First and second derivatives: drift vector and kinetic energy

José Antonio Quiñonero Gris

March 11, 2024

1 Definitions

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 $1s$ *Slater type function* centered at $\mathbf{R}$

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

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

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

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

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

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

$$\psi\left(\mathbf{r}\right) = \prod_{i=1}^{n} \left(\sum_{I=1}^{m} \phi_{iI}\right), \tag{4}$$

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.

The drif vector is given by

$$\frac{\nabla\psi\left(\mathbf{r}\right)}{\psi\left(\mathbf{r}\right)}, \tag{5}$$

where the gradient $\nabla\psi(\mathbf{r})$ reads

$$\nabla\psi(\mathbf{r}) = \nabla\psi(x_1, y_1, z_1, \dots, x_n, y_n, z_n) = \begin{pmatrix} \partial_{x_1}\psi \\ \partial_{y_1}\psi \\ \partial_{z_1}\psi \\ \vdots \\ \partial_{x_n}\psi \\ \partial_{y_n}\psi \\ \partial_{z_n}\psi \end{pmatrix}. \tag{6}$$

The local kinetic energy is defined as

$$T_{\mathrm{L}}(\mathbf{r}) = -\frac{1}{2}\frac{\nabla^2\psi(\mathbf{r})}{\psi(\mathbf{r})}, \tag{7}$$

where the laplacian reads

$$\nabla^2 = \partial_x^2 + \partial_y^2 + \partial_z^2. \tag{8}$$

To compute the drif vector and kinetic energy, the gradient and laplacian of the wavefunction over the electron positions, $\mathbf{r}$, are needed. Firstly, to easy the upcoming development, the first and second partial derivatives of the basis functions are calculated.

2 Partial derivatives of the AO's

The first partial derivative of the AO $\phi(\mathbf{r}_i - \mathbf{R}_I) \equiv \phi_{iI}$ over the x component of the i-th electron, x_i, is given by

$$\frac{\partial}{\partial x_i}\phi_{iI} \equiv \partial_{x_i}\phi_{iI}. \tag{9}$$

By definition

$$\partial_{x_i} f(\mathbf{r}_i) = \partial_{\mathbf{r}_i} f(\mathbf{r}_i)\, \partial_{x_i}\mathbf{r}_i, \tag{10}$$

then

$$\partial_{x_i}\phi_{iI} = \partial_{|\mathbf{r}_{iI}|}\phi_{iI}\partial_{x_i}|\mathbf{r}_{iI}|, \tag{11}$$

where the first partial derivative reads

$$\partial_{|\mathbf{r}_{iI}|}\phi_{iI} = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \partial_{|\mathbf{r}_{iI}|} e^{-\alpha|\mathbf{r}_{iI}|} = -\alpha\left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha|\mathbf{r}_{iI}|} = -\alpha\phi_{iI}, \tag{12}$$

and the second one reads

$$
\begin{aligned}
\partial_{x_i}|\mathbf{r}_{iI}| &= \partial_{x_i}\left[(x_i-X_I)^2+(y_i-Y_I)^2+(z_i-Z_I)^2\right]^{1/2} \\
&= \frac{1}{2}\partial_{x_i}\left[(x_i-X_I)^2+(y_i-Y_I)^2+(z_i-Z_I)^2\right]\left[(x_i-X_I)^2+(y_i-Y_I)^2+(z_i-Z_I)^2\right]^{-1/2} \\
&= \frac{1}{2}2\partial_{x_i}(x_i-X_I)(x_i-X_I)\frac{1}{|\mathbf{r}_{iI}|} \\
&= \frac{x_i-X_I}{|\mathbf{r}_{iI}|}.
\end{aligned}
\tag{13}
$$

Then, in eq. (11)

$$\partial_{x_i}\phi_{iI} = -\alpha\frac{x_i-X_I}{|\mathbf{r}_{iI}|}\phi_{iI}. \tag{14}$$

For the y_i and z_i components, the analogous result is obtained. Therefore, the first partial derivative over the $\lambda_i = \{x_i, y_i, z_i\}$ component is given by

$$\therefore \partial_{\lambda_i}\phi_{iI} = -\alpha C_{\lambda,iI}\phi_{iI}, \tag{15}$$

where

$$C_{\lambda,iI} = \frac{\lambda_i-\Lambda_I}{|\mathbf{r}_{iI}|}. \tag{16}$$

The second partial derivative is obtained as

$$\partial^2_{x_i}\phi_{iI} = -\alpha\partial_{x_i}\left(C_{x,iI}\phi_{iI}\right). \tag{17}$$

