Ground State Calculator: Mathematics and Development Notes

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Contents

1 Gaussian Functions

This section covers important properties of Gaussian functions generalized to any number of dimensions in cartesian coordinates.

For the purposes of this program and its documentation, a Gaussian function in n dimensions will be defined as

$$\mathcal{G}_n\left(\mathbf{x}\right) \equiv \exp\left[-\mathbf{x}^T\mathbf{A}\mathbf{x} + \mathbf{s}^T\mathbf{x}\right]$$

where

$$\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_{n-1} \\ x_n \end{bmatrix}$$

and is a column vector of input coordinates for the Gaussian function. $\mathbf{s}$ is a length n column vector that defines the shift of the function.

$$\mathbf{s} = \begin{bmatrix} s_1 \\ s_2 \\ \vdots \\ s_{n-1} \\ s_n \end{bmatrix}$$

$\mathbf{A}$ is an $n \times n$ matrix of values that define the shape of the Gaussian function.

$$\mathbf{A} = \begin{bmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn} \end{bmatrix}$$

This matrix is symmetric and positive definite, meaning that

$$\mathbf{z}^T\mathbf{A}\mathbf{z} > 0 \;\forall \sum_i \left|z_i\right| \; > 0,\; z_i \in \mathbb{R}$$

The integral of such a Gaussian function over all space

$$\int_{\mathbb{R}^n} \mathcal{G}_n\left(\mathbf{x}\right)\, d\mathbf{x} = \sqrt{\frac{\pi^n}{\det \mathbf{A}}} \exp\left[\frac{1}{4}\mathbf{s}^T\mathbf{A}^{-1}\mathbf{s}\right]$$

Where $\mathbf{A}^{-1}$ denotes the inverse of the matrix $\mathbf{A}$.

2 General Equations

This section defines equations that are generally applicable.

For a given normalized wavefunction

$$\psi = \psi\left(\mathbf{x}\right)$$

the expectation value of the Hamiltonian in cartesian coordinates is

$$\langle H \rangle = \int_{\mathbb{R}^n} \psi^* H \psi \, d\mathbf{x}$$

For a system of N_u atomic nuclei approximated as points with N_e electrons orbiting them and the Born-Oppenheimer approximation applied, the Hamiltonian of the system is

$$H = \frac{-\hbar^2}{2m_e} \left[\sum_{n=1}^{N_e} \nabla_n^2 \psi(\mathbf{x}) \right] + \frac{q_e}{4\pi\epsilon_0} \left[q_e \sum_{n=1}^{N_e} \sum_{m>n}^{N_e} |\mathbf{r}_n - \mathbf{r}_m|^{-1} - \sum_{n=1}^{N_u} \sum_{m=1}^{N_e} Q_n |\mathbf{R}_n - \mathbf{r}_m|^{-1} \right] \psi(\mathbf{x}) \tag{1}$$

where ∇_n^2 denotes the cartesian Laplacian of the wavefunction with respect to the nth electrons position, m_e denotes the mass of the electron, q_e denotes the charge of the electron (positive), $\mathbf{r}_n$ denotes the position of the nth electron w.r.t the origin, $\mathbf{R}_n$ denotes the position of the nth nucleus w.r.t the origin and Q_n denotes the charge of the nth nucleus. Because of the definition of the Laplacian in cartesian coordinates, this expression can be rewritten as

$$H = \frac{-\hbar^2}{2m_e} \left[\sum_{i=1}^{3N_e} \frac{\partial^2}{\partial x_i^2} \psi(\mathbf{x}) \right] + \frac{q_e}{4\pi\epsilon_0} \left[q_e \sum_{n=1}^{N_e} \sum_{m>n}^{N_e} |\mathbf{r}_n - \mathbf{r}_m|^{-1} - \sum_{n=1}^{N_u} \sum_{m=1}^{N_e} Q_n |\mathbf{R}_n - \mathbf{r}_m|^{-1} \right] \psi(\mathbf{x}) \tag{2}$$

Here, each Laplacian term has been replaced by three, 2nd partial derivative terms. In each term, x_n denotes the nth input coordinate of the trial wavefunction.

3 Gaussian Trial Function

The Gaussian Trial function is defined

$$\mathcal{G}_n^{(m)}(\mathbf{x}) \equiv B \sum_{j=1}^{m} C_j \exp\left[-\mathbf{x}^T \mathbf{A}^{(j)} \mathbf{x} + \mathbf{s}^{(j)T} \mathbf{x} \right]$$

Where m is the number of Gaussian terms in the trial function, B is a normalization constant, C_j is an arbitrary real constant, $\mathbf{A}^{(j)}$ defines the shape matrix of the jth term in the trial function and $\mathbf{s}^{(j)T}$ is the transpose of the shift vector of the jth term in the trial function.

3.1 Simplifying the Hamiltonian

In order to simplify the Hamiltonian, for the purposes of computing its expectation value, it is necessary to better define

$$\frac{\partial^2}{\partial x_i^2} \mathcal{G}_n^{(m)}(\mathbf{x}) = \frac{\partial^2}{\partial x_i^2} B \sum_{j=1}^{m} C_j \exp\left[-\mathbf{x}^T \mathbf{A}^{(j)} \mathbf{x} + \mathbf{s}^{(j)T} \mathbf{x} \right]$$

First, convert the interior of the exponential into a sum

$$-\mathbf{x}^T \mathbf{A}^{(j)} \mathbf{x} + \mathbf{s}^{(j)T} \mathbf{x} = -\sum_{k=1}^{n} x_k \left(\sum_{l=1}^{n} x_l A_{kl}^{(j)} \right) + \sum_{k=1}^{n} s_k^{(j)} x_k$$

