

Local Energy Calculation of the Slater-Jastrow wave function

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1 Slater-Jastrow wave function

This short paper summarizes the local energy calculation problem of the calculation of the Slater-Jastrow wave function. This wave function has number of desirable properties for many-body quantum Monte-Carlo calculations of electrons in the presence of ions.

The Slater-Jastrow wave function is a product of Slater determinants and the Jastrow correlation factor:

$$\Psi_T(\{\mathbf{r}_i\}) = \det(A^{\text{up}}) \det(A^{\text{down}}) \exp\left(\sum_{i<j} U_{ij}\right) \quad (1)$$

Here, the A^{up} and A^{down} are defined as the Slater matrices of the single particle *up* and *down* orbitals, respectively. That is

$$A = \begin{bmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \phi_1(\mathbf{r}_3) & \phi_1(\mathbf{r}_4) & \cdots \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \phi_2(\mathbf{r}_3) & \phi_2(\mathbf{r}_4) & \cdots \\ \phi_3(\mathbf{r}_1) & \phi_3(\mathbf{r}_2) & \phi_3(\mathbf{r}_3) & \phi_3(\mathbf{r}_4) & \cdots \\ \phi_4(\mathbf{r}_1) & \phi_4(\mathbf{r}_2) & \phi_4(\mathbf{r}_3) & \phi_4(\mathbf{r}_4) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (2)$$

Where ϕ_k are molecular orbitals centered at \mathbf{c}_k :

$$\phi_k(\mathbf{r}) = \exp\left(\frac{-(\mathbf{r} - \mathbf{c}_k)^2}{\omega_k^2 + \nu_k |\mathbf{r} - \mathbf{c}_k|}\right) \quad (3)$$

The Jastrow correlation factor U_{ij} terms are defined in the following manner:

$$U_{ij} = \frac{a_{ij} r_{ij}}{1 + b_{ij} r_{ij}}, \quad (4)$$

where $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ and

$$a_{ij} = \begin{cases} e^2/8D & \text{if } ij \text{ are like spins} \\ e^2/4D & \text{if } ij \text{ are unlike spins} \\ e^2/2D & \text{if } ij \text{ are electron-nuclear pairs} \end{cases} \quad (5)$$

This trial wave function (1) has a number of desirable properties:

1. The correct cusp conditions for both like and unlike electron spins.
2. The correct cusp behavior as the electron-nuclear separation becomes small.
3. The variational parameters in (1) have a simple physical interpretation at large separations.
 - (a) β can be related to the polarizability of a molecule
 - (b) ν^* the maximum value of ν is equal to $1/\sqrt{2I}$ where I is the first ionization potential.

2 Local Energy

We wish to compute the local energy of the wave function, defined by

$$E_{\text{local}} \equiv \frac{\hat{H}\Psi_T}{\Psi_T}, \quad (6)$$

where

$$\hat{H} \equiv \frac{\hbar^2}{2m}\nabla^2 + V \quad (7)$$

The calculation of the potential energy V is straightforward. Therefore, we will focus here the application of the Laplacian operator to the Jastrow wave function. Given the form of the trial wave function, it will prove convenient to define

$$\begin{aligned} \mathcal{L}_T &= \ln(\Psi_T) \\ &= \ln(\det(A^{\text{up}})) + \ln(\det(A_{\text{down}})) + \sum_{i<j} U_{ij} \end{aligned} \quad (8)$$

We now attempt to calculate the action of ∇^2 on Ψ_T in terms of \mathcal{L}_T .

$$\begin{aligned} \nabla^2\Psi_T(\mathbf{R}) &= \nabla^2\exp(\mathcal{L}_T(\mathbf{R})) \\ &= \nabla \cdot \nabla(\exp(\mathcal{L}_T(\mathbf{R}))) \\ &= \nabla \cdot [\exp(\mathcal{L}_T(\mathbf{R}))\nabla\mathcal{L}_T(\mathbf{R})] \\ &= \nabla^2\mathcal{L}_T(\mathbf{R})\exp(\mathcal{L}_T(\mathbf{R})) + (\nabla\mathcal{L}_T(\mathbf{R}))\nabla\exp(\mathcal{L}_T(\mathbf{R})) \\ &= [\nabla^2\mathcal{L}_T(\mathbf{R}) + (\nabla\mathcal{L}_T(\mathbf{R}))^2]\psi_T(\mathbf{R}) \end{aligned} \quad (9)$$

This leaves a particularly simple form for the local energy.

$$E_{\text{local}}(\mathbf{R}) = \frac{-\hbar^2}{2m} [\nabla^2\mathcal{L}_T(\mathbf{R}) + (\nabla\mathcal{L}_T(\mathbf{R}))^2] + V(\mathbf{R}) \quad (10)$$

Now, we are left with the task of computing $\nabla\mathcal{L}_T$ and $\nabla^2\mathcal{L}_T$.