Applying the product rule

$$\partial_{x_i}\left(C_{x,iI}\phi_{iI}\right) = \phi_{iI}\partial_{x_i}C_{x,iI} + C_{x,iI}\partial_{x_i}\phi_{iI}, \tag{18}$$

where, by the quotient rule

$$\partial_{x_i}C_{x,iI} = \partial_{x_i}\left(\frac{x_i-X_I}{|\mathbf{r}_{iI}|}\right) = \frac{|\mathbf{r}_{iI}|\,\partial_{x_i}(x_i-X_I)-(x_i-X_I)\,\partial_{x_i}|\mathbf{r}_{iI}|}{|\mathbf{r}_{iI}|^2}, \tag{19}$$

as $\partial_{x_i}(x_i-X_I) = 1$ and recalling eq. (13)

$$\partial_{x_i}C_{x,iI} = \frac{|\mathbf{r}_{iI}|-(x_i-X_I)\frac{x_i-X_I}{|\mathbf{r}_{iI}|}}{|\mathbf{r}_{iI}|^2} = \frac{1}{|\mathbf{r}_{iI}|}-\frac{(x_i-X_I)^2}{|\mathbf{r}_{iI}|^3} = \frac{1-C^2_{x,iI}}{|\mathbf{r}_{iI}|}, \tag{20}$$

In eq. (18)

$$\partial_{x_i}\left(C_{x,iI}\phi_{iI}\right) = \frac{1-C^2_{x,iI}}{|\mathbf{r}_{iI}|}\phi_{iI} + C_{x,iI}\partial_{x_i}\phi_{iI}, \tag{21}$$

and in eq. (17)

$$\partial^2_{x_i}\phi_{iI} = -\alpha\left(\frac{1-C^2_{x,iI}}{|\mathbf{r}_{iI}|}\phi_{iI} + C_{x,iI}\partial_{x_i}\phi_{iI}\right), \tag{22}$$

inserting the $-\alpha$ factor

$$\partial_{x_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \left(-\alpha\frac{C_{x,iI}^2}{|\mathbf{r}_{iI}|}\phi_{iI}\right) - \alpha C_{x,iI}\partial_{x_i}\phi_{iI}, \tag{23}$$

and recalling eq. (15), the second term reads

$$-\alpha\frac{C_{x,iI}^2}{|\mathbf{r}_{iI}|}\phi_{iI} = \frac{C_{x,iI}}{|\mathbf{r}_{iI}|}\left(-\alpha C_{x,iI}\phi_{iI}\right) = \frac{C_{x,iI}}{|\mathbf{r}_{iI}|}\partial_{x_i}\phi_{iI}. \tag{24}$$

In eq. (23)

$$\partial_{x_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \frac{C_{x,iI}}{|\mathbf{r}_{iI}|}\partial_{x_i}\phi_{iI} - \alpha C_{x,iI}\partial_{x_i}\phi_{iI}, \tag{25}$$

and taking $\partial_{x_i}\phi_{iI}$ as common factor

$$\partial_{x_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \left(\frac{C_{x,iI}}{|\mathbf{r}_{iI}|} + \alpha C_{x,iI}\right)\partial_{x_i}\phi_{iI}, \tag{26}$$

or

$$\partial_{x_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \frac{C_{x,iI}\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|}\partial_{x_i}\phi_{iI}. \tag{27}$$

The second partial derivative over the $\lambda_i = \{x_i, y_i, z_i\}$ component can be expressed in terms of the first partial derivative as

$$\therefore \partial_{\lambda_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \frac{C_{\lambda,iI}\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|}\partial_{\lambda_i}\phi_{iI}, \tag{28}$$

which can be usefull for testing.