Note that since $\mathbf{A}$ is symmetric, the term A_{kl} in the inner sum can also be written A_{lk}. The symmetry of $\mathbf{A}$ also means that all off diagonal terms in the sum have an identical term in the sum corresponing to their element in $\mathbf{A}^T$. This means that only one half of the off diagonal terms need to actually be computed. Their value can then be doubled. Re-writing the derivative

$$\frac{\partial^2}{\partial x_i^2}\mathcal{G}_n^{(m)}(\mathbf{x}) = B\sum_{j=1}^{m} C_j \frac{\partial^2}{\partial x_i^2}\exp\left[-\sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right]$$

$$let\ \exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x} + \mathbf{s}^{(j)T}\mathbf{x}\right] = \hat{\mathcal{G}}^{(j)}$$

$$\frac{\partial^2}{\partial x_i^2}\exp\left[-\sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right] = \frac{\partial}{\partial x_i}\left\{\hat{\mathcal{G}}^{(j)}\frac{\partial}{\partial x_i}\left[-\sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right]\right\}$$

$$\begin{aligned}
\frac{\partial}{\partial x_i}\left[-\sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right] &= -\sum_{k=1}^{n}\frac{\partial}{\partial x_i}x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n}\frac{\partial}{\partial x_i}s_k^{(j)} x_k \\
&= -\sum_{k=1}^{n}\frac{\partial}{\partial x_i}x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + s_i^{(j)}
\end{aligned}$$

$$\sum_{k=1}^{n}\frac{\partial}{\partial x_i}x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) = \sum_{k=1}^{n}\left[\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\frac{\partial}{\partial x_i}x_k + x_k\frac{\partial}{\partial x_i}\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\right]$$

$$\begin{aligned}
\sum_{k=1}^{n}\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\frac{\partial}{\partial x_i}x_k &= \sum_{k=1}^{n}\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\delta_{ik} \\
&= \sum_{l=1}^{n} x_l A_{il}^{(j)}
\end{aligned}$$

$$\begin{aligned}
\sum_{k=1}^{n} x_k\frac{\partial}{\partial x_i}\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) &= \sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n}\frac{\partial}{\partial x_i}x_l A_{kl}^{(j)}\right) \\
&= \sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} A_{kl}^{(j)}\delta_{li}\right) \\
&= \sum_{k=1}^{n} x_k A_{ki}^{(j)}
\end{aligned}$$

Combining all of the sub-terms derived above and applying the second derivative

$$\frac{\partial}{\partial x_i}\left\{\hat{\mathcal{G}}^{(j)}\frac{\partial}{\partial x_i}\left[-\sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right]\right\} = \frac{\partial}{\partial x_i}\left\{\hat{\mathcal{G}}^{(j)}\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]\right\}$$

$$= \left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]\frac{\partial}{\partial x_i}\hat{\mathcal{G}}^{(j)} + \hat{\mathcal{G}}^{(j)}\frac{\partial}{\partial x_i}\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]$$

As derived above,

$$\frac{\partial}{\partial x_i}\hat{\mathcal{G}}^{(j)} = \hat{\mathcal{G}}^{(j)}\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]$$

Completing the second derivative terms

$$\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right] \frac{\partial}{\partial x_i}\hat{\mathcal{G}}^{(j)} = \left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right] \hat{\mathcal{G}}^{(j)} \left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]$$

$$= \left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]^2 \hat{\mathcal{G}}^{(j)}$$

$$\hat{\mathcal{G}}^{(j)} \frac{\partial}{\partial x_i}\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right] = \hat{\mathcal{G}}^{(j)} \left\{-\sum_{l=1}^{n} \frac{\partial}{\partial x_i} x_l A_{il}^{(j)} - \sum_{k=1}^{n} \frac{\partial}{\partial x_i} x_k A_{ki}^{(j)}\right\}$$

$$= \hat{\mathcal{G}}^{(j)} \left\{-\sum_{l=1}^{n} A_{il}^{(j)} \delta_{li} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} \delta_{ki}\right\}$$

$$= \hat{\mathcal{G}}^{(j)} \left\{-A_{ii}^{(j)} - A_{ii}^{(j)}\right\}$$

$$= -2A_{ii}^{(j)} \hat{\mathcal{G}}^{(j)}$$

Finally

$$\frac{\partial^2}{\partial x_i^2}\hat{\mathcal{G}}^{(j)} = \left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]^2 \hat{\mathcal{G}}^{(j)} - 2A_{ii}^{(j)} \hat{\mathcal{G}}^{(j)}$$

Meaning that

$$\frac{\partial^2}{\partial x_i^2}\mathcal{G}_n^{(m)}(\mathbf{x}) = B\sum_{j=1}^{m} C_j \left\{\left[-\sum_{l=1}^{n} x_l A_{il}^{(j)} - \sum_{k=1}^{n} x_k A_{ki}^{(j)} + s_i^{(j)}\right]^2 \hat{\mathcal{G}}^{(j)} - 2A_{ii}^{(j)} \hat{\mathcal{G}}^{(j)}\right\}$$

$$= B\sum_{j=1}^{m} C_j \left\{\left[-\left(\sum_{k=1}^{n} x_k A_{ik}^{(j)} + x_k A_{ki}^{(j)}\right) + s_i^{(j)}\right]^2 \hat{\mathcal{G}}^{(j)} - 2A_{ii}^{(j)} \hat{\mathcal{G}}^{(j)}\right\}$$

Recalling that $\mathbf{A}$ is symmetric,

$$\frac{\partial^2}{\partial x_i^2}\mathcal{G}_n^{(m)}(\mathbf{x}) = B\sum_{j=1}^{m} C_j \hat{\mathcal{G}}^{(j)} \left\{\left[s_i^{(j)} - 2\sum_{k=1}^{n} x_k A_{ik}^{(j)}\right]^2 - 2A_{ii}^{(j)}\right\}$$

where

$$\hat{\mathcal{G}}^{(j)} = \exp\left[-\mathbf{x}^T \mathbf{A}^{(j)} \mathbf{x} + \mathbf{s}^{(j)T} \mathbf{x}\right]$$

Applying this definition to simplify the Hamiltonian, the kinetic energy portion

$$T\mathcal{G}_n^{(m)}(\mathbf{x}) = \frac{-\hbar^2}{2m_e}\left[\sum_{i=1}^{n} B \sum_{j=1}^{m} C_j \hat{\mathcal{G}}^{(j)} \left\{\left[s_i^{(j)} - 2\sum_{k=1}^{n} x_k A_{ik}^{(j)}\right]^2 - 2A_{ii}^{(j)}\right\}\right]$$

$$= \frac{-B\hbar^2}{2m_e} \sum_{i=1}^{n}\sum_{j=1}^{m} C_j \hat{\mathcal{G}}^{(j)} \left\{\left[s_i^{(j)} - 2\sum_{k=1}^{n} x_k A_{ik}^{(j)}\right]^2 - 2A_{ii}^{(j)}\right\}$$

No derivatives need to be calculated for the potential energy portion, so it can be written

$$V\mathcal{G}_n^{(m)}(\mathbf{x}) = \frac{q_e}{4\pi\epsilon_0}\left[q_e \sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \left|\mathbf{r}_i - \mathbf{r}_j\right|^{-1} - \sum_{i=1}^{N_u}\sum_{j=1}^{N_e} Q_i \left|\mathbf{R}_i - \mathbf{r}_j\right|^{-1}\right] \mathcal{G}_n^{(m)}(\mathbf{x})$$

