$$

where $\hat{\tau} = \sum_{i<j} u(\mathbf{r}_i,\mathbf{r}_j)$ and $\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i) + \sum_{i<j}\frac{1}{r_{ij}}$. This leads to the following similarity transformed Hamiltonian

$$\begin{aligned}\tilde{H} &= H - \sum_i \left(\frac{1}{2}\nabla_i^2\hat{\tau} + (\nabla_i\hat{\tau}) + \frac{1}{2}(\nabla_i\hat{\tau})^2\right)\\ &= H - \sum_{i<j}\hat{K}(\mathbf{r}_i,\mathbf{r}_j) - \sum_{i<j<k}\hat{L}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k),\end{aligned} \tag{2}$$

where the effective two- and three-body operators $\hat{K}(\mathbf{r}_i,\mathbf{r}_u)$ and $\hat{L}(\mathbf{r}_i,\mathbf{r}_u,\mathbf{r}_k)$ are defined as

$$\begin{aligned}\hat{K}(\mathbf{r}_1,\mathbf{r}_2)) = \frac{1}{2}\Big(&\nabla_1^2 u(\mathbf{r}_1,\mathbf{r}_2) + \nabla_2^2 u(\mathbf{r}_1,\mathbf{r}_2)\\ &+(\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2))^2 + (\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2))^2\Big)\\ &+\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1 + \nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2,\end{aligned} \tag{3}$$

$$\begin{aligned}\hat{L}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)) =&\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1 u(\mathbf{r}_1,\mathbf{r}_3) + \nabla_2 u(\mathbf{r}_2,\mathbf{r}_1)\cdot\nabla_2 u(\mathbf{r}_2,\mathbf{r}_3)\\ &+\nabla_3 u(\mathbf{r}_3,\mathbf{r}_1)\cdot\nabla_3 u(\mathbf{r}_3,\mathbf{r}_2).\end{aligned} \tag{4}$$

Here we propose to use a non-symmetric Jastrow factor $u(r_{12},\mu(\mathbf{r_1}))$ and therefore we need to compute the integrals of the $\hat{K}(\mathbf{r}_1,\mathbf{r}_2)$ and $\hat{L}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ operators with such a Jastrow factor. Here, we will give the equations for a general $\mu(\mathbf{r_1})$. To derive properly the integrals for such a new Jastrow factor, one needs to derive the different terms involving gradients and so on.

A. Gradients of $u(r_{12},\mu(\mathbf{r_1}))$

A fundamental quantity is the gradient of $u(\mathbf{r_1},\mathbf{r_2})$ which is

$$\nabla_1 u(\mathbf{r_1},\mathbf{r_2}) = \frac{\partial}{\partial x_1}u(\mathbf{r_1},\mathbf{r_2})\mathbf{e}_{x_1} + \frac{\partial}{\partial y_1}u(\mathbf{r_1},\mathbf{r_2})\mathbf{e}_{y_1} + \frac{\partial}{\partial z_1}u(\mathbf{r_1},\mathbf{r_2})\mathbf{e}_{z_1}. \tag{5}$$

Let us begin with the first term

$$\begin{aligned}\frac{\partial}{\partial x_1}u(r_{12};\mu(\mathbf{r_1})) =&\frac{\partial}{\partial r_{12}}u(r_{12};\mu(\mathbf{r_1}))\frac{\partial r_{12}}{\partial x_1}\\ &+\frac{\partial}{\partial\mu(\mathbf{r_1})}u(r_{12};\mu(\mathbf{r_1}))\frac{\partial\mu(\mathbf{r_1})}{\partial x_1},\end{aligned} \tag{6}$$

but as

$$\frac{\partial}{\partial\mu}u(r_{12};\mu) = \frac{e^{-(\mu r_{12})^2}}{2\sqrt{\pi}\mu^2} \tag{7}$$

one obtains

$$\begin{aligned}\frac{\partial}{\partial x_1}u(r_{12};\mu(\mathbf{r_1})) =&\frac{1-\mathrm{erf}(\mu(\mathbf{r_1})r_{12})}{2r_{12}}(x_1-x_2)\\ &+\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}\frac{\partial\mu(\mathbf{r_1})}{\partial x_1}.\end{aligned} \tag{8}$$

