First and second derivatives: drift vector and kinetic energy

José Antonio Quiñonero Gris

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The drif vector is given by

$$\frac{\nabla\psi(\mathbf{r})}{\psi(\mathbf{r})}, \tag{1}$$

where the gradient reads

$$\nabla = \partial_x + \partial_y + \partial_z. \tag{2}$$

The local kinetic energy is defined as

$$T_{\mathrm{L}}(\mathbf{r}) = -\frac{1}{2}\frac{\nabla^2\psi(\mathbf{r})}{\psi(\mathbf{r})}, \tag{3}$$

where the laplacian reads

$$\nabla^2 = \partial_x^2 + \partial_y^2 + \partial_z^2. \tag{4}$$

The molecular orbitals (MO's), our wavefunctions, ψ, are formed as Linear Combinations of atomic orbitals (AO's). The AO basis functions used are the normalized 1*s* *Slater type function* centered at $\mathbf{R}$

$$\phi(\mathbf{r}-\mathbf{R}) \equiv \phi(\mathbf{r}) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha|\mathbf{r}-\mathbf{R}|}, \tag{5}$$

where α is the *Slater orbital exponent* and $|\mathbf{r}-\mathbf{R}|$ is the distance between a point in space, $\mathbf{r}$ and $\mathbf{R}$

$$|\mathbf{r}-\mathbf{R}| = \sqrt{(x-X)^2+(y-Y)^2+(z-Z)^2}, \tag{6}$$

where lower case letters reffer to the cartesian coordinates of $\mathbf{r} = (x\ y\ z)$ and upper case to $\mathbf{R} = (X\ Y\ Z)$.

To simplify the notation, the value of the orbital in the i-th point in space, $\mathbf{r}_i = (x_i\ y_i\ z_i)$, centered on the j-th atom, at $\mathbf{R}_j = (X_j\ Y_j\ Z_j)$, is denoted as

$$\phi_{ij} \equiv \phi(\mathbf{r}_i - \mathbf{R}_j) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha|\mathbf{r}_i-\mathbf{R}_j|} \equiv \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha|\mathbf{r}_{ij}|}, \tag{7}$$

where it is important to note that the modulus $|\mathbf{r}_i - \mathbf{R}_j|$ is simply written as the two-indexed $|\mathbf{r}_{ij}|$.

Therefore, our MO's are constructed in the AO's basis functions $\{\phi_\mu\}$ as the product of the summed contributions of all the AO's at any given point in space. More specifically, as the product of the summed contributions of each orbital, centered at each atom position, for the position of each electron. Then, the wavefunction for n electrons and m atoms (nucleus) is given by

$$\psi(\mathbf{r}) = \prod_{i=1}^{n}\left(\sum_{I=1}^{m}\phi_{iI}\right), \tag{8}$$

where, to keep the notation simple, the electrons are indexed with lower case letters and the nucleus with upper case. For n electrons and m nucleus, $\mathbf{r}$ has $3n$ components and $\mathbf{R}$ has $3m$ components.

To compute the drif vector and kinetic energy, the gradient and laplacian of the wavefunction over the electron positions, $\mathbf{r}$, are needed.

The first derivative of the wavefunction $\psi(\mathbf{r}) \equiv \psi$ over the x component of the i-th electron, x_i, is given by

$$\frac{\partial}{\partial x_i}\psi \equiv \partial_{x_i}\psi = \partial_{x_i}\prod_{i=1}^{n}\left(\sum_{I=1}^{m}\phi_{iI}\right). \tag{9}$$

As the partial derivative of all the $j \neq i$ components over i is null

$$\partial_{x_j}\phi_{jI} = 0 \quad \forall j \neq i \text{ and } \forall I, \tag{10}$$

only the $j \neq i$ components that are not differentiated survive. Then

$$\partial_{x_i}\psi = \partial_{x_i}\prod_{i=1}^{n}\left(\sum_{I=1}^{m}\phi_{iI}\right) = \prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right)\partial_{x_i}\left(\sum_{I=1}^{m}\phi_{iI}\right) = \prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right)\sum_{I=1}^{m}\partial_{x_i}\phi_{iI}. \tag{11}$$

Since both in the drift vector and the kinetic energy (eqs. (1) and (3)) the gradient and the laplacian are divided by ψ, it is convinient to express those in terms of ψ.

