Mapping RS-DFT and F12

Emmanuel Giner[a)]

blabla

I. SIMILARITY TRANSFORMED HAMILTONIAN FOR HE

A. The regular Hamiltonian

Consider the Hamiltonian of He atom written in the $\mathbf{r}r_{12}$ and $\mathbf{r}s$ coordinates:

$$\begin{aligned} H = &- \frac{1}{2}\sum_{i=1}^{2}\Big(\frac{\partial^2}{\partial {r_i}^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} + \frac{2Z}{r_i}\Big) \\ &- \Big(\frac{\partial^2}{\partial {r_{12}}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{1}{r_{12}}\Big) \\ &- \Big(\frac{\mathbf{r_1}}{r_1}\cdot\frac{\mathbf{r_{12}}}{r_{12}}\frac{\partial}{\partial r_1} + \frac{\mathbf{r_2}}{r_2}\cdot\frac{\mathbf{r_{21}}}{r_{21}}\frac{\partial}{\partial r_2}\Big). \end{aligned} \tag{1}$$

Therefore, if one defines h_c as

$$\begin{aligned} h_c = &- \frac{1}{2}\sum_{i=1}^{2}\Big(\frac{\partial^2}{\partial {r_i}^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} + \frac{2Z}{r_i}\Big) \\ &- \Big(\frac{\partial^2}{\partial {r_{12}}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\Big) \\ &- \Big(\frac{\mathbf{r_1}}{r_1}\cdot\frac{\mathbf{r_{12}}}{r_{12}}\frac{\partial}{\partial r_1} + \frac{\mathbf{r_2}}{r_2}\cdot\frac{\mathbf{r_{21}}}{r_{21}}\frac{\partial}{\partial r_2}\Big), \end{aligned} \tag{2}$$

one can rewrite the Hamiltonian as

$$H = h_c + \frac{1}{r_{12}}. \tag{3}$$

B. The similarity transformed Hamiltonian

Now let us consider the Similarity transformed Hamiltonian $\tilde{H}[j]$

$$\tilde{H}[j] = e^{-j(r_{12})} H e^{j(r_{12})}, \tag{4}$$

where $j(r_{12})$ is a general jastrow factor depending only on r_{12}. Therefore, the only new terms arising in $\tilde{H}[j]$ are those coming from the differential operator in r_{12},

$$\mathcal{T}[j] = -e^{-j(r_{12})}\Big(\frac{\partial^2}{\partial {r_{12}}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\Big)e^{j(r_{12})}. \tag{5}$$

Let us compute the action on $\phi(r_{12})$ of $\mathcal{T}[j]$

$$\begin{aligned} \mathcal{T}[j]\phi(r_{12}) = &-e^{-j(r_{12})}\Big[\frac{\partial^2}{\partial {r_{12}}^2} + \frac{2}{r}\frac{\partial}{\partial r_{12}}\Big]e^{j(r_{12})}\phi(r_{12}) \\ = &-\frac{\partial^2 \phi}{\partial {r_{12}}^2} - \frac{2}{r_{12}}\frac{\partial \phi}{\partial r_{12}} \\ &- 2\frac{\partial j}{\partial r_{12}}\frac{\partial \phi}{\partial r_{12}} \\ &- \Big[\frac{2}{r_{12}}\frac{\partial j}{\partial r_{12}} + \frac{\partial^2 j}{\partial {r_{12}}^2} + \Big(\frac{\partial j}{\partial r_{12}}\Big)^2\Big]\phi(r_{12}). \end{aligned} \tag{6}$$

Now, let us define the following operators

$$\tilde{t}[j] = -2\frac{\partial j}{\partial r_{12}}\frac{\partial}{\partial r_{12}}, \tag{7}$$

$$\tilde{W}[j] = -\frac{2}{r_{12}}\frac{\partial j}{\partial r_{12}}, \tag{8}$$

$$\tilde{w}[j] = -\frac{\partial^2 j}{\partial {r_{12}}^2} - \Big(\frac{\partial j}{\partial r_{12}}\Big)^2. \tag{9}$$

Therefore, one can write the action of the Similarity transformed Hamiltonian on $\phi(r_{12})$ as

$$\tilde{H}[j]\phi(\mathbf{r}_1,\mathbf{r}_2) = H\phi(\mathbf{r}_1,\mathbf{r}_2) + \tilde{t}[j]\phi(\mathbf{r}_1,\mathbf{r}_2) + \tilde{w}[j]\phi(\mathbf{r}_1,\mathbf{r}_2) + \tilde{W}[j]\,\phi(\mathbf{r}_1,\mathbf{r}_2). \tag{10}$$

Now we choose $j(r_{12})$ such that it fulfills the following condition

$$\begin{aligned} \tilde{W}[j] + \frac{1}{r_{12}} &= \frac{\text{erf}(\mu r_{12})}{r_{12}} \\ \Leftrightarrow -\frac{2}{r_{12}}\frac{\partial j}{\partial r_{12}} + \frac{1}{r_{12}} &= \frac{\text{erf}(\mu r_{12})}{r_{12}} \end{aligned} \tag{11}$$

which is equivalent to

$$\frac{\partial j}{\partial r_{12}} = \frac{1-\text{erf}(\mu r_{12})}{2}. \tag{12}$$

The solution to Eq. (12) is

$$j(r_{12};\mu) = \frac{1}{2}r_{12}\Big(1-\text{erf}(\mu r_{12})\Big) - \frac{1}{2\sqrt{\pi}\mu}e^{-(r_{12}\mu)^2}. \tag{13}$$