Similarly, as by definition $\frac{\partial\mu(\mathbf{r_1})}{\partial x_2} = 0$, one obtains that

$$\frac{\partial}{\partial x_2}u(r_{12};\mu(\mathbf{r_1})) = -(x_1-x_2)\frac{1-\mathrm{erf}(\mu(\mathbf{r_1})r_{12})}{2r_{12}}. \tag{9}$$

One can summarize the gradients of $u(r_{12},\mu(\mathbf{r_1}))$ by the following formulas

$$\nabla_1 u(r_{12};\mu(\mathbf{r_1})) = \mathbf{u_0}(r_{12},\mu(\mathbf{r_1})) + \gamma(\mathbf{r}_1,r_{12}), \tag{10}$$

with

$$\mathbf{u_0}(r_{12},\mu(\mathbf{r_1})) = u_0^x(r_{12},\mu(\mathbf{r_1}))\mathbf{e}_{x_1} + u_0^y(r_{12},\mu(\mathbf{r_1}))\mathbf{e}_{y_1} + u_0^z(r_{12},\mu(\mathbf{r_1}))\mathbf{e}_{z_1}, \tag{11}$$

$$u_0^x(r_{12},\mu(\mathbf{r_1})) = \frac{1-\mathrm{erf}(\mu(\mathbf{r}_1)r_{12})}{2r_{12}}(x_1-x_2), \tag{12}$$

and

$$\gamma(\mathbf{r}_1,r_{12}) = \frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}\nabla_1\mu(\mathbf{r}_1), \tag{13}$$

and equivalently for $\nabla_2 u(r_{12};\mu(\mathbf{r_1}))$

$$\nabla_2 u(r_{12};\mu(\mathbf{r_1})) = -\mathbf{u_0}(r_{12},\mu(\mathbf{r_1})). \tag{14}$$

B. Computation of $\Big(\nabla_1 u(r_{12};\mu(\mathbf{r_1}))\Big)^2 + \Big(\nabla_2 u(r_{12};\mu(\mathbf{r_1}))\Big)^2$

According to Eq. (8) one has

$$\begin{aligned}\frac{\partial}{\partial x_1}u(r_{12};\mu(\mathbf{r_1})) =&\frac{1-\mathrm{erf}(\mu(\mathbf{r_1})r_{12})}{2r_{12}}(x_1-x_2)\\ &+\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}\frac{\partial\mu(\mathbf{r_1})}{\partial x_1}.\end{aligned} \tag{15}$$

Therefore, the computation of $(\frac{\partial}{\partial x_1}u(r_{12};\mu(\mathbf{r_1})))^2$ yields

$$\begin{aligned}\left(\frac{\partial}{\partial x_1}u(r_{12};\mu(\mathbf{r_1}))\right)^2 =&\frac{\Big(1-\mathrm{erf}(\mu(\mathbf{r_1})r_{12})\Big)^2}{4(r_{12})^2}(x_1-x_2)^2\\ &+\frac{e^{-2(\mu(\mathbf{r}_1)r_{12})^2}}{4\pi\mu(\mathbf{r}_1)^4}\left(\frac{\partial\mu(\mathbf{r_1})}{\partial x_1}\right)^2\\ &+\frac{1-\mathrm{erf}(\mu(\mathbf{r_1})r_{12})}{r_{12}}(x_1-x_2)\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}\frac{\partial\mu(\mathbf{r_1})}{\partial x_1}.\end{aligned} \tag{16}$$

a)Electronic mail: emmanuel.giner@lct.jussieu.fr

Therefore, the computation of $\left(\nabla_1 u(r_{12};\mu(\mathbf{r_1}))\right)^2$ yields

$$\begin{aligned}\left(\nabla_1 u(r_{12};\mu(\mathbf{r_1}))\right)^2 &= \frac{\left(1-\text{erf}(\mu(\mathbf{r}_1)r_{12})\right)^2}{4}\\ &+\frac{e^{-2(\mu(\mathbf{r}_1)r_{12})^2}}{4\pi\mu(\mathbf{r}_1)^4}\left(\nabla_1\mu(\mathbf{r_1})\right)^2\\ &+\nabla_1\mu(\mathbf{r_1})\cdot(\mathbf{r}_1-\mathbf{r}_2)\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{r_{12}}\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}\end{aligned} \tag{17}$$