Given the definition of ψ in eq. (8), the product can be separated as

$$\psi = \left(\sum_{I=1}^{m}\phi_{iI}\right)\prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right), \tag{12}$$

which implies that

$$\prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right) = \frac{\psi}{\left(\sum_{I=1}^{m}\phi_{iI}\right)}. \tag{13}$$

This way, eq. (11) can be rewritten in terms of ψ as

$$\partial_{x_i}\psi = \frac{\sum_{I=1}^{m}\partial_{x_i}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{14}$$

The first derivative of the Slater type function, given that, by definition

$$\partial_{x_i}f(\mathbf{r}_i) = \partial_{\mathbf{r}_i}f(\mathbf{r}_i)\,\partial_{x_i}\mathbf{r}_i, \tag{15}$$

is

$$\partial_{x_i}\phi_{iI} = \partial_{|\mathbf{r}_{iI}|}\phi_{iI}\partial_{x_i}|\mathbf{r}_{iI}|, \tag{16}$$

where the first partial derivative reads

$$\partial_{|\mathbf{r}_{iI}|}\phi_{iI} = \left(\frac{\alpha^3}{\pi}\right)^{1/2}\partial_{|\mathbf{r}_{iI}|}e^{-\alpha|\mathbf{r}_{iI}|} = -\alpha\left(\frac{\alpha^3}{\pi}\right)^{1/2}e^{-\alpha|\mathbf{r}_{iI}|} = -\alpha\phi_{iI}, \tag{17}$$

and the second one reads

$$\begin{aligned}
\partial_{x_i}\left|\mathbf{r}_{iI}\right| &= \partial_{x_i}\left[\left(x_i - X_I\right)^2 + \left(y_i - Y_I\right)^2 + \left(z_i - Z_I\right)^2\right]^{1/2} \\
&= \frac{1}{2}\partial_{x_i}\left[\left(x_i - X_I\right)^2 + \left(y_i - Y_I\right)^2 + \left(z_i - Z_I\right)^2\right]\left[\left(x_i - X_I\right)^2 + \left(y_i - Y_I\right)^2 + \left(z_i - Z_I\right)^2\right]^{-1/2} \\
&= \frac{1}{2}2\partial_{x_i}\left(x_i - X_I\right)\left(x_i - X_I\right)\frac{1}{\left|\mathbf{r}_{iI}\right|} \\
&= \frac{\left(x_i - X_I\right)}{\left|\mathbf{r}_{iI}\right|}.
\end{aligned} \tag{18}$$

Then, in eq. (16)

$$\partial_{x_i}\phi_{iI} = -\alpha\frac{\left(x_i - X_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}, \tag{19}$$

and in eq. (14)

$$\partial_{x_i}\psi = -\alpha\frac{\sum_{I=1}^{m}\frac{\left(x_i - X_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{20}$$

Analogously, it is easy to see that

$$\partial_{y_i}\psi = -\alpha\frac{\sum_{I=1}^{m}\frac{\left(y_i - Y_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi, \tag{21}$$

$$\partial_{z_i}\psi = -\alpha\frac{\sum_{I=1}^{m}\frac{\left(z_i - Z_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{22}$$

Then, the gradient given in eq. (2) is given by summing over all i electrons

$$\nabla\psi\left(\mathbf{r}\right) = \sum_{i=1}^{n}\partial_{x_i}\psi + \sum_{i=1}^{n}\partial_{y_i}\psi + \sum_{i=1}^{n}\partial_{z_i}\psi, \tag{23}$$

substituting eqs. (20) to (22) into eq. (23) and taking $-\alpha\psi$ as a common factor

$$\nabla\psi\left(\mathbf{r}\right) = -\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}\frac{\left(x_i - X_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}} + \frac{\sum_{I=1}^{m}\frac{\left(y_i - Y_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}} + \frac{\sum_{I=1}^{m}\frac{\left(z_i - Z_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi\left(\mathbf{r}\right), \tag{24}$$

which can be rewritten as

$$\nabla\psi\left(\mathbf{r}\right) = -\alpha\sum_{i=1}^{n}\left(\frac{\sum_{I=1}^{m}\frac{\left(x_i - X_I\right)+\left(y_i - Y_I\right)+\left(z_i - Z_I\right)}{\left|\mathbf{r}_{iI}\right|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right)\psi\left(\mathbf{r}\right). \tag{25}$$

Therefore, the drift vector defined in eq. (1) is given by

$$\therefore\frac{\nabla\psi\left(\mathbf{r}\right)}{\psi\left(\mathbf{r}\right)} = -\alpha\sum_{i=1}^{n}\left(\frac{\sum_{I=1}^{m}C_{iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right), \tag{26}$$

with

$$C_{iI} = \frac{\left(x_i - X_I\right) + \left(y_i - Y_I\right) + \left(z_i - Z_I\right)}{\left|\mathbf{r}_{iI}\right|}. \tag{27}$$