With $j(r_{12},\mu)$ defined as in (13), one obtains the following effective Hamiltonian

$$\begin{aligned} \tilde{H}[j] = &- \frac{1}{2}\sum_{i=1}^{2}\Big(\frac{\partial^2}{\partial {r_i}^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} + \frac{2Z}{r_i}\Big) \\ &- \Big(\frac{\partial^2}{\partial {r_{12}}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\Big) \\ &- \Big(\frac{\mathbf{r_1}}{r_1}\cdot\frac{\mathbf{r_{12}}}{r_{12}}\frac{\partial}{\partial r_1} + \frac{\mathbf{r_2}}{r_2}\cdot\frac{\mathbf{r_{21}}}{r_{21}}\frac{\partial}{\partial r_2}\Big) \\ &+ \tilde{t}[j] + \frac{\text{erf}(\mu r_{12})}{r_{12}} + \tilde{w}[j]. \end{aligned} \tag{14}$$

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

One can therefore rewrite the similarity transformed Hamiltonian as

$$\tilde{H}[j] = h_c + \frac{\text{erf}(\mu r_{12})}{r_{12}} + \tilde{t}[j] + \tilde{w}[j]. \tag{15}$$

C. Analysis of different terms

Let us consider the term $\tilde{t}[j]$

$$\tilde{t}[j] = -2\frac{\partial j}{\partial r_{12}}\frac{\partial}{\partial r_{12}}, \tag{16}$$

which, according to Eq. (12) becomes

$$\begin{aligned}\tilde{t}[j] &= -2\frac{\partial j}{\partial r_{12}}\frac{\partial}{\partial r_{12}},\\ &= \Big(\text{erf}(\mu r_{12}) - 1\Big)\frac{\partial}{\partial r_{12}}.\end{aligned} \tag{17}$$

This is short-range operator multiplying a derivative operator, therefore it can be approximated locally provided that μ is large enough. Then, one has the usual long-range interaction of RS-DFT, whose integrals can be computed analytically.

Then, one has the potential $\tilde{w}[j]$

$$\tilde{w}[j] = -\frac{\partial^2 j}{\partial {r_{12}}^2} - \Big(\frac{\partial j}{\partial r_{12}}\Big)^2, \tag{18}$$

which, according to Eq. (12) is simply

$$\tilde{w}[j] = -\frac{1}{4}\Big(1 - \text{erf}(\mu r_{12})\Big)^2 + \frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2} \tag{19}$$

II. GENERAL FORMULATION OF SIMILARITY TRANSFORMED HAMILTONIAN

A. General equations for a two-electron system

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

$$e^{-\hat{\tau}}\hat{H}e^{\hat{\tau}} = H + [H,\hat{\tau}] + \frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big] \tag{20}$$

where $\hat{\tau} = \sum_{i>j} u(\mathbf{r}_i,\mathbf{r}_j)$ and $\hat{H} = \sum_i -\frac{1}{2}\,\nabla_i^2 + v(\mathbf{r}_i) + \sum_{i>j}\frac{1}{r_{ij}}$. Of course, only the differential terms do not commute in Eq. (20). Let us compute each terms, beginning with the action of $[H,\hat{\tau}]$ on a function $\phi(\mathbf{r}_1,\dots\mathbf{r}_N)$.

$$\begin{aligned}\Big[H,\hat{\tau}\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N) &= \Big[-\frac{1}{2}\sum_i \nabla_i^2, \sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\\ &= -\frac{1}{2}\sum_i \nabla_i^2\Big(\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big)\\ &+ \frac{1}{2}\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\sum_i \nabla_i^2\phi(\mathbf{r}_1,\dots\mathbf{r}_N).\end{aligned} \tag{21}$$

The first term in the right-hand side of Eq. (21) is

$$\begin{aligned}&-\frac{1}{2}\sum_i \nabla_i^2\Big(\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big)\\ &= -\frac{1}{2}\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\sum_i\Big(\nabla_i^2\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big)\\ &-\frac{1}{2}\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big(\sum_i \nabla_i^2\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\\ &-\sum_i\Big(\nabla_i\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\cdot\Big(\nabla_i\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big).\end{aligned} \tag{22}$$

Inserting Eq. (22) in Eq. (21) leads to cancellation of the terms involving $\nabla_i^2\phi(\mathbf{r}_1,\dots\mathbf{r}_N)$

$$\begin{aligned}[H,\hat{\tau}]\phi(\mathbf{r}_1,\dots\mathbf{r}_N) &= \frac{1}{2}\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big(\sum_i \nabla_i^2\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\\ &-\sum_i\Big(\nabla_i\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\cdot\Big(\nabla_i\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\Big)\end{aligned} \tag{23}$$

and therefore one can write the first commutator of Eq. (20) as

$$\begin{aligned}[H,\hat{\tau}] &= -\frac{1}{2}\Big(\sum_i \nabla_i^2\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\\ &-\sum_i\Big(\nabla_i\sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big)\cdot\Big(\nabla_i\Big),\end{aligned} \tag{24}$$

and as $\nabla_i f(\mathbf{r}_j) = \delta_{ij}\nabla_i f(\mathbf{r}_i)$ one obtains

$$\begin{aligned}[H,\hat{\tau}] &= -\frac{1}{2}\Big(\sum_i \nabla_i^2 u(\mathbf{r}_i,\mathbf{r}_j) + \sum_j \nabla_j^2 u(\mathbf{r}_i,\mathbf{r}_j))\Big)\\ &-\sum_i\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_i\Big)\\ &-\sum_i\Big(\nabla_j u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_j\Big).\end{aligned} \tag{25}$$

Then, one has to compute the second-order commutator in Eq. (20):

$$\begin{aligned}&\Big[[H,\hat{\tau}],\hat{\tau}\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N) =\\ &\Big[-\frac{1}{2}\Big(\sum_i \nabla_i^2 u(\mathbf{r}_i,\mathbf{r}_j) + \sum_j \nabla_j^2 u(\mathbf{r}_i,\mathbf{r}_j))\Big), \sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\\ &+\Big[-\sum_i\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_i\Big), \sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N)\\ &+\Big[-\sum_i\Big(\nabla_j u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_j\Big), \sum_{j>k} u(\mathbf{r}_j,\mathbf{r}_k)\Big]\phi(\mathbf{r}_1,\dots\mathbf{r}_N).\end{aligned} \tag{26}$$