Eventually, the total operator yields

$$\begin{aligned}\frac{\left(\nabla_1 u(r_{12};\mu(\mathbf{r_1}))\right)^2+\left(\nabla_2 u(r_{12};\mu(\mathbf{r_1}))\right)^2}{2} &= \frac{\left(1-\text{erf}(\mu(\mathbf{r}_1)r_{12})\right)^2}{4}\\ &+\frac{1}{2}\frac{e^{-2(\mu(\mathbf{r}_1)r_{12})^2}}{4\pi\mu(\mathbf{r}_1)^4}\left(\nabla_1\mu(\mathbf{r_1})\right)^2\\ &+\frac{1}{2}\nabla_1\mu(\mathbf{r_1})\cdot(\mathbf{r}_1-\mathbf{r}_2)\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{r_{12}}\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2}.\end{aligned} \tag{18}$$

Note the $\frac{1}{2}$ factor in the second and third lines of Eq. (18) which is due to the fact that $\mu(\mathbf{r_1})$ depends only on $\mathbf{r}_1$. These integrals remain still possible through an analytical integration on $\mathbf{r}_2$ and numerical integration on $\mathbf{r}_1$.

C. Derivation of the Laplacian

We need to compute the following quantity

$$\nabla_1\cdot\nabla_1 u(r_{12};\mu(\mathbf{r_1}))+\nabla_2\cdot\nabla_2 u(r_{12};\mu(\mathbf{r_1})). \tag{19}$$

where $\nabla_1 u(r_{12};\mu(\mathbf{r_1}))$ and $\nabla_2 u(r_{12};\mu(\mathbf{r_1}))$ are given by the formulas (10) and (14), respectively. Therefore one needs to compute

$$\begin{aligned}&\nabla_1\cdot\nabla_1 u(r_{12};\mu(\mathbf{r_1}))+\nabla_2\cdot\nabla_2 u(r_{12};\mu(\mathbf{r_1}))\\ =&\nabla_1\cdot(\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))+\gamma(\mathbf{r}_1,r_{12}))-\nabla_2\cdot\mathbf{u_0}(r_{12},\mu(\mathbf{r_1})).\end{aligned} \tag{20}$$

The term in ∇_1 yields

$$\nabla_1\cdot(\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))+\gamma(\mathbf{r}_1,r_{12}))=\nabla_1\cdot\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))+\nabla_1\cdot\gamma(\mathbf{r}_1,r_{12}), \tag{21}$$

Therefore, when adding the two derivatives on has that

$$\begin{aligned}&\nabla_1\cdot\nabla_1 u(r_{12};\mu(\mathbf{r_1}))+\nabla_2\cdot\nabla_2 u(r_{12};\mu(\mathbf{r_1}))\\ &=\nabla_1\cdot\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))-\nabla_2\cdot\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))+\nabla_1\cdot\gamma(\mathbf{r}_1,r_{12}),\end{aligned} \tag{22}$$

The derivative of $u_0^x(r_{12},\mu(\mathbf{r_1}))$ with respect to x_1 yields

$$\begin{aligned}\frac{\partial}{\partial x_1}u_0^x(r_{12},\mu(\mathbf{r_1})) &= \frac{\partial}{\partial x_1}\bigg|_{\mu(\mathbf{r_1})=cst}\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{2r_{12}}(x_1-x_2)\\ &+(x_1-x_2)\frac{\partial}{\partial\mu(\mathbf{r_1})}\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{2r_{12}}\frac{\partial}{\partial x_1}\mu(\mathbf{r_1}),\end{aligned} \tag{23}$$

and correspondingly for x_2

$$\frac{\partial}{\partial x_2}u_0^x(r_{12},\mu(\mathbf{r_1}))=\frac{\partial}{\partial x_2}\left(\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{2r_{12}}(x_1-x_2)\right). \tag{24}$$