The gradient and Laplacian are linear operators, using (8), we can find action of these operators on each of the terms in the sum.

3 Jastro correlation factor

In this section we explicitly compute the gradient and Laplacian of the the correlation factor. We begin by calculating the gradient terms. Note that \mathbf{R} is a $3N$ dimensional vector, so that the gradient with respect to \mathbf{R} will have $3N$ components. For clarity, the $3N$ dimensional vector will be represented by N 3-dimensional vectors, $\{\mathbf{r}_i\}$. The i^{th} component of the gradient is simply

$$\nabla_i = \frac{\partial}{\partial x_i} \hat{x}_i + \frac{\partial}{\partial y_i} \hat{y}_i + \frac{\partial}{\partial z_i} \hat{z}_i \quad (11)$$

We will explicitly calculate the x_i component and symmetry considerations will give us the remainder. We begin by expanding the notation in our expression for U_{ij} .

$$U_{ij}(\mathbf{R}) = \sum_{i < j} \frac{a_{ij} [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}}{1 + b_{ij} [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}} \quad (12)$$

Since the summation is given for $i < j$, to calculate the i^{th} component, we will need to sum over the remaining j 's.

$$\begin{aligned} (\nabla_i)_x \sum_{i < j} U_{ij} &= \sum_{i < j} \partial_{x_i} \left[\frac{a_{ij} [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}}{1 + b_{ij} [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}} \right] \\ &= \sum_{i < j} \left[\frac{a_{ij} r_{ij}^{-1} (x_i - x_j)}{1 + b_{ij} r_{ij}} - \frac{a_{ij} b_{ij} (x_i - x_j)}{(1 + b_{ij} r_{ij})^2} \right] \\ &= \sum_{i < j} \left[\frac{a_{ij}}{1 + b_{ij} r_{ij}} \left(r_{ij}^{-1} - \frac{b_{ij}}{1 + b_{ij} r_{ij}} \right) (x_i - x_j) \right] \\ &= \sum_{i < j} \left[\frac{a_{ij}}{1 + b_{ij} r_{ij}} \left(\frac{r_{ij}^{-1} + b_{ij} - b_{ij}}{1 + b_{ij} r_{ij}} \right) (x_i - x_j) \right] \\ &= \sum_{i < j} \left[\frac{a_{ij}}{r_{ij} (1 + b_{ij} r_{ij})^2} (x_i - x_j) \right] \end{aligned} \quad (13)$$

With the form for the x component, we can generalize the calculation to the i^{th} component of the gradient.

$$\nabla_i \sum_{i < j} U_{ij} = \sum_{i < j} \frac{a_{ij}}{r_{ij} (1 + b_{ij} r_{ij})^2} (\mathbf{r}_i - \mathbf{r}_j) \quad (14)$$

For each gradient term $\nabla_{\mathbf{r}_i}$ we need to sum over all $j \neq i$.

Now we move on to the Laplacian. We begin by expanding out (13).

$$(\nabla_i)_x \sum_{i < j} U_{ij} = \sum_{i < j} \frac{a_{ij} (x_i - x_j)}{[(x_i - x_j)^2 + y_{ij}^2 + z_{ij}^2]^{\frac{1}{2}} \left\{ 1 + b_{ij} [(x_i - x_j)^2 + y_{ij}^2 + z_{ij}^2]^{\frac{1}{2}} \right\}^2} \quad (15)$$

This calculation is quite involved, so we begin by taking the derivative of the denominator.

$$\begin{aligned}\partial_{x_i} \text{denom} &= r_{ij}^{-1}(1 + b_{ij}r_{ij})^2(x_i - x_j) + 2b_{ij}(1 + b_{ij}r_{ij})(x_i - x_j) \\ &= (1 + b_{ij})(r_{ij}^{-1} + 3b_{ij})(x_i - x_j)\end{aligned}\quad (16)$$

With this derivative, we can compute the full second derivative.

$$\begin{aligned}\partial_{x_i}^2 U_{ij} &= \frac{a_{ij}}{r_{ij}(1 + b_{ij}r_{ij})^2} - \frac{(1 + b_{ij}r_{ij})(r_{ij}^{-1} + 3b_{ij})(x_i - x_j)^2 a_{ij}}{r_{ij}^2(1 + b_{ij}r_{ij})^4} \\ &= \frac{a_{ij}}{r_{ij}(1 + b_{ij}r_{ij})^2} \left[1 - \frac{(r_{ij}^{-1} + 3b_{ij})(x_i - x_j)^2}{r_{ij}(1 + b_{ij}r_{ij})} \right]\end{aligned}\quad (17)$$