For the laplacian, the second partial derivatives are needed. Following the same scheme, the partial derivative over the x_i component of $\partial_{x_i}\psi$ from eq. (20) is taken

$$\partial^2_{x_i}\psi = -\alpha\partial_{x_i}\left[\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi\right], \tag{28}$$

that, by the product rule

$$\partial^2_{x_i}\psi = -\alpha\left[\psi\,\underbrace{\partial_{x_i}\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}}_{\text{(a)}} + \frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\underbrace{\partial_{x_i}\psi}_{\text{(b)}}\right]. \tag{29}$$

The first partial derivative is treated separately. Applying the quotient rule

$$\text{(a)}\;\;\partial_{x_i}\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}} = \frac{\left(\sum_{I=1}^{m}\phi_{iI}\right)\overbrace{\partial_{x_i}\left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)}^{\text{(c)}}}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2} - \frac{\left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)\overbrace{\partial_{x_i}\left(\sum_{I=1}^{m}\phi_{iI}\right)}^{\text{(d)}}}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2}. \tag{30}$$

Again, each partial derivative is calculated separately. The first one is first rewritten as

$$\text{(c)}\;\;\partial_{x_i}\left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right) = \sum_{I=1}^{m}\partial_{x_i}\left[(x_i-X_I)\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\right], \tag{31}$$

applying the product rule

$$\text{(c)}\;\;\sum_{I=1}^{m}\partial_{x_i}\left[(x_i-X_I)\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\right] = \sum_{I=1}^{m}\left[\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\partial_{x_i}(x_i-X_I) + (x_i-X_I)\,\partial_{x_i}\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\right], \tag{32}$$

where $\partial_{x_i}(x_i-X_I)=1$ and, by the quotient rule

$$\partial_{x_i}\frac{\phi_{iI}}{|\mathbf{r}_{iI}|} = \frac{|\mathbf{r}_{iI}|\,\partial_{x_i}\phi_{iI} - \phi_{iI}\partial_{x_i}|\mathbf{r}_{iI}|}{(|\mathbf{r}_{iI}|)^2}, \tag{33}$$

and recalling eqs. (18) and (19)

$$\partial_{x_i}\frac{\phi_{iI}}{|\mathbf{r}_{iI}|} = \frac{|\mathbf{r}_{iI}|\left(-\alpha\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right) - \phi_{iI}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}}{(|\mathbf{r}_{iI}|)^2} = \frac{-(x_i-X_I)\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)\phi_{iI}}{(|\mathbf{r}_{iI}|)^2}, \tag{34}$$

in eq. (32)

$$\begin{aligned}\text{(c)}\;\;\sum_{I=1}^{m}\partial_{x_i}\left[(x_i-X_I)\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\right] &= \sum_{I=1}^{m}\left[\frac{\phi_{iI}}{|\mathbf{r}_{iI}|} + (x_i-X_I)\frac{-(x_i-X_I)\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)\phi_{iI}}{(|\mathbf{r}_{iI}|)^2}\right]\\ &= \sum_{I=1}^{m}\left[\frac{1}{|\mathbf{r}_{iI}|} - \frac{(x_i-X_I)^2\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)}{(|\mathbf{r}_{iI}|)^2}\right]\phi_{iI},\end{aligned} \tag{35}$$

then

$$(\mathrm{c})\ \sum_{I=1}^{m} \partial_{x_i}\left[(x_i - X_I)\frac{\phi_{iI}}{|\mathbf{r}_{iI}|}\right] = \sum_{I=1}^{m} D_{iI}^{(x)}\phi_{iI}, \tag{36}$$

where

$$D_{iI}^{(x)} = \left[\frac{1}{|\mathbf{r}_{iI}|} - \frac{(x_i - X_I)^2\left(\alpha + \frac{1}{|\mathbf{r}_{iI}|}\right)}{(|\mathbf{r}_{iI}|)^2}\right] \tag{37}$$

The second derivative that appears in eq. (30), recalling eq. (16), reads

$$(\mathrm{d})\ \partial_{x_i}\left(\sum_{I=1}^{m}\phi_{iI}\right) = \sum_{I=1}^{m}\partial_{x_i}\phi_{iI} = -\alpha\sum_{I=1}^{m}\frac{(x_i - X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}. \tag{38}$$

Now, substituting eqs. (36) and (38) into eq. (30)

$$\begin{aligned}(\mathrm{a})\ \partial_{x_i}\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}} &= \frac{\left(\sum_{I=1}^{m}\phi_{iI}\right)\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI} - \left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)\left(-\alpha\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2}\\ &= \frac{\left(\sum_{I=1}^{m}\phi_{iI}\right)\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI} + \alpha\left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)^2}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2}.\end{aligned} \tag{39}$$