3.2 Simplifying the Expectation Value of the Hamiltonian

The expectation value of the Hamiltonian for this system can be written

$$\int_{\mathbb{R}^q} \psi^* H\psi \, d\mathbf{x} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* H\psi \, dx_1 \, dx_2 \cdots dx_q$$
$$\psi^* H\psi = \psi^* \left(T\psi + V\psi\right)$$

Where n is the number of inputs to the trial function. Since the trial function is real, $\psi^* = \psi$

$$\psi^* \left(T\psi + V\psi\right) = \psi T\psi + V\psi^2$$
$$V\psi^2 = \frac{q_e}{4\pi\epsilon_0} \left[q_e \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} |\mathbf{r}_i - \mathbf{r}_j|^{-1} - \sum_{i=1}^{N_u} \sum_{j=1}^{N_e} Q_i \, |\mathbf{R}_i - \mathbf{r}_j|^{-1} \right] \left[\mathcal{G}_n^{(m)}\left(\mathbf{x}\right)\right]^2$$
$$\psi T\psi = \mathcal{G}_n^{(m)}\left(\mathbf{x}\right) \frac{-B\hbar^2}{2m_e} \sum_{i=1}^{n} \sum_{j=1}^{m} C_j \hat{\mathcal{G}}^{(j)} \left\{ \left[s_i^{(j)} - 2 \sum_{k=1}^{n} x_k A_{ik}^{(j)} \right]^2 - 2A_{ii}^{(j)} \right\}$$

Breaking up the integral

$$\int_{\mathbb{R}^q} \psi^* H\psi \, d\mathbf{x} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi T\psi \, dx_1 \, dx_2 \cdots dx_n + \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V\psi^2 \, dx_1 \, dx_2 \cdots dx_n$$

3.2.1 Kinetic Energy Integral

In order to calculate the integral,

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi T\psi \, dx_1 \, dx_2 \cdots dx_n$$

it is necessary to break it up into a product of integrals w.r.t each dx_n to the furthest extent that it is possible. In order to do this, it is necessary to express the function $\hat{\mathcal{G}}\left(\mathbf{x}\right)$ in terms of a product of multiple exponential functions.

$$
\begin{aligned}
\hat{\mathcal{G}}^{(j)} &= \exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x} + \mathbf{s}^{(j)T}\mathbf{x}\right] \\
&= \exp\left[-\sum_{k=1}^{n} x_k \left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right) + \sum_{k=1}^{n} s_k^{(j)} x_k\right] \\
&= \exp\left[-\sum_{k=1}^{n} x_k \left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\right] \exp\left[\sum_{k=1}^{n} s_k^{(j)} x_k\right] \\
\exp\left[\sum_{k=1}^{n} s_k^{(j)} x_k\right] &= \prod_{k=1}^{n} \exp\left[s_k^{(j)} x_k\right] \\
\exp\left[-\sum_{k=1}^{n} x_k \left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\right] &= \prod_{k=1}^{n} \exp\left[-x_k \left(\sum_{l=1}^{n} x_l A_{kl}^{(j)}\right)\right] \\
&= \prod_{k=1}^{n} \exp\left[-x_k^2 A_{kk}^{(j)} - x_k \left(\sum_{l\neq k}^{n} x_l A_{kl}^{(j)}\right)\right] \\
&= \prod_{k=1}^{n} \exp\left[-x_k^2 A_{kk}^{(j)}\right] \exp\left[-\sum_{l\neq k}^{n} x_k x_l A_{kl}^{(j)}\right] \\
&= \prod_{k=1}^{n} \left\{\exp\left[-x_k^2 A_{kk}^{(j)}\right] \left(\prod_{l\neq k}^{n} \exp\left[-x_k x_l A_{kl}^{(j)}\right]\right)\right\} \\
\therefore \hat{\mathcal{G}}^{(j)} &= \left[\prod_{k=1}^{n} \left\{\exp\left[-x_k^2 A_{kk}^{(j)}\right] \left(\prod_{l\neq k}^{n} \exp\left[-x_k x_l A_{kl}^{(j)}\right]\right)\right\}\right] \left[\prod_{k=1}^{n} \exp\left[s_k^{(j)} x_k\right]\right] \qquad (3)
\end{aligned}
$$

At this point, it becomes convenient to apply a significant simplification, at the expense of removing some generality from the trial function. Now, assume that $\mathbf{A}$ is a diagonal matrix, more explicitely

$$A_{ij} = 0 \; for \; i \neq j$$

Applying this to eq. 3.

$$
\begin{aligned}
\hat{\mathcal{G}}^{(j)} &= \left[\prod_{k=1}^{n} \left\{\exp\left[-x_k^2 A_{kk}^{(j)}\right] \left(\cancelto{1}{\prod_{l\neq k}^{n} \exp\left[-x_k x_l A_{kl}^{(j)}\right]}\right)\right\}\right] \left[\prod_{k=1}^{n} \exp\left[s_k^{(j)} x_k\right]\right] \\
&= \prod_{k=1}^{n} \exp\left[-x_k^2 A_{kk}^{(j)}\right] \prod_{k=1}^{n} \exp\left[s_k^{(j)} x_k\right] \\
&= \prod_{k=1}^{n} \exp\left[-x_k^2 A_{kk}^{(j)}\right] \exp\left[s_k^{(j)} x_k\right]
\end{aligned}
$$

Using this to write the expression $\psi T\psi$ as explicitely as possible

$$\begin{aligned}
\psi T\psi &= \mathcal{G}_n^{(m)}(\mathbf{x})\,\frac{-B\hbar^2}{2m_e}\sum_{i=1}^{n}\sum_{j=1}^{m}C_j\hat{\mathcal{G}}^{(j)}\left\{\left[s_i^{(j)}-2\sum_{k=1}^{n}x_kA_{ik}^{(j)}\right]^2-2A_{ii}^{(j)}\right\}\\
&= \mathcal{G}_n^{(m)}(\mathbf{x})\,\frac{-B\hbar^2}{2m_e}\sum_{i=1}^{n}\sum_{j=1}^{m}C_j\hat{\mathcal{G}}^{(j)}\left\{\left[s_i^{(j)}-2x_iA_{ii}^{(j)}\right]^2-2A_{ii}^{(j)}\right\}\\
&= \frac{-B^2\hbar^2}{2m_e}\left(\sum_{j'=1}^{m}C_{j'}\prod_{l=1}^{n}\exp\left[-x_l^2A_{ll}^{(j')}\right]\exp\left[s_l^{(j')}x_l\right]\right)\times\\
&\sum_{i=1}^{n}\sum_{j=1}^{m}C_j\left(\prod_{k=1}^{n}\exp\left[-x_k^2A_{kk}^{(j)}\right]\exp\left[s_k^{(j)}x_k\right]\right)\left\{\left[s_i^{(j)}-2x_iA_{ii}^{(j)}\right]^2-2A_{ii}^{(j)}\right\}\\
&= \frac{-B^2\hbar^2}{2m_e}\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_j\left(\prod_{l=1}^{n}\exp\left[-x_l^2A_{ll}^{(j')}\right]\exp\left[s_l^{(j')}x_l\right]\right)\left(\prod_{k=1}^{n}\exp\left[-x_k^2A_{kk}^{(j)}\right]\exp\left[s_k^{(j)}x_k\right]\right)\times\\
&\left(\left[s_i^{(j)}-2x_iA_{ii}^{(j)}\right]^2-2A_{ii}^{(j)}\right)
\end{aligned}$$