Now, we may sum over components to generate the Laplacian with respect to \mathbf{r}_i . This summation changes the 1 in brackets to a 3 and the $(x_i - x_j)^2$ to r_{ij}^2 .

$$\begin{aligned}\nabla_i^2 U_{ij} &= \frac{a_{ij}}{r_{ij}(1 + b_{ij}r_{ij})^2} \left[3 - \frac{(r_{ij}^{-1} + 3b_{ij})r_{ij}^2}{r_{ij}(1 + b_{ij}r_{ij})} \right] \\ &= \frac{a_{ij}}{r_{ij}(1 + b_{ij}r_{ij})^2} \left[\frac{3 + 3b_{ij}r_{ij} - 1 - 3b_{ij}r_{ij}}{1 + b_{ij}r_{ij}} \right] \\ &= \frac{2a_{ij}}{r_{ij}(1 + b_{ij}r_{ij})^3}\end{aligned}\quad (18)$$

We remember that we must sum over all $i \neq j$ to calculate the full Laplacian.

4 Slater determinants

In this section, we explicitly compute the gradient and Laplacian of the determinant of the trial wave function. In particular, we seek

$$\nabla[\ln \det(A)], \quad (19)$$

where A is either the *up* or *down* matrix. To simplify the analysis, we will initially work again in terms of components. Let ∂_i represent the derivative with respect to a single component of the $3N$ dimensional \mathbf{R} . Trivially, then,

$$\partial_i \ln[\det(A)] = \frac{1}{\det A} \partial_i \det(A) \quad (20)$$

At first glance, taking the derivative of a determinant appears a daunting task. Considerable simplification is possible with the following simple relation, which we state without proof:

$$\partial_i \det(A) = \det(A) \text{Tr}[A^{-1} \partial_i A] \quad (21)$$

Then

$$\partial_i \ln[\det(A)] = \text{Tr}[A^{-1} \partial_i A] \quad (22)$$

Given this form, we are left with the calculation of the the elements of $\partial_i A$. The elements of A are just

$$A_{kl} = \phi_k(\mathbf{r}_l) \quad (23)$$

It is quite easy to see that the elements of the derivative matrix will be zero unless $i \in x_l, y_l, z_l$. Then the derivative matrix will have a single non-zero column. By taking advantage of symmetry, we can calculate the x , y , and z components simultaneously by directly calculating $\nabla_l \phi_k(\mathbf{r}_l)$. If we make the substitution,

$$\tilde{\mathbf{r}} \equiv \mathbf{r}_l - \mathbf{c}_k \quad (24)$$

then $\phi_k(\tilde{\mathbf{r}})$ will be radially symmetric in $\tilde{\mathbf{r}}$. Since these vector operators are translationally invariant,

$$\nabla_{\tilde{\mathbf{r}}} = \nabla_{r_l}. \quad (25)$$

If we work in spherical coordinates, $\phi_k(\tilde{r}, \tilde{\theta}, \tilde{\phi})$ will be independent of $\tilde{\theta}$ and $\tilde{\phi}$. We can then express the gradient as

$$\nabla_{\tilde{\mathbf{r}}} \phi_k(\tilde{\mathbf{r}}) = \partial_{\tilde{r}} \phi_k(\tilde{r}) \hat{\mathbf{r}}, \quad (26)$$

where $\hat{\mathbf{r}}$ represent the unit vector in the direction of $\tilde{\mathbf{r}}$. Written in terms of $\tilde{\mathbf{r}}$, the orbitals take the form,

$$\phi_k(\tilde{\mathbf{r}}) = \exp\left(\frac{-\tilde{r}^2}{\omega_k^2 + \nu_k \tilde{r}}\right) \quad (27)$$

The derivative takes the form

$$\begin{aligned} \partial_{\tilde{r}} \phi_k(\tilde{r}) &= \phi_k(\tilde{r}) \partial_{\tilde{r}} \left[\frac{-\tilde{r}^2}{\omega_k^2 + \nu_k \tilde{r}} \right] \\ &= \phi_k(\tilde{r}) \left[\frac{-2\tilde{r}}{\omega_k^2 + \nu_k \tilde{r}} + \frac{\nu_k \tilde{r}^2}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \\ &= \phi_k(\tilde{r}) \left[\frac{-2\tilde{r}(\omega_k^2 + \nu_k \tilde{r}) + \nu_k \tilde{r}^2}{(\omega_k^2 + \nu_k)^2} \right] \\ &= \phi_k(\tilde{r}) \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \end{aligned} \quad (28)$$

and furthermore,

$$\begin{aligned} \nabla_{\tilde{\mathbf{r}}} \phi_k(\tilde{\mathbf{r}}) &= \phi_k(\tilde{r}) \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \hat{\mathbf{r}} \\ &= \phi_k(\tilde{r}) \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \left(\frac{\mathbf{r} - \mathbf{c}}{\tilde{r}} \right) \\ &= \phi_k(\tilde{r}) \left[\frac{-(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] (\mathbf{r} - \mathbf{c}). \end{aligned} \quad (29)$$