The first term in Eq. (26) is actually a potential term and therefore it cancels out, then it comes

$$\Big[[H,\hat{\tau}],\hat{\tau}\Big] = -\sum_i\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)^2 - \sum_j\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)^2 \tag{27}$$

and so the two commutators become

$$[H,\hat{\tau}]+\frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big]=$$
$$\sum_{i>j}-\frac{1}{2}\Big(\nabla_i^2 u(\mathbf{r}_i,\mathbf{r}_j)+\nabla_j^2 u(\mathbf{r}_i,\mathbf{r}_j)+\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)^2+\Big(\nabla_j u(\mathbf{r}_i,\mathbf{r}_j)\Big)^2\Big)$$
$$-\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_i\Big)-\Big(\nabla_j u(\mathbf{r}_i,\mathbf{r}_j)\Big)\cdot\Big(\nabla_j\Big). \tag{28}$$

III. COMPUTATIONS OF INTEGRALS

A. $\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)$

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)=\frac{\partial}{\partial x_1}u(r_{12})\mathbf{e}_{x1}+\frac{\partial}{\partial y_1}u(r_{12})\mathbf{e}_{y1}+\frac{\partial}{\partial z_1}u(r_{12})\mathbf{e}_{z1}, \tag{29}$$

and

$$\frac{\partial}{\partial x_1}u(r_{12})=\frac{\partial}{\partial r_{12}}u(r_{12})\frac{\partial r_{12}}{\partial x_1}, \tag{30}$$

and as $r_{12}=\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}$ one has

$$\frac{\partial r_{12}}{\partial x_1}=\frac{x_1-x_2}{r_{12}}=-\frac{\partial r_{12}}{\partial x_2}, \tag{31}$$

and according to Eq. (12)

$$\frac{\partial u}{\partial r_{12}}=\frac{1-\mathrm{erf}(\mu r_{12})}{2}, \tag{32}$$

one obtains

$$\frac{\partial}{\partial x_1}u(r_{12})=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big(x_1-x_2\Big). \tag{33}$$

Similarly,

$$\frac{\partial}{\partial x_2}u(r_{12})=\frac{\mathrm{erf}(\mu r_{12})}{2r_{12}-1}\Big(x_1-x_2\Big). \tag{34}$$

Therefore,

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big((x_1-x_2)\mathbf{e}_{x1}+(y_1-y_2)\mathbf{e}_{y1}+(z_1-z_2)\mathbf{e}_{z1}\Big)=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}(\mathbf{r}_1-\mathbf{r}_2) \tag{35}$$

B. $\Big(\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\Big)^2$

According to Eq. (35), one obtains

$$\Big(\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\Big)^2=\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big)^2\Big((x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2\Big)=\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4(r_{12})^2}\times(r_{12})^2=\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4} \tag{36}$$

and therefore

$$\Big(\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\Big)^2+\Big(\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\Big)^2=2\times\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4} \tag{37}$$

C. $\nabla_i u(\mathbf{r}_i,\mathbf{r}_j)\cdot\Big(\nabla_i\Big)$

According to Eq. (35), one obtains Therefore,

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big((x_1-x_2)\frac{\partial}{\partial x_1}+(y_1-y_2)\frac{\partial}{\partial y_1}+(z_1-z_2)\frac{\partial}{\partial z_1}\Big). \tag{38}$$

And noticing the minus sign coming from the derivative in $\mathbf{r}_2$, the total operator can be written as

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1+\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big((x_1-x_2)(\frac{\partial}{\partial x_1}-\frac{\partial}{\partial x_2})+(y_1-y_2)(\frac{\partial}{\partial y_1}-\frac{\partial}{\partial y_2})+(z_1-z_2)(\frac{\partial}{\partial z_1}-\frac{\partial}{\partial z_2})\Big), \tag{39}$$

but as

$$\frac{\partial}{\partial r_{12}^x}=\frac{1}{2}\Big(\frac{\partial}{\partial x_1}-\frac{\partial}{\partial x_2}\Big), \tag{40}$$

one can rewrite as

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1+\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2=\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_{\mathbf{r}_{12}}. \tag{41}$$

Then, introducing $\mathbf{e}_u=\frac{\mathbf{r}_1-\mathbf{r}_2}{r_{12}}$, can notice that

$$\nabla_{\mathbf{r}_{12}}=\frac{\partial}{\partial r_{12}}\mathbf{e}_u+\frac{1}{r_{12}}\frac{\partial}{\partial\theta}\mathbf{e}_\theta+\frac{1}{r_{12}\sin(\theta)}\frac{\partial}{\partial\phi}\mathbf{e}_\phi, \tag{42}$$

and as $\mathbf{r}_1-\mathbf{r}_2=r_{12}\mathbf{e}_u$ one obtains

$$(\mathbf{r}_1-\mathbf{r}_2)\cdot\nabla_{\mathbf{r}_{12}}=r_{12}\frac{\partial}{\partial r_{12}}, \tag{43}$$

and therefore

$$\nabla_1 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_1+\nabla_2 u(\mathbf{r}_1,\mathbf{r}_2)\cdot\nabla_2 = \frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}} r_{12}\frac{\partial}{\partial r_{12}} \\ =\Big(1-\mathrm{erf}(\mu r_{12})\Big)\frac{\partial}{\partial r_{12}}. \tag{44}$$