Next, we simplify the two product terms

$$\left(\prod_{l=1}^{n}\exp\left[-x_l^2A_{ll}^{(j')}\right]\exp\left[s_l^{(j')}x_l\right]\right)\left(\prod_{k=1}^{n}\exp\left[-x_k^2A_{kk}^{(j)}\right]\exp\left[s_k^{(j)}x_k\right]\right)$$

$$\begin{aligned}
&= \prod_{l=1}^{n}\exp\left[-x_l^2A_{ll}^{(j')}\right]\exp\left[s_l^{(j')}x_l\right]\exp\left[-x_l^2A_{ll}^{(j)}\right]\exp\left[s_l^{(j)}x_l\right]\\
&= \prod_{l=1}^{n}\exp\left[-x_l^2A_{ll}^{(j')}-x_l^2A_{ll}^{(j)}\right]\exp\left[s_l^{(j')}x_l+s_l^{(j)}x_l\right]\\
&= \prod_{l=1}^{n}\exp\left[-x_l^2\left(A_{ll}^{(j')}+A_{ll}^{(j)}\right)\right]\exp\left[x_l\left(s_l^{(j')}+s_l^{(j)}\right)\right]
\end{aligned}$$

Inserting this into the original expression.

$$\psi T\psi = \frac{-B^2\hbar^2}{2m_e}\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_j\left(\left[s_i^{(j)}-2x_iA_{ii}^{(j)}\right]^2-2A_{ii}^{(j)}\right)\prod_{l=1}^{n}\exp\left[-x_l^2\left(A_{ll}^{(j')}+A_{ll}^{(j)}\right)\right]\exp\left[x_l\left(s_l^{(j')}+s_l^{(j)}\right)\right]$$

Expanding the last term in the above expression.

$$\left[s_i^{(j)}-2x_iA_{ii}^{(j)}\right]^2-2A_{ii}^{(j)} = \left[s_i^{(j)}\right]^2+4x_i^2\left[A_{ii}^{(j)}\right]^2-4x_iA_{ii}^{(j)}s_i^{(j)}-2A_{ii}^{(j)}$$

This allows for the integral that defines the expectation value of the kinetic energy to be simplified significantly. First, recall that

$$\int\cdots\int\int\prod_{i=1}^{n}f_i(x_i)\,dx_1dx_2\cdots dx_N = \prod_{i=1}^{n}\int f_i(x_i)\,dx_i \tag{4}$$

Emphasis being on the fact that all functions in the integrand depend on a single variable of integration, never more, never less.

Before applying this, we allow the following definitions, in order to be concise.

$$
\begin{aligned}
let\ f\left(x_l\right) &= \exp\left[-x_l^2\left(A_{ll}^{(j')}+A_{ll}^{(j)}\right)\right]\exp\left[x_l\left(s_l^{(j')}+s_l^{(j)}\right)\right] \\
let\ g\left(x_i\right) &= \left[s_i^{(j)}\right]^2+4x_i^2\left[A_{ii}^{(j)}\right]^2-4x_iA_{ii}^{(j)}s_i^{(j)}-2A_{ii}^{(j)}
\end{aligned}
$$

We now write the expectation value of the kinetic energy

$$
\begin{aligned}
\langle T\rangle &= \frac{-B^2\hbar^2}{2m_e}\int\cdots\int\int\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_jg\left(x_i\right)\prod_{l=1}^{n}f\left(x_l\right)\right\}dx_1dx_2\cdots dx_n \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_j\int\cdots\int\int g\left(x_i\right)\prod_{l=1}^{n}f\left(x_l\right)\ dx_1dx_2\cdots dx_n\right\} \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_j\int\cdots\int\int g\left(x_i\right)f\left(x_i\right)\prod_{l\neq i}^{n}f\left(x_l\right)\ dx_1dx_2\cdots dx_n\right\} \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n}C_{j'}C_j\int g\left(x_i\right)f\left(x_i\right)\ dx_i\prod_{l\neq i}^{n}\int f\left(x_l\right)\ dx_l\right\}
\end{aligned}
$$

This now leaves us with only the following two integrals to calculate.

$$
\begin{aligned}
\int_{-\infty}^{\infty}f\left(x_l\right)\ dx_l &= \int_{-\infty}^{\infty}\exp\left[-x_l^2\left(A_{ll}^{(j')}+A_{ll}^{(j)}\right)\right]\exp\left[x_l\left(s_l^{(j')}+s_l^{(j)}\right)\right]\ dx_l \\
\int_{-\infty}^{\infty}g\left(x_i\right)f\left(x_i\right)\ dx_i &= \int_{-\infty}^{\infty}\left(\left[s_i^{(j)}\right]^2+4x_i^2\left[A_{ii}^{(j)}\right]^2-4x_iA_{ii}^{(j)}s_i^{(j)}-2A_{ii}^{(j)}\right)\exp\left[-x_i^2\left(A_{ii}^{(j')}+A_{ii}^{(j)}\right)+x_i\left(s_i^{(j')}+s_i^{(j)}\right)\right]\ dx_i
\end{aligned}
$$

