FYS-4411: Computational Physics II
Project 1

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Abstract

1 Theorystuff

1.1 Efficient calculation of derivatives

Calculating the derivatives involved in the VMC calculation numerically is slow in that they entail several calls to the wavefunctions in addition to introducing an extra numerical error. Here we will show how we have found divided up the derivatives and found analytic expressions for all the parts.

The trialfunction can be factorized as

$$\Psi_T(\mathbf{x}) = \Psi_D \Psi_C = |D_\uparrow||D_\downarrow|\Psi_C \tag{1}$$

where $D_\uparrow$, $D_\downarrow$ and Ψ_C is the spin up and down part of the Slater determinant and the Jastrow factor respectively.

1.1.1 Gradient ratio

For quantum force we need to calculate the gradient ratio of the trialfunction which is given by

$$\frac{\nabla \Psi_T}{\Psi_T} = \frac{\nabla(\Psi_D \Psi_C)}{\Psi_D \Psi_C} = \frac{\nabla \Psi_D}{\Psi_D} + \frac{\nabla \Psi_C}{\Psi_C} \tag{2}$$

$$= \frac{\nabla |D_\uparrow|}{|D_\uparrow|} + \frac{\nabla |D_\downarrow|}{|D_\downarrow|} + \frac{\nabla \Psi_C}{\Psi_C} \tag{3}$$

1.1.2 Kinetic Energy

From the Hamiltonian the expectation value of kinetic energy for each electron is given by

$$K_i = -\frac{1}{2}\frac{\nabla_i^2 \Psi}{\Psi} \tag{4}$$

Using the factorization of of the trialfunction from (1) we can calculated the ratio needed for the kinetic energy.

$$\frac{1}{\Psi_T}\frac{\partial^2\Psi_T}{\partial x_k^2} = \frac{1}{\Psi_D\Psi_C}\frac{\partial^2(\Psi_D\Psi_C)}{\partial x_k^2} = \frac{1}{\Psi_D\Psi_C}\frac{\partial}{\partial x_k}\left(\frac{\partial\Psi_D}{\partial x_k}\Psi_C + \Psi_D\frac{\partial\Psi_C}{\partial x_k}\right) \tag{5}$$

$$= \frac{1}{\Psi_D\Psi_C}\left(\frac{\partial^2\Psi_D}{\partial x_k^2}\Psi_C + 2\frac{\partial\Psi_D}{\partial x_k}\frac{\partial\Psi_C}{\partial x_k} + \Psi_D\frac{\partial^2\Psi_C}{\partial x_k^2}\right) \tag{6}$$

$$= \frac{1}{\Psi_D}\frac{\partial^2\Psi_D}{\partial x_k^2} + 2\frac{1}{\Psi_D}\frac{\partial\Psi_D}{\partial x_k}\cdot\frac{1}{\Psi_C}\frac{\partial\Psi_C}{\partial x_k} + \frac{1}{\Psi_C}\frac{\partial^2\Psi_C}{\partial x_k^2} \tag{7}$$

Since the Slater determinant part of the trialfunction is seperable into a spin up and down part we can simplify it further.

$$\frac{1}{\Psi_D}\frac{\partial^2\Psi_D}{\partial x_k^2} = \frac{1}{|D_\uparrow||D_\downarrow|}\frac{\partial^2|D_\uparrow||D_\downarrow|}{\partial x_k^2} = \frac{1}{|D_\uparrow|}\frac{\partial^2|D_\uparrow|}{\partial x_k^2} + \frac{1}{|D_\downarrow|}\frac{\partial^2|D_\downarrow|}{\partial x_k^2} \tag{8}$$

$$\frac{1}{\Psi_D}\frac{\partial\Psi_D}{\partial x_k} = \frac{1}{|D_\uparrow||D_\downarrow|}\frac{\partial|D_\uparrow||D_\downarrow|}{\partial x_k} = \frac{1}{|D_\uparrow|}\frac{\partial|D_\uparrow|}{\partial x_k} + \frac{1}{|D_\downarrow|}\frac{\partial|D_\downarrow|}{\partial x_k} \tag{9}$$