D. $\nabla_i^2 u(\mathbf{r}_i,\mathbf{r}_j)$

$$\nabla_1^2 u(\mathbf{r}_1,\mathbf{r}_2) = \frac{\partial^2}{\partial {x_1}^2}u(\mathbf{r}_1,\mathbf{r}_2)+\frac{\partial^2}{\partial {y_1}^2}u(\mathbf{r}_1,\mathbf{r}_2)+\frac{\partial^2}{\partial {z_1}^2}u(\mathbf{r}_1,\mathbf{r}_2) \\ =\frac{\partial}{\partial x_1}\Big(\frac{\partial}{\partial x_1}u(\mathbf{r}_1,\mathbf{r}_2)\Big)+\frac{\partial}{\partial y_1}\Big(\frac{\partial}{\partial y_1}u(\mathbf{r}_1,\mathbf{r}_2)\Big)+\frac{\partial}{\partial z_1}\Big(\frac{\partial}{\partial z_1}u(\mathbf{r}_1,\mathbf{r}_2)\Big). \tag{45}$$

But according to Eq. (33), one obtains

$$\begin{aligned}\frac{\partial^2}{\partial {x_1}^2}u(\mathbf{r}_1,\mathbf{r}_2) &= \frac{\partial}{\partial x_1}\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}(x_1-x_2)\Big)\\ &=\Big(\frac{\partial}{\partial x_1}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big)(x_1-x_2)+\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}.\end{aligned} \tag{46}$$

Similarly, according to Eq. (34) one obtains for the second order derivative in x_2

$$\begin{aligned}\frac{\partial^2}{\partial {x_2}^2}u(\mathbf{r}_1,\mathbf{r}_2) &= \frac{\partial}{\partial x_2}\Big(\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}}(x_1-x_2)\Big)\\ &=\Big(\frac{\partial}{\partial x_2}\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}}\Big)(x_1-x_2)-\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}}\\ &=\Big(\frac{\partial}{\partial x_2}\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}}\Big)(x_1-x_2)+\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}.\end{aligned} \tag{47}$$

Also

$$\begin{aligned}\frac{\partial}{\partial x_1}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}} &=\frac{\partial}{\partial r_{12}}\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big)\frac{\partial r_{12}}{\partial x_1}\\ &=\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\end{aligned} \tag{48}$$

and similarly

$$\begin{aligned}\frac{\partial}{\partial x_2}\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}} &=\frac{\partial}{\partial r_{12}}\Big(\frac{\mathrm{erf}(\mu r_{12})-1}{2r_{12}}\Big)\frac{\partial r_{12}}{\partial x_2}\\ &=(-1)\frac{x_1-x_2}{r_{12}}(-1)\frac{\partial}{\partial r_{12}}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\\ &=\frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\\ &=\frac{\partial}{\partial x_1}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}},\end{aligned} \tag{49}$$

which implies that

$$\frac{\partial^2}{\partial {x_2}^2}u(\mathbf{r}_1,\mathbf{r}_2)=\frac{\partial^2}{\partial {x_1}^2}u(\mathbf{r}_1,\mathbf{r}_2). \tag{50}$$

To continue, as

$$\frac{\partial}{\partial r_{12}}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}} = -\frac{1}{r_{12}}\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\Big), \tag{51}$$

one obtains

$$\begin{aligned}\frac{\partial}{\partial x_1}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}} &= \frac{x_1-x_2}{r_{12}}\frac{\partial}{\partial r_{12}}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\\ &=-\frac{(x_1-x_2)}{(r_{12})^2}\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\Big).\end{aligned} \tag{52}$$

Therefore, Eq. (46) becomes

$$\begin{aligned}\frac{\partial^2}{\partial {x_1}^2}u(\mathbf{r}_1,\mathbf{r}_2) &= \Big(\frac{\partial}{\partial x_1}\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big)(x_1-x_2)+\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\\ &=-\frac{(x_1-x_2)^2}{(r_{12})^2}\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\Big)+\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\\ &=\frac{1-\mathrm{erf}(\mu r_{12})}{2r_{12}}\Big(1-\frac{(x_1-x_2)^2}{(r_{12})^2}\Big)-\frac{(x_1-x_2)^2}{(r_{12})^2}\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\end{aligned} \tag{53}$$

and so

$$\Big(\frac{\partial^2}{\partial {x_1}^2}+\frac{\partial^2}{\partial {x_2}^2}\Big)u(\mathbf{r}_1,\mathbf{r}_2) = \frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}\Big(1-\frac{(x_1-x_2)^2}{(r_{12})^2}\Big) \\ -2\frac{(x_1-x_2)^2}{(r_{12})^2}\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}. \tag{54}$$

Therefore,

$$\begin{aligned}&\Big(\frac{\partial^2}{\partial {x_1}^2}+\frac{\partial^2}{\partial {x_2}^2}+\frac{\partial^2}{\partial {y_1}^2}+\frac{\partial^2}{\partial {y_2}^2}+\frac{\partial^2}{\partial {z_1}^2}+\frac{\partial^2}{\partial {z_2}^2}\Big)u(\mathbf{r}_1,\mathbf{r}_2)\\ &=\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}\Big(3-\frac{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}{(r_{12})^2}\Big)\\ &-2\frac{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}{(r_{12})^2}\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\\ &=\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}\Big(3-\frac{(r_{12})^2}{(r_{12})^2}\Big)-2\frac{(r_{12})^2}{(r_{12})^2}\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\\ &=\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}\times 2-2\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\\ &=2\times\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{12})^2}\Big)\end{aligned} \tag{55}$$