The second integral can be split into a sum of three integrals, making the full list of integrals to be computed

$$
\begin{aligned}
I_1 &\equiv \int_{-\infty}^{\infty}\exp\left[-x_l^2\left(A_{ll}^{(j')}+A_{ll}^{(j)}\right)\right]\exp\left[x_l\left(s_l^{(j')}+s_l^{(j)}\right)\right]\ dx_l \\
I_2 &\equiv \left(\left[s_i^{(j)}\right]^2-2A_{ii}^{(j)}\right)\int_{-\infty}^{\infty}\exp\left[-x_i^2\left(A_{ii}^{(j')}+A_{ii}^{(j)}\right)\right]\exp\left[x_i\left(s_i^{(j')}+s_i^{(j)}\right)\right]\ dx_i \\
I_3 &\equiv 4\left[A_{ii}^{(j)}\right]^2\int_{-\infty}^{\infty}x_i^2\exp\left[-x_i^2\left(A_{ii}^{(j')}+A_{ii}^{(j)}\right)\right]\exp\left[x_i\left(s_i^{(j')}+s_i^{(j)}\right)\right]\ dx_i \\
I_4 &\equiv -4A_{ii}^{(j)}s_i^{(j)}\int_{-\infty}^{\infty}x_i\exp\left[-x_i^2\left(A_{ii}^{(j')}+A_{ii}^{(j)}\right)\right]\exp\left[x_i\left(s_i^{(j')}+s_i^{(j)}\right)\right]\ dx_i
\end{aligned}
$$

All of which can be computed analytically. First,

$$
\begin{aligned}
let\ D_{ljj'} &= A_{ll}^{(j')} + A_{ll}^{(j)} \\
let\ F_{ljj'} &= s_l^{(j')} + s_l^{(j)} \\
I_1 &= \sqrt{\frac{\pi}{D_{ljj'}}} \exp\left[\frac{F_{ljj'}^2}{4D_{ljj'}}\right] \\
I_2 &= \left(\left[s_i^{(j)}\right]^2 - 2A_{ii}^{(j)}\right)\sqrt{\frac{\pi}{D_{ijj'}}} \exp\left[\frac{F_{ijj'}^2}{4D_{ijj'}}\right] \\
I_3 &= \left[A_{ii}^{(j)}\right]^2 \exp\left[\frac{F_{ijj'}^2}{4D_{ijj'}}\right]\left(2D_{ijj'} + F_{ijj'}^2\right)\sqrt{\frac{\pi}{D_{ijj'}^5}} \\
I_4 &= -4A_{ii}^{(j)} s_i^{(j)} \exp\left[\frac{F_{ijj'}^2}{4D_{ijj'}}\right] F_{ijj'} \sqrt{\frac{\pi}{4D_{ijj'}^3}}
\end{aligned}
$$

We are now equipped to write a complete, closed form solution to the expectation value of the kinetic energy.

$$
\langle T \rangle = \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\left(I_2 + I_3 + I_4\right)\prod_{l\neq i}^{n} I_1\right\}
$$

The completely expanded form being

$$
\begin{aligned}
\langle T \rangle &= \frac{-B^2\hbar^2}{2m_e}\pi^{\frac{n+1}{2}}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\Gamma_{ijj'}\prod_{l\neq i}^{n} D_{ljj'}^{-1/2}\exp\left[\frac{F_{ljj'}^2}{4D_{ljj'}}\right]\right\} \\
\Gamma_{ijj'} &\equiv \exp\left[\frac{F_{ijj'}^2}{4D_{ijj'}}\right]\left\{\left(\left[s_i^{(j)}\right]^2 - 2A_{ii}^{(j)}\right)D_{ijj'}^{-1/2} + \left[A_{ii}^{(j)}\right]^2\left(2D_{ijj'} + F_{ijj'}^2\right)D_{ijj'}^{-5/2} - 2A_{ii}^{(j)}s_i^{(j)}F_{ijj'}D_{ijj'}^{-3/2}\right\} \\
D_{kjj'} &\equiv A_{kk}^{(j')} + A_{kk}^{(j)} \\
F_{kjj'} &= s_k^{(j')} + s_k^{(j)}
\end{aligned}
$$

3.2.2 Potential Energy Integral

The integral that defines the expectation value of the potential energy can be written as follows (in cartesian coordinates). In order to better formulate it, I will rewrite the Hamiltonian in terms of individual coordinates, rather than cartesian vectors in three dimensions.

$$
\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} V\psi^2\, dx_1\, dx_2\cdots dx_n
$$

The original definition of the potential energy portion of the integrand was

$$
V\psi^2 = \frac{q_e}{4\pi\epsilon_0}\left[q_e\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\left|\mathbf{r}_i - \mathbf{r}_j\right|^{-1} - \sum_{i=1}^{N_u}\sum_{j=1}^{N_e} Q_i\left|\mathbf{R}_i - \mathbf{r}_j\right|^{-1}\right]\left[\mathcal{G}_n^{(m)}(\mathbf{x})\right]^2
$$

Now, rewritten

$$
\begin{aligned}
V\psi^2 =& \frac{q_e}{4\pi\epsilon_0}\left[q_e\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\mathcal{D}_{ij} - \sum_{i=1}^{N_u}\sum_{j=1}^{N_e}Q_i\mathcal{J}_{ij}\right]\left[\mathcal{G}_n^{(m)}\left(\mathbf{x}\right)\right]^2 \\
\mathcal{D}_{ij} =& \frac{1}{\sqrt{\left(x_{3i}-x_{3j}\right)^2+\left(x_{3i+1}-x_{3j+1}\right)^2+\left(x_{3i+2}-x_{3j+2}\right)^2}} \\
\mathcal{J}_{ij} =& \frac{1}{\sqrt{\left(R_{3i}-x_{3j}\right)^2+\left(R_{3i+1}-x_{3j+1}\right)^2+\left(R_{3i+2}-x_{3j+2}\right)^2}}
\end{aligned}
$$