One can notice that

$$\begin{aligned}&\nabla_1\bigg|_{\mu(\mathbf{r_1})=cst}\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))-\nabla_2\cdot\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))\\ =&2\times\left(\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{r_{12}}-\frac{\mu(\mathbf{r_1})}{\sqrt{\pi}}e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2}\right),\end{aligned} \tag{25}$$

as it is the scalar potential obtained with the previously derived Jastrow factor but with $\mu(\mathbf{r_1})$ instead of μ. Then, as

$$\frac{\partial}{\partial\mu}\left(1-\text{erf}(\mu r_{12})\right)=-2\frac{r_{12}}{\sqrt{\pi}}e^{-\left(\mu r_{12}\right)^2}, \tag{26}$$

the second term yields

$$\begin{aligned}&\frac{\partial}{\partial\mu(\mathbf{r_1})}\frac{1-\text{erf}(\mu(\mathbf{r}_1)r_{12})}{2r_{12}}(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_1\mu(\mathbf{r_1})\\ &=-\frac{e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2}}{\sqrt{\pi}}(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_1\mu(\mathbf{r_1}).\end{aligned} \tag{27}$$

Eventually the computation of the Laplacian leads to

$$\begin{aligned}&\nabla_1\cdot\nabla_1 u(r_{12};\mu(\mathbf{r_1}))+\nabla_2\cdot\nabla_2 u(r_{12};\mu(\mathbf{r_1}))\\ &=2\times\left(\frac{1-\text{erf}(\mu(\mathbf{r_1})r_{12})}{r_{12}}-\frac{\mu(\mathbf{r_1})}{\sqrt{\pi}}e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2}\right)\\ &-\frac{e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2}}{\sqrt{\pi}}(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_1\mu(\mathbf{r_1})+\nabla_1\cdot\gamma(\mathbf{r}_1,r_{12}).\end{aligned} \tag{28}$$

D. Derivation of the non hermitian term

The non hermitian term can be written as

$$\begin{aligned}&\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1+\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2\\ &=\left(\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))+\gamma(\mathbf{r}_1,r_{12})\right)\cdot\nabla_1-\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))\cdot\nabla_2\\ &=\mathbf{u_0}(r_{12},\mu(\mathbf{r_1}))\cdot\left(\nabla_1-\nabla_2\right)+\gamma(\mathbf{r}_1,r_{12})\cdot\nabla_1.\end{aligned} \tag{29}$$

One recognizes the non hermitian term of Ref. **?** evaluated with a $\mu(\mathbf{r_1})$ and an additional term. Therefore, one can rewrite the non hermitian term as

$$\begin{aligned}&\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1+\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2=\\ &\left(1-\text{erf}(\mu(\mathbf{r_1})r_{12})\right)\frac{\partial}{\partial r_{12}}+\gamma(\mathbf{r}_1,r_{12})\cdot\nabla_1.\end{aligned} \tag{30}$$