Now, recalling eq. (15)

$$\partial_{x_i}^2 \phi_{iI} = -\frac{\alpha}{|\mathbf{r}_{iI}|}\phi_{iI} - \frac{C_{x,iI}\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|}\left(-\alpha C_{\lambda,iI}\phi_{iI}\right), \tag{29}$$

and taking $-\alpha\phi_{iI}$ as common factor

$$\partial_{x_i}^2 \phi_{iI} = -\alpha\left(\frac{1}{|\mathbf{r}_{iI}|} - \frac{C_{x,iI}^2\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|}\right)\phi_{iI}. \tag{30}$$

the second partial derivative over the $\lambda_i = \{x_i, y_i, z_i\}$ component is given by

$$\therefore \partial_{\lambda_i}^2 \phi_{iI} = -\alpha D_{\lambda,iI}\phi_{iI}, \tag{31}$$

where

$$D_{\lambda,iI} = \frac{1}{|\mathbf{r}_{iI}|} - \frac{C_{\lambda,iI}^2\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|}, \tag{32}$$

or, recalling the definition of $C_{\lambda,iI}$ in eq. (16)

$$D_{\lambda,iI} = \frac{1}{|\mathbf{r}_{iI}|} - \frac{\left(\lambda_i - \Lambda_I\right)^2\left(1+\alpha\left|\mathbf{r}_{iI}\right|\right)}{|\mathbf{r}_{iI}|^3}. \tag{33}$$

3 Partial derivatives of the wavefunction

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

$$\partial_{x_i}\psi = \partial_{x_i}\prod_{i=1}^{n}\left(\sum_{I=1}^{m}\phi_{iI}\right). \tag{34}$$

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

$$\partial_{x_j}\phi_{jI} = 0 \quad \forall j \neq i \text{ and } \forall I, \tag{35}$$

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

$$\partial_{x_i}\psi = \partial_{x_i}\prod_{i=1}^{n}\left(\sum_{I=1}^{m}\phi_{iI}\right) = \prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right)\partial_{x_i}\left(\sum_{I=1}^{m}\phi_{iI}\right) = \prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right)\sum_{I=1}^{m}\partial_{x_i}\phi_{iI}. \tag{36}$$

Since both in the drift vector and the kinetic energy (eqs. (5) and (7)) 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. (4), the product can be separated as

$$\psi = \left(\sum_{I=1}^{m}\phi_{iI}\right)\prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right), \tag{37}$$

which implies that

$$\prod_{j\neq i}^{n}\left(\sum_{I=1}^{m}\phi_{jI}\right) = \frac{\psi}{\sum_{I=1}^{m}\phi_{iI}}. \tag{38}$$

This way, eq. (36) can be rewritten in terms of ψ and $\partial_{x_i}\phi_{iI}$ as

$$\partial_{x_i}\psi = \frac{\sum_{I=1}^{m}\partial_{x_i}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{39}$$

Recalling eq. (15) in eq. (39)

$$\partial_{x_i}\psi = -\alpha\frac{\sum_{I=1}^{m}C_{x,iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi. \tag{40}$$

Therefore, the first partial derivative over the $\lambda_i = \{x_i, y_i, z_i\}$ components reads

$$\therefore \partial_{\lambda_i}\psi = -\alpha\frac{\sum_{I=1}^{m}C_{\lambda,iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi, \tag{41}$$

where $C_{\lambda,iI}$ is given by eq. (16).

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. (39) is taken

$$\partial_{x_i}^2\psi = \partial_{x_i}\left(\frac{\sum_{I=1}^{m}\partial_{x_i}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\psi\right), \tag{42}$$

that, by the product rule

$$\partial^2_{x_i}\psi = \psi\,\underbrace{\partial_{x_i}\left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right)}_{\text{(a)}} + \underbrace{\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\partial_{x_i}\psi}_{\text{(b)}}\,. \tag{43}$$

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

$$\text{(a)}\;\; \partial_{x_i}\left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right) = \frac{\left(\sum_{I=1}^m \phi_{iI}\right)\partial_{x_i}\left(\sum_{I=1}^m \partial_{x_i}\phi_{iI}\right)}{\left(\sum_{I=1}^m \phi_{iI}\right)^2} - \frac{\left(\sum_{I=1}^m \partial_{x_i}\phi_{iI}\right)\partial_{x_i}\left(\sum_{I=1}^m \phi_{iI}\right)}{\left(\sum_{I=1}^m \phi_{iI}\right)^2}, \tag{44}$$

which simplifies to

$$\text{(a)}\;\; \partial_{x_i}\left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right) = \underbrace{\frac{\sum_{I=1}^m \partial^2_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}}_{\text{(c)}} - \frac{\left(\sum_{I=1}^m \partial_{x_i}\phi_{iI}\right)^2}{\left(\sum_{I=1}^m \phi_{iI}\right)^2}. \tag{45}$$