Next, we simplify the square of the wavefunction

$$
\begin{aligned}
\mathcal{G}_n^{(m)}\left(\mathbf{x}\right) \equiv& B\sum_{j=1}^{m}C_j\exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x}+\mathbf{s}^{(j)T}\mathbf{x}\right] \\
-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x}+\mathbf{s}^{(j)T}\mathbf{x} =& -\sum_{k=1}^{n}x_k^2A_{kk}^{(j)}+\sum_{k=1}^{n}s_k^{(j)}x_k \\
\left[\mathcal{G}_n^{(m)}\left(\mathbf{x}\right)\right]^2 =& \left(B\sum_{j=1}^{m}C_j\exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x}+\mathbf{s}^{(j)T}\mathbf{x}\right]\right)\left(B\sum_{l=1}^{m}C_l\exp\left[-\mathbf{x}^T\mathbf{A}^{(l)}\mathbf{x}+\mathbf{s}^{(l)T}\mathbf{x}\right]\right) \\
=& B^2\sum_{j=1}^{m}\sum_{l=1}^{m}C_jC_l\exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x}+\mathbf{s}^{(j)T}\mathbf{x}\right]\exp\left[-\mathbf{x}^T\mathbf{A}^{(l)}\mathbf{x}+\mathbf{s}^{(l)T}\mathbf{x}\right] \\
=& B^2\sum_{j=1}^{m}\sum_{l=1}^{m}C_jC_l\exp\left[-\mathbf{x}^T\mathbf{A}^{(j)}\mathbf{x}+\mathbf{s}^{(j)T}\mathbf{x}-\mathbf{x}^T\mathbf{A}^{(l)}\mathbf{x}+\mathbf{s}^{(l)T}\mathbf{x}\right] \\
=& B^2\sum_{j=1}^{m}\sum_{l=1}^{m}C_jC_l\exp\left[-\sum_{k=1}^{n}x_k^2A_{kk}^{(j)}+\sum_{k=1}^{n}s_k^{(j)}x_k-\sum_{k=1}^{n}x_k^2A_{kk}^{(l)}+\sum_{k=1}^{n}s_k^{(l)}x_k\right] \\
=& B^2\sum_{j=1}^{m}\sum_{l=1}^{m}C_jC_l\exp\left[\sum_{k=1}^{n}\left(-x_k^2A_{kk}^{(j)}+s_k^{(j)}x_k-x_k^2A_{kk}^{(l)}+s_k^{(l)}x_k\right)\right] \\
=& B^2\sum_{j=1}^{m}\sum_{l=1}^{m}C_jC_l\exp\left[\sum_{k=1}^{n}\left\{-x_k^2\left(A_{kk}^{(j)}+A_{kk}^{(l)}\right)+x_k\left(s_k^{(j)}+s_k^{(l)}\right)\right\}\right]
\end{aligned}
$$

For formatting purposes, I will make the following definition

$$
\mathcal{K}_{lj} \equiv \sum_{k=1}^{n}\left\{-x_k^2\left(A_{kk}^{(j)}+A_{kk}^{(l)}\right)+x_k\left(s_k^{(j)}+s_k^{(l)}\right)\right\}
$$

The full expression for the expectation value of the potential energy can then be written,

$$
\langle V\rangle = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{q_e}{4\pi\epsilon_0}\left[q_e\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\mathcal{D}_{ij}-\sum_{i=1}^{N_u}\sum_{j=1}^{N_e}Q_i\mathcal{J}_{ij}\right]B^2\sum_{w=1}^{m}\sum_{l=1}^{m}C_wC_l\exp\left[\mathcal{K}_{lw}\right]\,dx_1\,dx_2\cdots\,dx_n
$$

Performing some basic simplification of this expressions,

$$
\langle V\rangle = \frac{q_eB^2}{4\pi\epsilon_0}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[q_e\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\mathcal{D}_{ij}-\sum_{i=1}^{N_u}\sum_{j=1}^{N_e}Q_i\mathcal{J}_{ij}\right]\sum_{w=1}^{m}\sum_{l=1}^{m}C_wC_l\exp\left[\mathcal{K}_{lw}\right]\,dx_1\,dx_2\cdots\,dx_n
$$

Next, it is convenient to split this into two integrals,

$$
\begin{aligned}
\langle V \rangle &= \frac{q_e B^2}{4\pi\epsilon_0}(\mathcal{I}_1 + \mathcal{I}_2) \\
\mathcal{I}_1 &= q_e \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \mathcal{D}_{ij} \left(\sum_{w=1}^{m} \sum_{l=1}^{m} C_w C_l \exp\left[\mathcal{K}_{lw}\right] \right) dx_1\, dx_2 \cdots dx_n \\
\mathcal{I}_2 &= - \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{i=1}^{N_u} \sum_{j=1}^{N_e} Q_i \mathcal{J}_{ij} \left(\sum_{w=1}^{m} \sum_{l=1}^{m} C_w C_l \exp\left[\mathcal{K}_{lw}\right] \right) dx_1\, dx_2 \cdots dx_n
\end{aligned}
$$

Neither or these integrals can be computed analytically, except for the most trivial values of the shape matrix and shift matrix. In order to to determine their value, numerical methods must be applied. Before developing an approximation for these expressions, they must be simplified further. Before performing any simplifications, I will make the following observation, which will be helpful.

$$
\begin{aligned}
\exp\left[\mathcal{K}_{lw}\right] &= \exp\left[\sum_{k=1}^{n} \left\{ -x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) + x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right\} \right] \\
\exp\left[\mathcal{K}_{lw}\right] &= \prod_{k=1}^{n} \exp\left[-x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) \right] \exp\left[x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right] \qquad (5)
\end{aligned}
$$

3.2.3 The Electron - Electron Integral

I will refer to $\mathcal{I}_1$ as the electron - electron integral, because it is used to calculate the potential energy due to electron - electron interactions.

$$
\mathcal{I}_1 = q_e \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \sum_{w=1}^{m} \sum_{l=1}^{m} \mathcal{D}_{ij} C_w C_l \exp\left[\mathcal{K}_{lw}\right] dx_1\, dx_2 \cdots dx_n
$$

Applying eq. 5,

$$
\mathcal{I}_1 = q_e \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \sum_{w=1}^{m} \sum_{l=1}^{m} \mathcal{D}_{ij} C_w C_l \prod_{k=1}^{n} \exp\left[-x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) \right] \exp\left[x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right] dx_1\, dx_2 \cdots dx_n
$$

Moving the integrals inside of the sums,

$$
\mathcal{I}_1 = q_e \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \sum_{w=1}^{m} \sum_{l=1}^{m} C_w C_l \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathcal{D}_{ij} \prod_{k=1}^{n} \exp\left[-x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) \right] \exp\left[x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right] dx_1\, dx_2 \cdots dx_n
$$

Next, we apply the fact that an integral of a product of independent factors is equivalent to a product of integrals of independent factors. First, I will extract the integral term from the expression above in order to keep the expression on a single line.

$$
\hat{\mathcal{I}}_1 \equiv \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathcal{D}_{ij} \prod_{k=1}^{n} \exp\left[-x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) \right] \exp\left[x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right] dx_1\, dx_2 \cdots dx_n
$$

It is important to note that in the above expression, the integrals can be separated into a number of integrals that do not depend on $\mathcal{D}_{ij}$ and six integrals that do.

$$
\begin{aligned}
\hat{\mathcal{I}}_1 &= \left(\prod_{k \notin \mathbb{X}} \int_{-\infty}^{\infty} \mathcal{W}_{kwl}\, dx_k \right) \left(\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathcal{D}_{ij} \prod_{k \in \mathbb{X}} \mathcal{W}_{kwl}\, d\mathbb{X}_1 \cdots d\mathbb{X}_n \right) \\
\mathcal{W}_{kwl} &\equiv \exp\left[-x_k^2 \left(A_{kk}^{(w)} + A_{kk}^{(l)} \right) \right] \exp\left[x_k \left(s_k^{(w)} + s_k^{(l)} \right) \right]
\end{aligned}
$$