E. Sum of all terms for $\hat{K}(\mathbf{r}_i, \mathbf{r}_j)$

Adding all terms reads

$$\begin{aligned}\hat{K}(\mathbf{r}_i, \mathbf{r}_j) =& \frac{1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{12})}{r_{12}} - \frac{\mu(\mathbf{r_1})}{\sqrt{\pi}} e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2} \\ &- \frac{e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2}}{2\sqrt{\pi}}(\mathbf{r}_1 - \mathbf{r}_2)\cdot\nabla_1\mu(\mathbf{r_1}) + \frac{1}{2}\Big(\nabla_1\cdot\gamma(\mathbf{r}_1, r_{12})\Big) \\ &+ \frac{\Big(1 - \mathrm{erf}(\mu(\mathbf{r}_1)r_{12})\Big)^2}{4} \\ &+ \frac{1}{2}\frac{e^{-2(\mu(\mathbf{r}_1)r_{12})^2}}{4\pi\mu(\mathbf{r}_1)^4}\Big(\nabla_1\mu(\mathbf{r_1})\Big)^2 \\ &+ \frac{1}{2}\nabla_1\mu(\mathbf{r_1})\,\cdot\,(\mathbf{r}_1 - \mathbf{r}_2)\frac{1 - \mathrm{erf}(\mu(\mathbf{r}_1)r_{12})}{r_{12}}\frac{e^{-(\mu(\mathbf{r}_1)r_{12})^2}}{2\sqrt{\pi}\mu(\mathbf{r}_1)^2} \\ &+ \Big(1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{12})\Big)\frac{\partial}{\partial r_{12}} + \gamma(\mathbf{r}_1, r_{12})\cdot\nabla_1.\end{aligned} \tag{31}$$

Summing $\frac{1}{r_{12}} - \hat{K}(\mathbf{r}_i, \mathbf{r}_j)$ leads to

$$\begin{aligned}\frac{1}{r_{12}} - \hat{K}(\mathbf{r}_i, \mathbf{r}_j) =& \tilde{\mathcal{W}}_{ee}(r_{ij}, \mu(\mathbf{r_1})) + \tilde{t}(r_{12}, \mu(\mathbf{r_1})) \\ &+ \tilde{\mathcal{U}}(r_{ij}, \mu(\mathbf{r_1})) + \tilde{\mathcal{V}}(r_{ij}, \mu(\mathbf{r_1}))\end{aligned} \tag{32}$$

with

$$\begin{aligned}\tilde{\mathcal{W}}_{ee}(r_{ij}, \mu(\mathbf{r_1})) =& \frac{\mathrm{erf}(\mu(\mathbf{r_1})r_{ij})}{r_{ij}} + \frac{\mu(\mathbf{r_1})}{\sqrt{\pi}} e^{-\left(\mu(\mathbf{r_1})r_{ij}\right)^2} \\ &- \frac{\Big(1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2}{4},\end{aligned} \tag{33}$$

$$\tilde{t}(r_{12}, \mu(\mathbf{r_1})) = \Big(\mathrm{erf}(\mu(\mathbf{r_1})r_{ij}) - 1\Big)\frac{\partial}{\partial r_{ij}}, \tag{34}$$

$$\begin{aligned}\tilde{\mathcal{U}}(r_{ij}, \mu(\mathbf{r_1})) =& -\frac{1}{2\sqrt{\pi}}\nabla_1\mu(\mathbf{r_1})\cdot(\mathbf{r}_1 - \mathbf{r}_2)e^{-\left(\mu(\mathbf{r_1})r_{12}\right)^2} \\ &\left(\frac{1 - \mathrm{erf}(\mu(\mathbf{r}_1)r_{12})}{2\mu(\mathbf{r}_1)^2 r_{12}} - 1\right)\end{aligned} \tag{35}$$

$$\begin{aligned}\tilde{\mathcal{V}}(r_{ij}, \mu(\mathbf{r_1})) =& -\frac{1}{2}\Big(\nabla_1\cdot\gamma(\mathbf{r}_1, r_{12})\Big) - \gamma(\mathbf{r}_1, r_{12})\cdot\nabla_1 \\ &- \frac{1}{2}\frac{e^{-2(\mu(\mathbf{r}_1)r_{12})^2}}{4\pi\mu(\mathbf{r}_1)^4}\Big(\nabla_1\mu(\mathbf{r_1})\Big)^2\end{aligned} \tag{36}$$