E. Sum of all terms

According to Eq. (28), Eq. (44), Eq. (37) and Eq. (54), the additional terms arising from the commutators in $\tilde{H}[j]$ are (for a two-electron system)

$$
\begin{aligned}
&[H,\hat{\tau}]+\frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big]=\\
&-\frac{1}{2}2\times\Big(\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}-\frac{\mu}{\sqrt{\pi}}e^{-\left(\mu r_{12}\right)^2}+\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4}\Big)\\
&-\Big(1-\mathrm{erf}(\mu r_{12})\Big)\frac{\partial}{\partial r_{12}},
\end{aligned}
\tag{56}
$$

or equivalently

$$
\begin{aligned}
&[H,\hat{\tau}]+\frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big]=\\
&-\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-\left(\mu r_{12}\right)^2}-\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4}\\
&+\Big(\mathrm{erf}(\mu r_{12})-1\Big)\frac{\partial}{\partial r_{12}}.
\end{aligned}
\tag{57}
$$

Therefore, the full similarity transformed Hamiltonian can be written as

$$
\begin{aligned}
\tilde{H}[j]=&\sum_{i=1,2}\Big(-\frac{1}{2}(\nabla_i)^2+v(\mathbf{r}_i)\Big)+\frac{1}{r_{12}}\\
&-\frac{1-\mathrm{erf}(\mu r_{12})}{r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-\left(\mu r_{12}\right)^2}-\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4}\\
&+\Big(\mathrm{erf}(\mu r_{12})-1\Big)\frac{\partial}{\partial r_{12}}
\end{aligned}
\tag{58}
$$

or equivalently

$$
\begin{aligned}
\tilde{H}[j]=&h_c+\frac{\mathrm{erf}(\mu r_{12})}{r_{12}}+\frac{\mu}{\sqrt{\pi}}e^{-\left(\mu r_{12}\right)^2}-\frac{\Big(1-\mathrm{erf}(\mu r_{12})\Big)^2}{4}\\
&+\Big(\mathrm{erf}(\mu r_{12})-1\Big)\frac{\partial}{\partial r_{12}},
\end{aligned}
\tag{59}
$$

which corresponds precisely to Eq. (15).

IV. NUMERICAL COMPUTATION OF INTEGRALS

A. Fit of functions

1. Fit of $1-\mathrm{erf}(x)$

At some point we would like to fit the following function

$$g(x)=1-\mathrm{erf}(x) \tag{60}$$

which can be done, for instance by

$$h(x,\alpha,\beta,c)=e^{-\alpha x-\beta x^2} \tag{61}$$

with $\alpha = 1.09529$ and $\beta = 0.756023$. So by posing $y=\mu x$, $x=y/\mu$ then

$$
\begin{aligned}
g(x,\mu)=&1-\mathrm{erf}(\mu x)\approx e^{-\alpha\mu x-\beta(\mu x)^2}\\
=&e^{-\alpha\mu x}e^{-\beta\mu^2x^2}\\
=&h(x,\alpha\mu,\beta\mu^2).
\end{aligned}
\tag{62}
$$

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

$$
\begin{aligned}
g(x,\mu)^2=&\Big(1-\mathrm{erf}(\mu x)\Big)^2\\
&=\Big(e^{-\alpha\mu x}e^{-\beta\mu^2x^2}\Big)^2\\
&=e^{-2\alpha\mu x}e^{-2\beta\mu^2x^2}\\
&=h(x,2\alpha\mu,2\beta\mu^2).
\end{aligned}
\tag{63}
$$

2. Fit of e^{-x}

The fit of $1-\mathrm{erf}(\mu x)$ in Eq. (62) involves a Slater function, which is always rather complex to integrate. Nevertheless, we can fit a Slater function with Gaussian functions (that is what quantum chemistry is about):

$$e^{-X}=\sum_{m=1}^{N_s}c_m e^{-\zeta_m X^2}, \tag{64}$$

and, by posing $X=\gamma x$ one can fit any Slater function as

$$e^{-\gamma x}=\sum_{m=1}^{N_s}c_m e^{-\zeta_m\gamma^2x^2}. \tag{65}$$

To find the $\{c_m,\zeta_m\}$ parameters, I performed a Hartree Fock calculation on the Hydrogen atom using the s functions of the ANO-RCC basis set which contains 8 gaussians.

B. Computation of integrals with $\exp(-\alpha r_{12}^2)$

As essentially all functions of r_{12} involve directly or indirectly (*i.e.* through a fit) gaussian functions, we will have to evaluate such integrals

$$
\begin{aligned}
&\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2(x_1-A_x)^{a_x}(x_2-B_x)^{b_x}(y_1-A_y)^{a_y}(y_2-B_y)^{b_y}(z_1-A_z)^{a_z}(z_2-B_z)^{b_z}\\
&\exp(-\alpha(\mathbf{r}_1-\mathbf{A})^2)\exp(-\beta(\mathbf{r}_2-\mathbf{B})^2)\exp(-\delta(\mathbf{r}_1-\mathbf{r}_2)^2)
\end{aligned}
\tag{66}
$$

which can be transformed into product of types

$$
\begin{aligned}
&\int \mathrm{d}x_1\mathrm{d}x_2(x_1-A_x)^{a_x}(x_2-B_x)^{b_x}\\
&\exp(-\alpha(x_1-A_x)^2)\exp(-\alpha(x_2-B_x)^2)\exp(-\delta(x_1-x_2)^2)
\end{aligned}
\tag{67}
$$

V. NEW FORM OF JASTROW FACTOR

We want the jastrow factor $j(r_{12})$ to fulfil such equation

$$-\left[\frac{2}{r_{12}}\frac{\partial j}{\partial r_{12}} + \frac{\partial^2 j}{\partial {r_{12}}^2}\right] + \frac{1}{r_{12}} = \frac{\mathrm{erf}(\mu r_{12})}{r_{12}}. \tag{68}$$

The solution for such an equation is

$$j(r_{12}) = \frac{1}{2}r_{12}\Big(1-\mathrm{erf}(\mu r_{12})\Big) - \frac{1}{2\sqrt{\pi}\mu}e^{-(\mu r_{12})^2} + \frac{1}{4 r_{12}}\Big(c_1 - \frac{\mathrm{erf}(\mu r_{12})}{\mu^2}\Big). \tag{69}$$

The constant c_1 can be found to impose that

$$\lim_{r_{12}\to 0} j(r_{12}) < \infty, \tag{70}$$

which means $c_1 = 0$. Therefore the new jastrow factor is

$$j(r_{12}) = \frac{1}{2}r_{12}\Big(1-\mathrm{erf}(\mu r_{12})\Big) - \frac{1}{2\sqrt{\pi}\mu}e^{-(\mu r_{12})^2} - \frac{\mathrm{erf}(\mu r_{12})}{4\mu^2 r_{12}}. \tag{71}$$

VI. ONE BODY TERM JASTROW

A. The case of the Hydrogen atom

We want to find a Jastrow factor which will take care of the nuclear-electron cusp condition, and we will begin by the Hydrogen atom.