In the expressions above, the set $\mathbb{X}$ is the set of six input coordinates $\{x_1,\, x_2,\, \cdots,\, x_n\}$ that are the same as the input coordinates in $\mathcal{D}_{ij}$. All of the integrals in the left term of $\hat{\mathcal{I}}_1$ can be calculated analytically. The integral in the right term cannot be calculated analytically. The integral in the left term,

$$
\begin{aligned}
\int_{-\infty}^{\infty} \mathcal{W}_{kwl}\, dx_k &= \int_{-\infty}^{\infty} \exp\left[-x_k^2\left(A_{kk}^{(w)} + A_{kk}^{(l)}\right)\right] \exp\left[x_k\left(s_k^{(w)} + s_k^{(l)}\right)\right] dx_k \\
&= \sqrt{\frac{\pi}{Y_{wkl}}} \exp\left[\frac{V_{wkl}^2}{4Y_{wkl}}\right] \\
Y_{wkl} &\equiv A_{kk}^{(w)} + A_{kk}^{(l)} \\
V_{wkl} &\equiv s_k^{(w)} + s_k^{(l)}
\end{aligned}
$$

The integral $\hat{\mathcal{I}}_1$ now reads,

$$
\hat{\mathcal{I}}_1 = \left(\prod_{k \notin \mathbb{X}} \sqrt{\frac{\pi}{Y_{wkl}}} \exp\left[\frac{V_{wkl}^2}{4Y_{wkl}}\right]\right) \left(\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathcal{D}_{ij} \prod_{k \in \mathbb{X}} \mathcal{W}_{kwl}\, d\mathbb{X}_1 \cdots d\mathbb{X}_n\right)
$$

What remains is to simplify the integral on the right and put it in a form that is reasonable to integrate numerically. The full integral can be written,

$$
\begin{aligned}
\hat{\mathcal{I}}_1^{(1)} &\equiv \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\prod_{k \in \mathbb{X}} \exp\left[-x_k^2\left(A_{kk}^{(w)} + A_{kk}^{(l)}\right)\right] \exp\left[x_k\left(s_k^{(w)} + s_k^{(l)}\right)\right]}{\sqrt{\left(x_{3i} - x_{3j}\right)^2 + \left(x_{3i+1} - x_{3j+1}\right)^2 + \left(x_{3i+2} - x_{3j+2}\right)^2}} dx_{3i}\, dx_{3j}\, dx_{3i+1}\, dx_{3j+1}\, dx_{3i+2}\, dx_{3j+2} \\
\mathbb{X} &= \{x_{3i},\, x_{3j},\, x_{3i+1},\, x_{3j+1},\, x_{3i+2},\, x_{3j+2}\}
\end{aligned}
$$

As states above, this cannot be computed analytically, but it can be re-written in a form that is readily computed numerically. First, we move the integral from six cartesian coordinates to six polar coordinates. In this case, we treat x_{3i}, x_{3i+1} and x_{3i+2} as the cartesian coordinates corresponding to the first set of polar coordinates and we treet the remaining coordinates as corresponding to the second set of polar coordinates. More explicitely,

$$
\begin{aligned}
x_{3i} &= r_1 \sin\theta_1 \cos\phi_1 \\
x_{3i+1} &= r_1 \sin\theta_1 \sin\phi_1 \\
x_{3i+2} &= r_1 \cos\theta_1 \\
x_{3j} &= r_2 \sin\theta_2 \cos\phi_2 \\
x_{3j+1} &= r_2 \sin\theta_2 \sin\phi_2 \\
x_{3j+2} &= r_2 \cos\theta_2
\end{aligned}
$$

The term $|\mathbf{r}_i - \mathbf{r}_j|$ in spherical coordinates can be rewritten

$$
|\mathbf{r}_i - \mathbf{r}_j| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\left(\theta_1 - \theta_2\right)}
$$

The integral $\hat{\mathcal{I}}_1^{(1)}$ can now be written

$$
\hat{\mathcal{I}}_1^{(1)} = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{\infty} \frac{\prod_{k \in \mathbb{X}} \exp\left[-x_k^2\left(A_{kk}^{(w)} + A_{kk}^{(l)}\right)\right] \exp\left[x_k\left(s_k^{(w)} + s_k^{(l)}\right)\right]}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\left(\theta_1 - \theta_2\right)}} r_1^2 r_2^2 \sin\theta_1 \sin\theta_2\, dr_1\, dr_2\, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2
$$

The numerator term must still be re-written in order to complete the explicit definition of the integral.

$$\prod_{k\in\mathbb{X}} \exp\left[-x_k^2\left(A_{kk}^{(w)}+A_{kk}^{(l)}\right)\right]\exp\left[x_k\left(s_k^{(w)}+s_k^{(l)}\right)\right]\equiv \mathcal{P}_1\mathcal{P}_2$$

$$\begin{aligned}
\mathcal{P}_1 &\equiv \exp\left[-x_{3i}^2 Y_{w(3i)l} + x_{3i}V_{w(3i)l} - x_{3i+1}^2 Y_{w(3i+1)l} + x_{3i+1}V_{w(3i+1)l} - x_{3i+2}^2 Y_{w(3i+2)l} + x_{3i+2}V_{w(3i+2)l}\right] \\
&= \exp\left[r_1\left\{\sin\theta_1\left[-r_1\sin\theta_1\cos^2\phi_1 Y_{wUl} + \cos\phi_1 V_{wUl} - r_1\sin\theta_1\sin^2\phi_1 Y_{wVl} + \sin\phi_1 V_{wVl}\right] - \cos\theta_1\left[r_1\cos\theta_1 Y_{wQl} + V_{wQl}\right]\right\}\right] \\
U &\equiv 3i \\
V &\equiv 3i+1 \\
Q &\equiv 3i+2 \\
\mathcal{P}_2 &\equiv \exp\left[-x_{3j}^2 Y_{w(3j)l} + x_{3j}V_{w(3j)l} - x_{3j+1}^2 Y_{w(3j+1)l} + x_{3j+1}V_{w(3j+1)l} - x_{3j+2}^2 Y_{w(3j+2)l} + x_{3j+2}V_{w(3j+2)l}\right] \\
&= \exp\left[r_2\left\{\sin\theta_2\left[-r_2\sin\theta_2\cos^2\phi_2 Y_{w\mathcal{U}l} + \cos\phi_2 V_{w\mathcal{U}l} - r_2\sin\theta_2\sin^2\phi_2 Y_{w\mathcal{V}l} + \sin\phi_2 V_{w\mathcal{V}l}\right] - \cos\theta_2\left[r_2\cos\theta_2 Y_{w\mathcal{Q}l} + V_{w\mathcal{Q}l}\right]\right\}\right] \\
\mathcal{U} &\equiv 3j \\
\mathcal{V} &\equiv 3j+1 \\
\mathcal{Q} &\equiv 3j+2
\end{aligned}$$