The second partial derivative in eq. (29), recalling eq. (20), reads

$$(\mathrm{b})\ \partial_{x_i}\psi = -\alpha\frac{(x_i - X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}, \tag{40}$$

and substituting eqs. (39) and (40) into eq. (29)

$$\begin{aligned}\partial_{x_i}^2\psi &= -\alpha\left[\psi\frac{\left(\sum_{I=1}^{m}\phi_{iI}\right)\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI} + \alpha\left(\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}\right)^2}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2} + \frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\left(-\alpha\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi\right)\right]\\ &= -\alpha\left[\psi\frac{\left(\sum_{I=1}^{m}\phi_{iI}\right)\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI}}{\left(\sum_{I=1}^{m}\phi_{iI}\right)^2} + \alpha\left(\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right)^2\psi - \alpha\left(\frac{\sum_{I=1}^{m}\frac{(x_i-X_I)}{|\mathbf{r}_{iI}|}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right)^2\psi\right],\end{aligned} \tag{41}$$

resulting in

$$\partial_{x_i}^2\psi = -\alpha\frac{\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{42}$$

Repeating the same process for ∂_{y_i} and ∂_{z_i}, one gets to

$$\partial_{y_i}^2\psi = -\alpha\frac{\sum_{I=1}^{m}D_{iI}^{(y)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi, \tag{43}$$

$$\partial_{z_i}^2\psi = -\alpha\frac{\sum_{I=1}^{m}D_{iI}^{(z)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{44}$$

Then, the laplacian given in eq. (4) is given by summing over all i electrons

$$\nabla^2\psi\left(\mathbf{r}\right)=\sum_{i=1}^{n}\partial_{x_i}^2\psi+\sum_{i=1}^{n}\partial_{y_i}^2\psi+\sum_{i=1}^{n}\partial_{z_i}^2\psi, \tag{45}$$

substituting eqs. (42) to (44) into eq. (45) and taking $-\alpha\psi$ as a common factor

$$\nabla^2\psi\left(\mathbf{r}\right)=-\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}D_{iI}^{(x)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}+\frac{\sum_{I=1}^{m}D_{iI}^{(y)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}+\frac{\sum_{I=1}^{m}D_{iI}^{(z)}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi\left(\mathbf{r}\right), \tag{46}$$

which can be rewritten as

$$\nabla^2\psi\left(\mathbf{r}\right)=-\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}\left(D_{iI}^{(x)}+D_{iI}^{(y)}+D_{iI}^{(z)}\right)\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi\left(\mathbf{r}\right). \tag{47}$$

Now, recalling eq. (37)

$$\begin{aligned}D_{iI}^{(x)}+D_{iI}^{(y)}+D_{iI}^{(z)}=&\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{\left(x_i-X_I\right)^2\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)}{\left(|\mathbf{r}_{iI}|\right)^2}\right]\\&+\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{\left(y_i-Y_I\right)^2\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)}{\left(|\mathbf{r}_{iI}|\right)^2}\right]\\&+\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{\left(z_i-Z_I\right)^2\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)}{\left(|\mathbf{r}_{iI}|\right)^2}\right],\end{aligned} \tag{48}$$

which can be simplified to

$$D_{iI}^{(x)}+D_{iI}^{(y)}+D_{iI}^{(z)}=\frac{3}{|\mathbf{r}_{iI}|}-\frac{\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)}{\left(|\mathbf{r}_{iI}|\right)^2}\left[\left(x_i-X_I\right)^2+\left(y_i-Y_I\right)^2+\left(z_i-Z_I\right)^2\right], \tag{49}$$

where, by the definition given in eq. (6)

$$|\mathbf{r}_{iI}|^2=\left(x_i-X_I\right)^2+\left(y_i-Y_I\right)^2+\left(z_i-Z_I\right)^2, \tag{50}$$

and

$$D_{iI}^{(x)}+D_{iI}^{(y)}+D_{iI}^{(z)}=\frac{3}{|\mathbf{r}_{iI}|}-\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right). \tag{51}$$

Then, in eq. (47)

$$\nabla^2\psi\left(\mathbf{r}\right)=-\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}\left(\frac{3}{|\mathbf{r}_{iI}|}-\left(\alpha+\frac{1}{|\mathbf{r}_{iI}|}\right)\right)\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi\left(\mathbf{r}\right). \tag{52}$$

Therefore, the kinetic energy defined in eq. (3) is given by

$$\therefore T_{\mathrm{L}}\left(\mathbf{r}\right)=-\frac{1}{2}\sum_{i=1}^{n}\left(\frac{\sum_{I=1}^{m}D_{iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right), \tag{53}$$

where

$$D_{iI} = -\alpha \left[\frac{3}{|\mathbf{r}_{iI}|} - \left(\alpha + \frac{1}{|\mathbf{r}_{iI}|} \right) \right] = \alpha^2 - \frac{2\alpha}{|\mathbf{r}_{iI}|}. \tag{54}$$