Let us write the Hamiltonian of the hydrogenoid atom in the radial coordinate for the $l = 0$ sector

$$H = -\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) - \frac{Z}{r}. \tag{72}$$

To do so, we have to compute the kinetic part acting on the Jastrow factor acting on a function depending only on the radial coordinate $\phi(r)$

$$\begin{aligned}
&-\frac{1}{2}e^{-j(r)}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r})e^{j(r)}\phi(r) = \\
&-\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r})\phi(r) \\
&-\frac{\partial j(r)}{\partial r}\frac{\partial}{\partial r}\phi(r) \\
&-\frac{1}{r}\frac{\partial j(r)}{\partial r}\phi(r) - \frac{1}{2}\frac{\partial^2 j(r)}{\partial r^2}\phi(r) - \frac{1}{2}\Big(\frac{\partial j(r)}{\partial r}\Big)^2\phi(r).
\end{aligned} \tag{73}$$

Therefore the full similarity transformed Hamiltonian $\tilde{H}[j]$ is

$$\begin{aligned}
&e^{-j(r)}H\,e^{j(r)} = \\
&-\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) - \frac{\partial j(r)}{\partial r}\frac{\partial}{\partial r} \\
&-\frac{1}{r}\Big(\frac{\partial j(r)}{\partial r} + Z\Big) \\
&-\frac{1}{2}\frac{\partial^2 j(r)}{\partial r^2} - \frac{1}{2}\Big(\frac{\partial j(r)}{\partial r}\Big)^2.
\end{aligned} \tag{74}$$

Similarly to what have been proposed in Section I B, we want to find the Jastrow factor $j(r,\mu,Z)$ such that

$$-\frac{1}{r}\Big(\frac{\partial j(r,\mu,Z)}{\partial r} + Z\Big) = -Z\frac{\mathrm{erf}(\mu r)}{r}, \tag{75}$$

or equivalently

$$\frac{\partial}{\partial r}j(r,\mu,Z) = Z\Big(\mathrm{erf}(\mu r) - 1\Big). \tag{76}$$

The Jastrow factor fulfilling Eq. (76) is

$$j(r,\mu,Z) = -Zr\Big(1-\mathrm{erf}(\mu r)\Big) + \frac{Z}{\sqrt{\pi}\mu}e^{-(\mu r)^2}. \tag{77}$$

Now, we can plug $j(r,\mu,Z)$ into Eq. (74) in order to compute the explicit form of the similarity transformed Hamiltonian. To do so, we use Eq. (76), and also that

$$\frac{\partial^2}{\partial r^2}j(r) = \frac{2\mu Z}{\sqrt{\pi}}e^{-(\mu r)^2}. \tag{78}$$

One obtains then the similarity transformed Hamiltonian

$$\begin{aligned}
\tilde{H}[j] =& e^{-j(r)}He^{j(r)} \\
=& -\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) - \frac{Z}{r} \\
&+ Z\Big(1-\mathrm{erf}(\mu r)\Big)\frac{\partial}{\partial r} \\
&- Z\frac{\mathrm{erf}(\mu r) - 1}{r} \\
&- Z\frac{\mu}{\sqrt{\pi}}e^{-(\mu r)^2} \\
&- \frac{1}{2}Z^2\Big(\mathrm{erf}(\mu r) - 1\Big)^2,
\end{aligned} \tag{79}$$

and one can notice that the $\frac{-Z}{r}$ interaction cancels out to give

$$\begin{aligned}
\tilde{H}[j] =& e^{-j(r)}He^{j(r)} \\
=& -\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) \\
&- Z\Big[\frac{\mu}{\sqrt{\pi}}e^{-(\mu r)^2} + \frac{\mathrm{erf}(\mu r)}{r} + \frac{1}{2}Z\Big(\mathrm{erf}(\mu r) - 1\Big)^2\Big] \\
&+ Z\Big(1-\mathrm{erf}(\mu r)\Big)\frac{\partial}{\partial r}.
\end{aligned} \tag{80}$$

Therefore, compared to the usual Hamiltonian, the similarity transformed Hamiltonian contains a different local interaction which is clearly non divergent, but also a new short-range differential operator.

B. General equation

Now that we know the general form of the one-body Jastrow factor for a one electron system, we can generalize it to an