Inserting equations (9) and (8) into (7) we get

$$\frac{\nabla^2\Psi_T}{\Psi_T} = \frac{\nabla^2|D_\uparrow|}{|D_\uparrow|} + \frac{\nabla^2|D_\downarrow|}{|D_\downarrow|} + 2\left(\frac{\nabla|D_\uparrow|}{|D_\uparrow|} + \frac{\nabla|D_\downarrow|}{|D_\downarrow|}\right)\cdot\frac{\nabla\Psi_C}{\Psi_C} + \frac{\nabla^2\Psi_C}{\Psi_C} \tag{10}$$

Now we have 4 different types of ratios we need to find an expression for $\frac{\nabla^2|D|}{|D|}$, $\frac{\nabla|D|}{|D|}$, $\frac{\nabla^2\Psi_C}{\Psi_C}$ and $\frac{\nabla\Psi_C}{\Psi_C}$ to calculate both the gradient and laplacian ratios of the wavefunction.

1.1.3 Determinant ratios

To tackle the determinant ratios we need to introduce some notation. Let an element in the determinant matrix, $|D|$, be described by

$$D_{ij} = \phi_j(\mathbf{r}_i) \tag{11}$$

where ϕ_j is the j'th single particle wavefunction and $\mathbf{r}_i$ is the position of the i'th particle.

The inverse of a matrix is given by transposing it and dividing by the determinant, so the determinant can be written as

$$|D| = \frac{\mathbf{D}^T}{\mathbf{D^{-1}}} = \sum_{j=1}^{N}\frac{C_{ji}}{D_{ij}^{-1}} = \sum_{j=1}^{N}D_{ij}C_{ji} \tag{12}$$

This gives the ratio of the new and old Slater determinants the following

$$R_{SD} = \frac{|\mathbf{D}^{new}|}{|\mathbf{D}^{old}|} = \frac{\sum_{j=0}^{N}D_{ij}^{new}C_{ji}^{new}}{\sum_{j=0}^{N}D_{ij}^{old}C_{ji}^{old}} \tag{13}$$

Since we are only moving one particle at a time and the cofactor term relies on the other rows it doesn't change, $C_{ij}^{new} = C_{ij}^{old}$ in one movement. Combining this with equation (12) we get

$$R_{SD} = \frac{\sum_{j=0}^{N} D_{ij}^{new} (D_{ji}^{old})^{-1} |D^{old}|}{\sum_{j=0}^{N} D_{ij}^{old} (D_{ji}^{old})^{-1} |D^{old}|} \tag{14}$$

Since $\mathbf{D}$ is invertible, $\mathbf{D}\mathbf{D}^{-1} = \mathbf{1}$, the ratio becomes

$$R_{SD} = \sum_{j=0}^{N} D_{ij}^{new} (D_{ji}^{old})^{-1} = \sum_{j=0}^{N} \phi_j(\mathbf{x}_i^{new}) D_{ji}^{-1}(\mathbf{x}^{old}) \tag{15}$$

1.1.4 Gradient determinant Ratio

1.1.5 Derivatives of single particle wavefunctions

Calculated in derivatives.py.

ψ_i	$\frac{\partial \psi_i}{\partial r_i}$	$\frac{\partial^2 \psi_i}{\partial r_i^2}$
$e^{-\alpha ri}$	$-\frac{\alpha}{r_i}\left(x_i + y_i + z_i\right) e^{-\alpha r_i}$	$\frac{\alpha}{r_i}\left(\alpha r_i - 2\right) e^{-\alpha r_i}$
$\left(-\frac{\alpha r_i}{2} + 1\right) e^{-\alpha r_i}$	$\frac{\alpha e^{-\alpha r_i}}{2r_i}\left(\alpha r_i - 3\right)\left(x_i + y_i + z_i\right)$	$-\frac{\alpha e^{-\alpha r_i}}{2r_i}\left(\alpha^2 r_i^2 - 6\alpha r_i + 6\right)$
$\alpha r_i e^{-\frac{\alpha r_i}{2}}$	$-\frac{\alpha e^{-\frac{\alpha r_i}{2}}}{2r_i}\left(\alpha r_i - 2\right)\left(x_i + y_i + z_i\right)$	$\frac{\alpha e^{-\frac{\alpha r_i}{2}}}{4r_i}\left(\alpha^2 r_i^2 - 8\alpha r_i + 8\right)$

1.1.6 Gradient ratio of Padé-Jastrow factor

When derivating the Padé-Jastrow factor all the factors not involving the particle we are derivating with respect to will be canceled by the corresponding terms in the denominator.