II. INTEGRALS COMPUTATIONS

A. Integrals of $\tilde{\mathcal{W}}_{ee}(r_{ij}, \mu(\mathbf{r_1}))$

One needs to compute the integrals of that type

$$\begin{aligned}&\langle kl|\tilde{\mathcal{W}}_{ee}(r_{ij}, \mu(\mathbf{r_1}))|ij\rangle \\ &= \int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi_i(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\tilde{\mathcal{W}}_{ee}(r_{ij}, \mu(\mathbf{r_1}))\phi_i(\mathbf{r}_2)\phi_l(\mathbf{r}_2) \\ &\langle kl|\frac{\mathrm{erf}(\mu(\mathbf{r_1})r_{ij})}{r_{ij}}|ij\rangle + \langle kl|\frac{\mu(\mathbf{r_1})}{\sqrt{\pi}}e^{-\left(\mu(\mathbf{r_1})r_{ij}\right)^2}|ij\rangle \\ &- \frac{1}{4}\langle kl|\Big(1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2|ij\rangle.\end{aligned} \tag{37}$$

By defining the following integrals

$$w_{jl}(\mathbf{r}, \mu) = \int \mathrm{d}\mathbf{r}'\phi_j(\mathbf{r}')\phi_l(\mathbf{r}')\frac{\mathrm{erf}(\mu|\mathbf{r} - \mathbf{r}'\,|)}{|\mathbf{r} - \mathbf{r}'\,|}, \tag{38}$$

$$G_{jl}(\mathbf{r}, \alpha) = \int \mathrm{d}\mathbf{r}'\phi_j(\mathbf{r}')\phi_l(\mathbf{r}')e^{-\left(\alpha|\mathbf{r} - \mathbf{r}'\,|\right)^2}, \tag{39}$$

one can compute the two first integrals in Eq. (37) as

$$\langle kl|\frac{\mathrm{erf}(\mu(\mathbf{r_1})r_{ij})}{r_{ij}}|ij\rangle = \int \mathrm{d}\mathbf{r}\phi_i(\mathbf{r})\phi_k(\mathbf{r})w_{jl}(\mathbf{r}, \mu(\mathbf{r})), \tag{40}$$

$$\langle kl|\frac{\mu(\mathbf{r_1})}{\sqrt{\pi}}e^{-\left(\mu(\mathbf{r_1})r_{ij}\right)^2}|ij\rangle = \int \mathrm{d}\mathbf{r}\phi_i(\mathbf{r})\phi_k(\mathbf{r})\frac{\mu(\mathbf{r})}{\sqrt{\pi}}G_{jl}(\mathbf{r}, (\mu(\mathbf{r}))^2). \tag{41}$$

The last term $\langle kl|\Big(1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2|ij\rangle$ can be computed as

$$\begin{aligned}&\langle kl|\Big(1 - \mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2|ij\rangle \\ &= \int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)(g(r_{12}, \mu(\mathbf{r_1})))^2\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2),\end{aligned} \tag{42}$$

with

$$g(x, \mu) = 1 - \mathrm{erf}(\mu x). \tag{43}$$

To make integrals analytical, we first fit the function $\mathrm{erfc}(x)$ with a simple Slater-Gaussian function

$$\mathrm{erfc}(x) \approx h(x, \alpha, \beta, c) \tag{44}$$

with

$$h(x, \alpha, \beta, c) = e^{-\alpha x - \beta x^2} \tag{45}$$

and $\alpha = 1.09529$ and $\beta = 0.756023$. Then, by posing $y = \mu x$, one obtains

$$\begin{aligned}g(x, \mu) \approx& e^{-\alpha\mu x - \beta(\mu x)^2} \\ =& h(x, \alpha\mu, \beta\mu^2).\end{aligned} \tag{46}$$

TABLE I. Set of coefficients c_m and exponents ζ_m for the fit of e^{-X}

ζ_m	c_m
30573.77073	0.00338925525
5608.452381	0.00536433869
1570.956734	0.00818702846
541.3978511	0.01202047655
212.4346963	0.01711289568
91.31444574	0.02376001022
42.04087246	0.03229121736
20.43200443	0.04303646818
10.37775161	0.05624657578
5.468807545	0.07192311571
2.973735292	0.08949389001
1.661441902	0.10727599240
0.9505256082	0.12178961750
0.5552868397	0.12740141870
0.3304336002	0.11759168160
0.1998230323	0.08953504394
0.1224684076	0.05066721317
0.07575825322	0.01806363869
0.04690146243	0.00305632563
0.02834749861	0.00013317513