The substitutions made for the indices above are meant to keep each expression on a single line. We can now write $\hat{\mathcal{I}}_1^{(1)}$

$$\hat{\mathcal{I}}_1^{(1)} = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{\infty}\frac{\mathcal{P}_1\mathcal{P}_2 r_1^2 r_2^2\sin\theta_1\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\left(\theta_1-\theta_2\right)}}dr_1\,dr_2\,d\theta_1\,d\theta_2\,d\phi_1\,d\phi_2$$

In order to make this integral more manageable numerically, it is helpful to define a subsitution that brings the range of the integrals down to a finite number. For this purpose, I will make the following subsitutions,

$$\begin{aligned}
u_1 &= \frac{1}{1+r_1} \\
u_2 &= \frac{1}{1+r_2}
\end{aligned}$$

These substitutions will bring the range of the integral from $[0, \infty)$ to $[1, 0]$, making them much more maneageable for a numerical integration method. They will however, introduce poles to the resulting integrand, which will need to be managed carefully.

$$\begin{aligned}
du_1 &= -\frac{1}{\left(1+r_1\right)^2}dr_1 \\
dr_1 &= -\left(1+r_1\right)^2\,du_1 \\
r_1 &= \frac{1}{u_1}-1 \\
dr_1 &= -\frac{1}{u_1^2}du_1 \\
du_2 &= -\frac{1}{\left(1+r_2\right)^2}dr_2 \\
dr_2 &= -\left(1+r_2\right)^2\,du_2 \\
r_2 &= \frac{1}{u_2}-1 \\
dr_2 &= -\frac{1}{u_2^2}du_2
\end{aligned}$$

Subsituting these into the integral and omitting an explicit redefinition of $\mathcal{P}_1$ and $\mathcal{P}_2$ (because they are trivial),

$$\hat{\mathcal{I}}_1^{(1)} = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_1^{0}\int_1^{0} \frac{\mathcal{P}_1\mathcal{P}_2\left(\frac{1}{u_1}-1\right)^2\left(\frac{1}{u_2}-1\right)^2\sin\theta_1\sin\theta_2}{\sqrt{\left(\frac{1}{u_1}-1\right)^2+\left(\frac{1}{u_2}-1\right)^2-2\left(\frac{1}{u_1}-1\right)\left(\frac{1}{u_2}-1\right)\cos\left(\theta_1-\theta_2\right)}}\frac{1}{u_1^2u_2^2}\,du_1\,du_2\,d\theta_1\,d\theta_2\,d\phi_1\,d\phi_2$$

This expression is now significantly easier to integrate numerically. It does have a few poles, which must be treated carefully. The poles are at the following points,

$$\begin{aligned} u_1 &= 0 \\ u_2 &= 0 \\ u_1 = u_2 &= 1 \end{aligned}$$

In order to mitigate the effects of these poles, it is necessary to adopt an integration technique that increases the resolution of its step with proportion to the change in the integrand. More specifically,

$$\begin{aligned} \Delta u_1 &\propto \frac{\partial}{\partial u_1}\,\mathsf{Integrand} \\ \Delta u_2 &\propto \frac{\partial}{\partial u_2}\,\mathsf{Integrand} \end{aligned}$$

The exact method applied for this integration will be discussed in detail later. The full expression for the electron - electron integral can now be written,

$$\begin{aligned}
\mathcal{I}_1 &= q_e\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\sum_{w=1}^{m}\sum_{l=1}^{m}C_wC_l\left(\prod_{k\notin\mathbb{X}}\sqrt{\frac{\pi}{Y_{wkl}}}\exp\left[\frac{V_{wkl}^2}{4Y_{wkl}}\right]\right)\hat{\mathcal{I}}_1^{(1)} \\
\hat{\mathcal{I}}_1^{(1)} &\equiv \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{1}\int_0^{1} \frac{\mathcal{P}_1\mathcal{P}_2\left(\frac{1}{u_1}-1\right)^2\left(\frac{1}{u_2}-1\right)^2\sin\theta_1\sin\theta_2}{\sqrt{\left(\frac{1}{u_1}-1\right)^2+\left(\frac{1}{u_2}-1\right)^2-2\left(\frac{1}{u_1}-1\right)\left(\frac{1}{u_2}-1\right)\cos\left(\theta_1-\theta_2\right)}}\frac{1}{u_1^2u_2^2}\,du_1\,du_2\,d\theta_1\,d\theta_2\,d\phi_1\,d\phi_2 \\
\mathcal{P}_1 &\equiv \exp\left[r_1\left\{\sin\theta_1\left[-r_1\sin\theta_1\cos^2\phi_1Y_{wUl}+\cos\phi_1V_{wUl}-r_1\sin\theta_1\sin^2\phi_1Y_{wVl}+\sin\phi_1V_{wVl}\right]-\cos\theta_1\left[r_1\cos\theta_1Y_{wQl}+V_{wQl}\right]\right\}\right] \\
\mathcal{P}_2 &\equiv \exp\left[r_2\left\{\sin\theta_2\left[-r_2\sin\theta_2\cos^2\phi_2Y_{w\mathcal{U}l}+\cos\phi_2V_{w\mathcal{U}l}-r_2\sin\theta_2\sin^2\phi_2Y_{w\mathcal{V}l}+\sin\phi_2V_{w\mathcal{V}l}\right]-\cos\theta_2\left[r_2\cos\theta_2Y_{w\mathcal{Q}l}+V_{w\mathcal{Q}l}\right]\right\}\right] \\
r_1 &\equiv \frac{1}{u_1}-1 \\
r_2 &\equiv \frac{1}{u_2}-1 \\
U &\equiv 3i \\
V &\equiv 3i+1 \\
Q &\equiv 3i+2 \\
\mathcal{U} &\equiv 3j \\
\mathcal{V} &\equiv 3j+1 \\
\mathcal{Q} &\equiv 3j+2
\end{aligned}$$

It's worth noting that I flipped the range on two of the integrals, but this is allowed because both of the negative signs will cancel eachother.

3.2.4 The Electron - Nucleus Integral

I will refer to $\mathcal{I}_2$ as the electron - nucleus integral, because it is used to calculate the potential energy due to electron - nucleus interactions. I will omit many steps in this derivation, because it is a more simple case of the electron - electron integral.