N-electron system and an M nucleus system by just taking the following form

$$e^{\hat{\tau}(\mathbf{r}_1,\ldots,\mathbf{r}_i,\mathbf{r}_N)} = e^{-\sum_i^N J(\mathbf{r}_i)} \tag{81}$$

where $J(\mathbf{r}_i)$ has the following form

$$J(\mathbf{r}_i) = \sum_A j(r_{iA}, \mu, Z_A) \tag{82}$$

where $j(r,\mu,Z)$ is given by Eq. (77) and $r_{iA} = \left|\mathbf{r}_i - \mathbf{R}_A\right|$. According to Eq. (2) of Ref. 1, the equation of the similarity transformed Hamiltonian is similar to that of Eq. (20) but with a new form of Jastrow factor. Therefore one needs to compute $[H,\hat{\tau}]$ and $\frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big]$. Let us begin by $[H,\hat{\tau}]$, and as before, we apply it to a general function $\phi(\mathbf{r}_1,\ldots\mathbf{r}_N)$:

$$\begin{aligned}\Big[H,\hat{\tau}\Big]\phi(\mathbf{r}_1,\ldots\mathbf{r}_N) &= \Big[-\frac{1}{2}\sum_i \nabla_i^2, \sum_j J(\mathbf{r}_j)\Big]\phi(\mathbf{r}_1,\ldots\mathbf{r}_N) \\ &= -\frac{1}{2}\sum_i\Big((\nabla_i^2 J(\mathbf{r}_i)) + 2\nabla_i J(\mathbf{r}_i)\cdot\nabla_i\phi(\mathbf{r}_1,\ldots\mathbf{r}_N)\Big).\end{aligned} \tag{83}$$

Therefore, one can write that term as

$$\begin{aligned}[H,\hat{\tau}] = &-\frac{1}{2}\Big(\sum_i \nabla_i^2 J(\mathbf{r}_i)\Big) \\ &-\sum_i\Big(\nabla_i J(\mathbf{r}_i)\Big)\cdot\Big(\nabla_i\Big).\end{aligned} \tag{84}$$

After some math, the second-order commutator is simply

$$\Big[[H,\hat{\tau}],\hat{\tau}\Big] = -\sum_i \nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i) \tag{85}$$

So eventually, the similarity transformed operator becomes

$$\begin{aligned}&H + [H,\hat{\tau}] + \frac{1}{2}\Big[[H,\hat{\tau}],\hat{\tau}\Big] = \\ &H - \frac{1}{2}\Big(\sum_i \nabla_i^2 J(\mathbf{r}_i)\Big) - \sum_i\Big(\nabla_i J(\mathbf{r}_i)\Big)\cdot\Big(\nabla_i\Big) - \frac{1}{2}\sum_i \nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i)\end{aligned} \tag{86}$$

Therefore, the addition of the jastrow operator does not add extra two-body terms.

C. Computation of the total operator

1. *Computation of* $\nabla_i J(\mathbf{r}_i)$

$$\begin{aligned}\nabla_i J(\mathbf{r}_i) &= \sum_A \nabla_i J(r_{iA}, Z_A) \\ &= \sum_A \frac{\partial}{\partial x_i}J(r_{iA},Z_A)\mathbf{e}_{x_i} + \frac{\partial}{\partial y_i}J(r_{iA},Z_A)\mathbf{e}_{y_i} + \frac{\partial}{\partial z_i}J(r_{iA},Z_A)\mathbf{e}_{z_i},\end{aligned} \tag{87}$$

and

$$\frac{\partial}{\partial x_i}J(r_{iA}) = \frac{\partial}{\partial r_{iA}}J(r_{iA})\frac{\partial r_{iA}}{\partial x_i}, \tag{88}$$

and as $r_{iA} = \sqrt{(x_1-x_A)^2 + (y_1-y_A)^2 + (z_1-z_A)^2}$ one has

$$\frac{\partial r_{iA}}{\partial x_1} = \frac{x_1 - x_A}{r_{iA}} \tag{89}$$

and therefore according to Eq. (76), one has

$$\frac{\partial}{\partial x_i}J(r_{iA},Z_A) = -\sum_A Z_A(x_i - x_A)\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}. \tag{90}$$

2. *Computation of* $\nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i)$

The computation of $\nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i)$ leads to

$$\begin{aligned}\nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i) = \sum_{A,B} Z_B Z_A &(x_i - x_A)(x_i - x_B)\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\frac{1-\mathrm{erf}(\mu r_{iB})}{r_{iB}} \\ &+ (y_i - y_A)(y_i - y_B)\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\frac{1-\mathrm{erf}(\mu r_{iB})}{r_{iB}} \\ &+ (z_i - z_A)(z_i - z_B)\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\frac{1-\mathrm{erf}(\mu r_{iB})}{r_{iB}}.\end{aligned} \tag{91}$$

The diagonal part of such integrals is simply

$$\begin{aligned}&\sum_A (Z_A)^2\Big((x_i - x_A)^2 + (y_i - y_A)^2 + (z_i - z_A)^2\Big)\frac{\Big(\mathrm{erf}(\mu r_{iA}) - 1\Big)^2}{(r_{iA})^2} \\ &= \sum_A (Z_A)^2\Big(\mathrm{erf}(\mu r_{iA}) - 1\Big)^2\end{aligned} \tag{92}$$

3. *Computation of* $\nabla_i^2 J(\mathbf{r}_i)$

We need to compute

$$\begin{aligned}\frac{\partial^2}{\partial {x_i}^2}J(\mathbf{r}_i) &= -\sum_A Z_A\frac{\partial}{\partial x_i}\Big[(x_i - x_A)\frac{1-\mathrm{erf}(\mu r)}{r_{iA}}\Big] \\ &= -\sum_A Z_A\Big[\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}} + (x_i - x_A)\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big]\end{aligned} \tag{93}$$

But, one has that

$$\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}} = -\frac{(x_i - x_A)}{(r_{iA})^2}\Big(\frac{2\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2} + \frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big). \tag{94}$$

Therefore,

$$(x_i - x_A)\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}} = -\frac{(x_i - x_A)^2}{(r_{iA})^2}\Big(\frac{2\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2} + \frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big) \tag{95}$$

. Therefore, the Laplacian is

$$\frac{\partial^2}{\partial x_i^2}J(\mathbf{r}_i)+\frac{\partial^2}{\partial y_i^2}J(\mathbf{r}_i)+\frac{\partial^2}{\partial z_i^2}J(\mathbf{r}_i)=-\sum_A Z_A\Big[3\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}$$
$$+(x_i-x_A)\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}$$
$$+(y_i-y_A)\frac{\partial}{\partial y_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}$$
$$+(z_i-z_A)\frac{\partial}{\partial z_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big] \tag{96}$$