Again, the first term is calculated separately. Recalling eq. (31)

$$\text{(c)}\;\; \frac{\sum_{I=1}^m \partial^2_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}} = -\alpha\frac{\sum_{I=1}^m D_{x,iI}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}, \tag{46}$$

in eq. (45)

$$\text{(a)}\;\; \partial_{x_i}\left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right) = -\alpha\frac{\sum_{I=1}^m D_{x,iI}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}} - \left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right)^2. \tag{47}$$

The second term in eq. (43), recalling eq. (39), reads

$$\text{(b)}\;\; \frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\partial_{x_i}\psi = \frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\psi = \left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right)^2\psi. \tag{48}$$

Substituting eqs. (47) and (48) into eq. (43)

$$\partial^2_{x_i}\psi = \left[-\alpha\frac{\sum_{I=1}^m D_{\lambda,iI}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}} - \left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right)^2\right]\psi + \left(\frac{\sum_{I=1}^m \partial_{x_i}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\right)^2\psi, \tag{49}$$

which reduces to

$$\partial^2_{x_i}\psi = -\alpha\frac{\sum_{I=1}^m D_{x,iI}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\psi. \tag{50}$$

Therefore, the second partial derivative over the $\lambda_i = \{x_i, y_i, z_i\}$ components reads

$$\therefore\, \partial^2_{\lambda_i}\psi = -\alpha\frac{\sum_{I=1}^m D_{\lambda,iI}\phi_{iI}}{\sum_{I=1}^m \phi_{iI}}\psi, \tag{51}$$

where $D_{\lambda,iI}$ is given by eq. (33).

4 Gradient & drift vector

Substituting eq. (41) into the definition of the gradient given in eq. (6)

$$\nabla\psi\left(\mathbf{r}\right)=\begin{pmatrix}\partial_{x_1}\psi\\ \partial_{y_1}\psi\\ \partial_{z_1}\psi\\ \vdots\\ \partial_{x_n}\psi\\ \partial_{y_n}\psi\\ \partial_{z_n}\psi\end{pmatrix}=\begin{pmatrix}-\alpha\left(\sum_{I=1}^{m}C_{x,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\psi\\ -\alpha\left(\sum_{I=1}^{m}C_{y,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\psi\\ -\alpha\left(\sum_{I=1}^{m}C_{z,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\psi\\ \vdots\\ -\alpha\left(\sum_{I=1}^{m}C_{x,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\psi\\ -\alpha\left(\sum_{I=1}^{m}C_{y,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\psi\\ -\alpha\left(\sum_{I=1}^{m}C_{z,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\psi\end{pmatrix},\tag{52}$$

and taking $-\alpha\psi$ as a common factor

$$\nabla\psi\left(\mathbf{r}\right)=-\alpha\begin{pmatrix}\left(\sum_{I=1}^{m}C_{x,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{y,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{z,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \vdots\\ \left(\sum_{I=1}^{m}C_{x,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{y,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{z,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\end{pmatrix}\psi,\tag{53}$$

Therefore, the drift vector defined in eq. (5) is given by

$$\therefore\frac{\nabla\psi\left(\mathbf{r}\right)}{\psi\left(\mathbf{r}\right)}=-\alpha\begin{pmatrix}\left(\sum_{I=1}^{m}C_{x,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{y,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{z,1I}\phi_{1I}\right)\left(\sum_{I=1}^{m}\phi_{1I}\right)^{-1}\\ \vdots\\ \left(\sum_{I=1}^{m}C_{x,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{y,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\\ \left(\sum_{I=1}^{m}C_{z,nI}\phi_{nI}\right)\left(\sum_{I=1}^{m}\phi_{nI}\right)^{-1}\end{pmatrix},\tag{54}$$

where $C_{\lambda,iI}$ is given by eq. (16).

