# 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 $\nabla_n^2$ denotes the cartesian Laplacian of the wavefunction with respect to the $n$th 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 $n$th electron w.r.t the origin, $\mathbf{R}_n$ denotes the position of the $n$th nucleus w.r.t the origin and $Q_n$ denotes the charge of the $n$th 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 $n$th 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 $j$th term in the trial function and $\mathbf{s}^{(j)T}$ is the transpose of the shift vector of the $j$th 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

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

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

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

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

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

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

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

$$= \sum_{l=1}^{n} x_l A_{il}^{(j)}$$

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

$$= \sum_{k=1}^{n} x_k\left(\sum_{l=1}^{n} A_{kl}^{(j)}\delta_{li}\right)$$

$$= \sum_{k=1}^{n} x_k A_{ki}^{(j)}$$

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

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

## 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, $\psi^* = \psi$

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

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 $\hat{\mathcal{G}}(\mathbf{x})$ 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

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

Next, we simplify the two product terms

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

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

Inserting this into the original expression.

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

Expanding the last term in the above expression.

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

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

$$\int \cdots \int \int \prod_{i=1}^{n} f_i(x_i)\, dx_1 dx_2 \cdots dx_N = \prod_{i=1}^{n} \int f_i(x_i)\, dx_i \tag{4}$$

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.

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

We now write the expectation value of the kinetic energy

$$
\begin{aligned}
\langle T\rangle &= \frac{-B^2\hbar^2}{2m_e}\int\cdots\int\int\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\, g\left(x_i\right)\prod_{l=1}^{n} f\left(x_l\right)\right\} dx_1 dx_2\cdots dx_n \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\int\cdots\int\int g\left(x_i\right)\prod_{l=1}^{n} f\left(x_l\right)\, dx_1 dx_2\cdots dx_n\right\} \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\int\cdots\int\int g\left(x_i\right) f\left(x_i\right)\prod_{l\neq i}^{n} f\left(x_l\right)\, dx_1 dx_2\cdots dx_n\right\} \\
&= \frac{-B^2\hbar^2}{2m_e}\left\{\sum_{j'=1}^{m}\sum_{j=1}^{m}\sum_{i=1}^{n} C_{j'}C_j\int g\left(x_i\right) f\left(x_i\right)\, dx_i\prod_{l\neq i}^{n}\int f\left(x_l\right)\, dx_l\right\}
\end{aligned}
$$

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

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

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

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

# 4 Appendix A: Generalized Integration By Parts

$$
\begin{aligned}
\frac{d}{dx} \prod_{i=1}^{n} f_i(x) &= f_1(x) \frac{d}{dx} \prod_{i=2}^{n} f_i(x) + \left(\prod_{i=2}^{n} f_i(x)\right) \frac{d}{dx} f_1(x) \\
&= \left(\prod_{i=2}^{n} f_i(x)\right) \frac{d}{dx} f_1(x) + f_1(x) \left[\left(\prod_{i=3}^{n} f_i(x)\right) \frac{d}{dx} f_2(x) + f_2(x) \frac{d}{dx} \prod_{i=3}^{n} f_i(x)\right] \\
&= \left(\prod_{i=2}^{n} f_i(x)\right) \frac{d}{dx} f_1(x) + f_1(x) \left(\prod_{i=3}^{n} f_i(x)\right) \frac{d}{dx} f_2(x) + f_1(x) f_2(x) \frac{d}{dx} \prod_{i=3}^{n} f_i(x)
\end{aligned}
$$

From this, we can define the derivative of the generalized product to be a sum of terms

$$
\frac{d}{dx} \prod_{i=1}^{n} f_i(x) = \sum_{i=1}^{n} F_{i-1}(x) \left(\prod_{i'=i+1}^{n} f_{i'}(x)\right) \frac{d}{dx} f_i(x)
$$

Where

$$\begin{aligned}
&F_n(x) \equiv f_n(x) f_{n-1}(x) \cdots f_1(x) \\
&F_0(x) \equiv 1
\end{aligned}$$

This can be simplified as follows

$$\frac{d}{dx}\prod_{i=1}^{n} f_i(x) = \sum_{i=1}^{n}\left(\prod_{i' \neq i}^{n} f_{i'}(x)\right)\frac{d}{dx} f_i(x)$$

Recall the derivation of integration by parts

$$\begin{aligned}
\frac{d}{dx} f(x) g(x) &= g(x) \frac{d}{dx} f(x) + f(x) \frac{d}{dx} g(x) \\
\int \frac{d}{dx} f(x) g(x) &= \int g(x) \frac{d}{dx} f(x) + \int f(x) \frac{d}{dx} g(x) \\
f(x) g(x) &= \int g(x) \frac{d}{dx} f(x) + \int f(x) \frac{d}{dx} g(x) \\
\int g(x) \frac{d}{dx} f(x) &= f(x) g(x) - \int f(x) \frac{d}{dx} g(x)
\end{aligned}$$

Or, in the more common notation

$$\int g f' = f g - \int f g'$$

Next, using the same argument, we derive a generalization for any number of products in the intgrand.

$$\begin{aligned}
\int \frac{d}{dx}\prod_{i=1}^{n} f_i(x) &= \int \sum_{i=1}^{n}\left(\prod_{i' \neq i}^{n} f_{i'}(x)\right)\frac{d}{dx} f_i(x) \\
\prod_{i=1}^{n} f_i(x) &= \sum_{i=1}^{n}\int\left(\prod_{i' \neq i}^{n} f_{i'}(x)\right)\frac{d}{dx} f_i(x)
\end{aligned}$$

From the expression on the right of the equal sign, we can extract any chosen element of the sum and move it to the left hand side.

$$\int\left(\prod_{i' \neq \gamma}^{n} f_{i'}(x)\right)\frac{d}{dx} f_\gamma(x) = \prod_{i=1}^{n} f_i(x) - \sum_{i \neq \gamma}^{n}\int\left(\prod_{i' \neq i}^{n} f_{i'}(x)\right)\frac{d}{dx} f_i(x) \tag{5}$$

This provides us with a means of reasoning about the products in the integrand of the kinetic energy function.