But according to Eq. (95), one has that

$$+(x_i-x_A)\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}$$
$$+(y_i-y_A)\frac{\partial}{\partial y_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}$$
$$+(z_i-z_A)\frac{\partial}{\partial z_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}=$$
$$-\frac{(x_i-x_A)^2+(y_i-y_A)^2+(z_i-z_A)^2}{(r_{iA})^2}\Big(\frac{2\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}+\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big) \tag{97}$$

which is simply

$$\begin{aligned}&+(x_i-x_A)\frac{\partial}{\partial x_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\\&+(y_i-y_A)\frac{\partial}{\partial y_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\\&+(z_i-z_A)\frac{\partial}{\partial z_i}\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}=\\&-\Big(\frac{2\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}+\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big).\end{aligned} \tag{98}$$

Then, coming back to Eq. (96) with Eq. (98) one has

$$\Delta_i J(\mathbf{r}_i)=-\sum_A Z_A\Big[3\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}-\Big(\frac{2\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}+\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big)\Big] \tag{99}$$

which becomes

$$\Delta_i J(\mathbf{r}_i)=-\sum_A 2\,Z_A\Big[\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}\Big] \tag{100}$$

4. Computation of the total operator

$$H+[H,\hat{\tau}]+\frac{1}{2}\Big[[H,\hat{\tau}],J\Big]=$$
$$H-\frac{1}{2}\Big(\sum_i\nabla_i^2 J(\mathbf{r}_i)\Big)-\sum_i\Big(\nabla_i J(\mathbf{r}_i)\Big)\cdot\Big(\nabla_i\Big)-\frac{1}{2}\sum_i\nabla_i J(\mathbf{r}_i)\cdot\nabla_i J(\mathbf{r}_i) \tag{101}$$

which becomes

$$\tilde{H}=H+\sum_i\sum_A Z_A\Big[\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}\Big]$$
$$+\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big[(x_i-x_A)\frac{\partial}{\partial x_i}+(y_i-y_A)\frac{\partial}{\partial y_i}+(z_i-z_A)\frac{\partial}{\partial z_i}\Big]$$
$$-\frac{1}{2}\sum_B Z_B\Big[(x_1-x_A)(x_1-x_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}$$
$$+(y_1-y_A)(y_1-y_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}$$
$$+(z_1-z_A)(z_1-z_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}\Big]. \tag{102}$$

and as $H=\sum_i-\frac{1}{2}\Delta_i-\sum_A\frac{Z_A}{r_{iA}}+\sum_{i>j}\frac{1}{r_{ij}}$ the total interaction becomes

$$\tilde{H}=\sum_i-\frac{1}{2}\Delta_i+\sum_A Z_A\tilde{v}_A(\mathbf{r}_i)+\sum_{i>j}\frac{1}{r_{ij}} \tag{103}$$

where the new effective potential is

$$\tilde{v}_A(\mathbf{r}_i)=-\frac{\mathrm{erf}(\mu r_{iA})}{r_{iA}}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r_{iA})^2}$$
$$+\frac{1-\mathrm{erf}(\mu r_{iA})}{r_{iA}}\Big[(x_i-x_A)\frac{\partial}{\partial x_i}+(y_i-y_A)\frac{\partial}{\partial y_i}+(z_i-z_A)\frac{\partial}{\partial z_i}\Big]$$
$$-\frac{1}{2}\sum_B Z_B\Big[(x_i-x_A)(x_i-x_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}$$
$$+(y_i-y_A)(y_i-y_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}$$
$$+(z_i-z_A)(z_i-z_B)\frac{\mathrm{erf}(\mu r_{iA})-1}{r_{iA}}\frac{\mathrm{erf}(\mu r_{iB})-1}{r_{iB}}\Big]. \tag{104}$$

5. Verification with the Hydrogen atom

Let us apply the general equations (see Eqs. (103) and (104)) to the case of the Hydrogen atom, which is supposed to be in the center of the frame of reference (*i.e.* $\mathbf{r}_A=\vec{0}$)

$$\begin{aligned}\tilde{v}(\mathbf{r})=&-\frac{\mathrm{erf}(\mu r)}{r}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r)^2}\\&+\frac{1-\mathrm{erf}(\mu r)}{r}\Big[x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\Big]\\&-\frac{1}{2}Z(x^2+y^2+z^2)\frac{(\mathrm{erf}(\mu r)-1)^2}{r^2},\end{aligned} \tag{105}$$

but as $r^2=x^2+y^2+z^2$ one obtains that

$$-\frac{1}{2}Z(x^2+y^2+z^2)\frac{(\mathrm{erf}(\mu r)-1)^2}{r^2}=-\frac{1}{2}Z(\mathrm{erf}(\mu r)-1)^2 \tag{106}$$

and also as

$$\begin{aligned}x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}&=\mathbf{r}\cdot\nabla\\&=r\frac{\partial}{\partial r},\end{aligned} \tag{107}$$

one obtains

$$+\frac{1-\operatorname{erf}(\mu r)}{r}\left[x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right]=\Big(1-\operatorname{erf}(\mu r)\Big)\frac{\partial}{\partial r}, \quad (108)$$

and therefore the total potential is

$$\begin{aligned}\tilde{v}(\mathbf{r}) = &-\frac{\operatorname{erf}(\mu r)}{r}-\frac{\mu}{\sqrt{\pi}}e^{-(\mu r)^2}\\ &+\Big(1-\operatorname{erf}(\mu r)\Big)\frac{\partial}{\partial r}\\ &-\frac{1}{2}Z(\operatorname{erf}(\mu r)-1)^2,\end{aligned} \quad (109)$$

which coincides with Eq. (80).

[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.