The total Laplacian will be a sum of the Laplacian's with respect to each electronic coordinate, \mathbf{r}_i . Let i represent a particular component of the $3N$ dimensional vector, \mathbf{R} , eg. the x component of \mathbf{r}_4 . Then we have that

$$\begin{aligned}\partial_i \ln[\det(A)] &= \text{Tr}[A^{-1}\partial_i A] \\ \partial_i^2 \ln[\det(A)] &= \partial_i \text{Tr}[A^{-1}\partial_i A] \\ &= \text{Tr}[A^{-1}\partial_i^2 A] + \text{Tr}[(\partial_i A^{-1})(\partial_i A)]\end{aligned}\quad (30)$$

where $\partial_i^2 A$ actually denotes the Laplacian of the components of the matrix A . For the latter term, we utilize the fundamental property of inverses,

$$\begin{aligned}A^{-1}A &= \mathbf{1} \\ (\partial_i A^{-1})A + A^{-1}\partial_i A &= 0 \\ \partial_i A^{-1} &= -A^{-1}(\partial_i A)A^{-1}\end{aligned}\quad (31)$$

Using this new relation

$$\begin{aligned}\partial_i^2 \ln[\det(A)] &= \text{Tr}[A^{-1}\partial_i^2 A] - \text{Tr}[A^{-1}(\partial_i A)A^{-1}(\partial_i A)] \\ &= \text{Tr}[A^{-1}\partial_i^2 A] - \text{Tr}[(A^{-1}(\partial_i A))^2]\end{aligned}\quad (32)$$

Now, to calculate the Laplacian with respect to \mathbf{r}_m , we sum over the three components, j , of the \mathbf{r}_m .

$$\nabla_{\mathbf{r}_m}^2 \ln[\det(A)] = \text{Tr}[A^{-1}\nabla_{\mathbf{r}_m}^2 A] - \sum_{j=\{x,y,z\}} \text{Tr}[(A^{-1}(\partial_{\mathbf{r}_m^j} A))^2],\quad (33)$$

where \mathbf{r}_m^j refers to the j^{th} component of \mathbf{r}_m .

We already have the first derivative of A , which we found in the gradient part of the calculation. Next we calculate the Laplacian of the components of A . Specifically, we seek $\nabla_{\mathbf{r}_m}^2 A_{kl}$, where $A_{kl} = \phi_k(\mathbf{r}_l)$. We have that

$$\nabla_{\mathbf{r}_m}^2 A_{kl} = \delta_{lm} \nabla_{\mathbf{r}_l}^2 \phi_k(\mathbf{r}_l)\quad (34)$$

What remains is the Laplacian of the molecular orbitals, ϕ_k , with respect to \mathbf{r}_l . If we make the definition, $\mathbf{r}_{kl} \equiv \mathbf{r}_l - \mathbf{c}_k$, we recognize that $\phi_k(\mathbf{r}_{kl})$ will be spherically symmetric. Differential operators are invariant under translations, so we simplify the calculation our calculation by exploiting this translational invariance

$$\begin{aligned}\nabla_{\mathbf{r}_m}^2 A_{kl} &= \frac{1}{r_{kl}^2} \partial_{r_{kl}} r_{kl}^2 \partial_{r_{kl}} \phi_k(r_{kl}) \\ &= \frac{2}{r_{kl}} \partial_{r_{kl}} \phi_k(r_{kl}) + \partial_{r_{kl}}^2 \phi_k(r_{kl})\end{aligned}\quad (35)$$

The first derivative of the molecular orbitals were computed earlier in this

paper, so we finally turn to computing the second derivative of the ϕ_k 's.

$$\begin{aligned}
\partial_{\tilde{r}}^2 \phi_k(\tilde{r}) &= \partial_{\tilde{r}} \phi_k(\tilde{r}) \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \\
&= \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \partial_{\tilde{r}} \phi_k(\tilde{r}) + \phi_k(\tilde{r}) \partial_{\tilde{r}} \left[\frac{-\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^2} \right] \\
&= \phi_k(\tilde{r}) \frac{[\tilde{r}(2\omega_k^2 + \nu_k \tilde{r})]^2}{(\omega_k^2 + \nu_k \tilde{r})^4} \\
&\quad - 2\phi_k(\tilde{r}) \left[\frac{(\omega_k^2 + \nu_k \tilde{r})^3 - \tilde{r}\nu_k(\omega_k^2 + \nu_k \tilde{r})(2\omega_k^2 + \nu_k \tilde{r})}{(\omega_k^2 + \nu_k \tilde{r})^4} \right] \quad (36)
\end{aligned}$$