Therefore, one can fit $g(x)^2$ as

$$\begin{aligned} g(x,\mu)^2 &= \Big(1-\mathrm{erf}(\mu x)\Big)^2 \\ &= \Big(e^{-\alpha\mu x}e^{-\beta\mu^2x^2}\Big)^2 \\ &= e^{-2\alpha\mu x}e^{-2\beta\mu^2x^2} \\ &= h(x, 2\alpha\mu, 2\beta\mu^2). \end{aligned} \tag{47}$$

Then we fit the Slater function as a linear combination of Gaussians

$$e^{-X} = \sum_{m=1}^{N_s} c_m e^{-\zeta_m X^2}. \tag{48}$$

In the present work, we use $N_s = 20$ and the $\{c_m, \zeta_m\}$ parameters are reported in Table II A. By posing $X = \gamma x$ one can fit any Slater function as

$$e^{-\gamma x} = \sum_{m=1}^{N_s} c_m e^{-\zeta_m \gamma^2 x^2}. \tag{49}$$

Eventually, the function $g(x,\mu)^2$ is obtained as a linear combination of Gaussian

$$g(x,\mu)^2 \approx \sum_{m=1}^{N_s} c_m e^{-2\mu^2\big(2\alpha\zeta_m+\beta\big)x^2}, \tag{50}$$

which makes then the integrals analytical

$$\begin{aligned} \langle kl|\Big(1-\mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2|ij\rangle \approx \sum_{m=1}^{N_s} c_m \int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \\ \phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2)e^{-2\mu(\mathbf{r})^2\big(2\alpha\zeta_m+\beta\big)(r_{12})^2}, \end{aligned} \tag{51}$$

which then can be computed as

$$\begin{aligned} &\langle kl|\Big(1-\mathrm{erf}(\mu(\mathbf{r_1})r_{ij})\Big)^2|ij\rangle \\ &\approx \int \mathrm{d}\mathbf{r}\phi_i(\mathbf{r})\phi_k(\mathbf{r})\sum_{m=1}^{N_s} c_m G_{jl}(\mathbf{r}, 2\mu(\mathbf{r})^2(2\alpha\zeta_m+\beta)). \end{aligned} \tag{52}$$

All numerical tests performed for $\mu > 0.1$ show that this fit is highly accurate.

B. Integrals of $\tilde{t}(r_{12},\mu(\mathbf{r_1}))$

A more practical point of view for the computation of the non hermitian term is the following

$$\begin{aligned} \tilde{t}(r_{12},\mu(\mathbf{r_1})) =& \frac{\mathrm{erf}(\mu(\mathbf{r})r_{12})-1}{2r_{12}} \\ &\Big((x_1-x_2)\frac{\partial}{\partial x_1} + (y_1-y_2)\frac{\partial}{\partial y_1} + (z_1-z_2)\frac{\partial}{\partial z_1}\Big), \end{aligned} \tag{53}$$

$$\begin{aligned} &\tilde{t}(r_{12},\mu(\mathbf{r_1})) = \frac{\mathrm{erf}(\mu(\mathbf{r})r_{12})-1}{2r_{12}} \\ &\Big((x_1-x_2)(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2}) + (y_1-y_2)(\frac{\partial}{\partial y_1} - \frac{\partial}{\partial y_2}) \\ &+ (z_1-z_2)(\frac{\partial}{\partial z_1} - \frac{\partial}{\partial z_2})\Big). \end{aligned} \tag{54}$$