5 Laplacian & kinetic energy

The laplacian given in eq. (8) is given by summing over all i electrons

$$\nabla^2\psi\left(\mathbf{r}\right)=\sum_{i=1}^{n}\partial_{x_i}^2\psi+\sum_{i=1}^{n}\partial_{y_i}^2\psi+\sum_{i=1}^{n}\partial_{z_i}^2\psi,\tag{55}$$

substituting eq. (51) into eq. (55) and taking $-\alpha\psi$ as a common factor

$$\nabla^2\psi\left(\mathbf{r}\right)=-\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}D_{x,iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}+\frac{\sum_{I=1}^{m}D_{y,iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}+\frac{\sum_{I=1}^{m}D_{z,iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi\left(\mathbf{r}\right),\tag{56}$$

which can be rewritten as

$$\nabla^2\psi(\mathbf{r}) = -\alpha\sum_{i=1}^{n}\left[\frac{\sum_{I=1}^{m}\left(D_{x,iI}+D_{y,iI}+D_{z,iI}\right)\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right]\psi(\mathbf{r}). \tag{57}$$

Now, recalling eq. (32)

$$\begin{aligned} D_{iI} = D_{x,iI}+D_{y,iI}+D_{z,iI} = &\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{C_{x,iI}^2\left(1+\alpha\,|\mathbf{r}_{iI}|\right)}{|\mathbf{r}_{iI}|}\right] \\ &+\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{C_{y,iI}^2\left(1+\alpha\,|\mathbf{r}_{iI}|\right)}{|\mathbf{r}_{iI}|}\right] \\ &+\left[\frac{1}{|\mathbf{r}_{iI}|}-\frac{C_{z,iI}^2\left(1+\alpha\,|\mathbf{r}_{iI}|\right)}{|\mathbf{r}_{iI}|}\right], \end{aligned} \tag{58}$$

which can be simplified to

$$D_{iI} = \frac{3}{|\mathbf{r}_{iI}|}-\frac{\left(1+\alpha\,|\mathbf{r}_{iI}|\right)}{|\mathbf{r}_{iI}|}\left(C_{x,iI}^2+C_{y,iI}^2+C_{z,iI}^2\right). \tag{59}$$

Recalling the definition of $C_{\lambda,iI}$ in eq. (16)

$$C_{x,iI}^2+C_{y,iI}^2+C_{z,iI}^2 = \frac{(x_i-X_I)^2}{|\mathbf{r}_{iI}|^2}+\frac{(y_i-Y_I)^2}{|\mathbf{r}_{iI}|^2}+\frac{(z_i-Z_I)^2}{|\mathbf{r}_{iI}|^2}, \tag{60}$$

or, taking $1/|\mathbf{r}_{iI}|^2$ as common factor

$$C_{x,iI}^2+C_{y,iI}^2+C_{z,iI}^2 = \frac{1}{|\mathbf{r}_{iI}|^2}\left[(x_i-X_I)^2+(y_i-Y_I)^2+(z_i-Z_I)^2\right]. \tag{61}$$

By the definition given in eq. (2)

$$|\mathbf{r}_{iI}|^2 = (x_i-X_I)^2+(y_i-Y_I)^2+(z_i-Z_I)^2, \tag{62}$$

it results in

$$C_{x,iI}^2+C_{y,iI}^2+C_{z,iI}^2 = 1. \tag{63}$$

In eq. (59)

$$D_{iI} = \frac{3}{|\mathbf{r}_{iI}|}-\frac{\left(1+\alpha\,|\mathbf{r}_{iI}|\right)}{|\mathbf{r}_{iI}|}. \tag{64}$$

Then, in eq. (57)

$$\nabla^2\psi(\mathbf{r}) = -\alpha\sum_{i=1}^{n}\left(\frac{\sum_{I=1}^{m}D_{iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right)\psi(\mathbf{r}). \tag{65}$$

Therefore, the kinetic energy defined in eq. (7) is given by

$$\therefore T_{\mathrm{L}}(\mathbf{r}) = -\frac{1}{2}\sum_{i=1}^{n}\left(\frac{\sum_{I=1}^{m}-\alpha D_{iI}\phi_{iI}}{\sum_{I=1}^{m}\phi_{iI}}\right), \tag{66}$$

where D_{iI} is defined in eq. (64).