We define the following integrals

$$w^x_{jl}(\mathbf{r},\mu) = \int \mathrm{d}\mathbf{r}'\phi_l(\mathbf{r}')x'\frac{\mathrm{erf}(\mu|\mathbf{r}'-\mathbf{r}|)-1}{|\mathbf{r}'-\mathbf{r}|}\phi_j(\mathbf{r}'), \tag{55}$$

$$w'^x_{jl}(\mathbf{r},\mu) = \int \mathrm{d}\mathbf{r}'\phi_l(\mathbf{r}')\frac{\mathrm{erf}(\mu|\mathbf{r}'-\mathbf{r}|)-1}{|\mathbf{r}'-\mathbf{r}|}\frac{\partial}{\partial x'}\phi_j(\mathbf{r}'), \tag{56}$$

$$w'^{xx}_{jl}(\mathbf{r},\mu) = \int \mathrm{d}\mathbf{r}'x' \;\phi_l(\mathbf{r}')\frac{\mathrm{erf}(\mu|\mathbf{r}'-\mathbf{r}|)-1}{|\mathbf{r}'-\mathbf{r}|}\frac{\partial}{\partial x'}\phi_j(\mathbf{r}'), \tag{57}$$

and we decompose the integral $\langle kl|\tilde{t}(r_{12},\mu(\mathbf{r_1}))|ij\rangle$ in x, y, z components

$$\begin{aligned} \langle kl|\tilde{t}(r_{12},\mu(\mathbf{r_1}))|ij\rangle =& \langle kl|\tilde{t}_x(r_{12},\mu(\mathbf{r_1}))|ij\rangle + \langle kl|\tilde{t}_y(r_{12},\mu(\mathbf{r_1}))|ij\rangle \\ &+ \langle kl|\tilde{t}_z(r_{12},\mu(\mathbf{r_1}))|ij\rangle, \end{aligned} \tag{58}$$

with

$$\begin{aligned} \langle kl|\tilde{t}_x(r_{12},\mu(\mathbf{r_1}))|ij\rangle = \int \mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\phi_l(\mathbf{r}_2)\phi_k(\mathbf{r}_1)\frac{\mathrm{erf}(\mu(\mathbf{r})r_{12})-1}{2r_{12}} \\ (x_1-x_2)(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2})\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2). \end{aligned} \tag{59}$$

The integral $\langle kl|\tilde{t}_x(r_{12},\mu(\mathbf{r_1}))|ij\rangle$ can then be computed as

$$\begin{aligned}
&\langle kl|\tilde{t}_x(r_{12},\mu(\mathbf{r_1}))|ij\rangle \\
&\quad= \int \mathrm{d}\mathbf{r}\phi_k(\mathbf{r})x\frac{\partial}{\partial x}\phi_i(\mathbf{r})\frac{1}{2}(w_{jl}(\mathbf{r},\infty) - w_{jl}(\mathbf{r},\mu(\mathbf{r}))) \\
&\quad+ \int \mathrm{d}\mathbf{r}\phi_k(\mathbf{r})\phi_i(\mathbf{r})\frac{1}{2}(w'^{xx}_{jl}(\mathbf{r},\infty) - w'^{xx}_{jl}(\mathbf{r},\mu(\mathbf{r}))) \\
&\quad- \int \mathrm{d}\mathbf{r}\phi_k(\mathbf{r})x\phi_i(x)\frac{1}{2}(w'^{x}_{jl}(\mathbf{r},\infty) - w'^{x}_{jl}(\mathbf{r},\mu(\mathbf{r}))) \\
&\quad- \int \mathrm{d}\mathbf{r}\phi_k(\mathbf{r})\frac{\partial}{\partial x}\phi_i(\mathbf{r})\frac{1}{2}(w^{x}_{jl}(\mathbf{r},\infty) - w^{x}_{jl}(\mathbf{r},\mu(\mathbf{r})))
\end{aligned} \tag{60}$$

[1] A. J. Cohen, H. Luo, K. Guther, W. Dobrautz, D. P. Tew, and A. Alavi, The Journal of Chemical Physics **151**, 061101 (2019), https://doi.org/10.1063/1.5116024.