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{1}{g_{ik}}\frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N} \frac{1}{g_{ki}}\frac{\partial g_{ki}}{\partial x_k} \tag{16}$$

1.1.7 Correlation-to-correlation ratio

We have $N(N-1)/2$ relative distances r_{ij}. We can write these in a matrix storage format, where they form a strictly upper triangular matrix

$$\mathbf{r} \equiv \begin{pmatrix} 0 & r_{1,2} & r_{1,3} & \dots & r_{1,N} \\ \vdots & 0 & r_{2,3} & \dots & r_{2,N} \\ \vdots & \vdots & 0 & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & r_{N-1,N} \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}$$

This upper triangular matrix form also applies to $g = g(r_{ij})$.

The correlation-to-correlation ratio, or ratio between Jastrow factors is given by

$$R_C = \frac{\Psi_C^{new}}{\Psi_C^{cur}} = \prod_{i=1}^{k-1} \frac{g_{ik}^{new}}{g_{ik}^{cur}} \prod_{i=k+1}^{N} \frac{g_{ki}^{new}}{g_{ki}^{cur}}$$

or in the Padé-Jastrow form

$$R_C = \frac{\Psi_C^{\text{new}}}{\Psi_C^{\text{cur}}} = \frac{\exp U_{new}}{\exp U_{cur}} = \exp \Delta U$$

where

$$\Delta U = \sum_{i=1}^{k-1} \left(f_{ik}^{\mathrm{new}} - f_{ik}^{\mathrm{cur}} \right) + \sum_{i=k+1}^{N} \left(f_{ki}^{\mathrm{new}} - f_{ki}^{\mathrm{cur}} \right)$$

1.1.8 The $\nabla \Psi_C / \Psi_C$ ratio

We continue by finding a useful expression for the quantum force and kinetic energy, the ratio $\nabla \Psi_C / \Psi_C$. It has, for all dimensions, the form

$$\frac{\nabla_i \Psi_C}{\Psi_C} = \frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_i}$$

where i runs over all particles. Since the g-terms aren't differentiated they cancel with their corresponding terms in the denominator, so only $N-1$ terms survive the first derivative. We get

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{1}{g_{ik}} \frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N} \frac{1}{g_{ki}} \frac{\partial g_{ki}}{\partial x_k}$$

For the exponential form we get almost the same, by just replacing g_{ij} with $\exp(f_{ij})$ and we get

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N} \frac{\partial g_{ki}}{\partial x_k}$$

We now use the identity

$$\frac{\partial}{\partial x_i} g_{ij} = -\frac{\partial}{\partial x_j} g_{ij}$$

and get expressions where the derivatives that act on the particle are represented by the second index of g

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{1}{g_{ik}} \frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N} \frac{1}{g_{ki}} \frac{\partial g_{ki}}{\partial x_i}$$

and for the exponential case

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N} \frac{\partial g_{ki}}{\partial x_i}$$

Since we have that the correlation function is depending on the relative distance we use the chain rule

$$\frac{\partial g_{ij}}{\partial x_j} = \frac{\partial g_{ij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_j} = \frac{x_j - x_i}{r_{ij}} \frac{\partial g_{ij}}{\partial r_{ij}}$$

After substitution we get

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{1}{g_{ik}} \frac{\mathbf{r_{ik}}}{r_{ik}} \frac{\partial g_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N} \frac{1}{g_{ki}} \frac{\mathbf{r_{ki}}}{r_{ki}} \frac{\partial g_{ki}}{\partial r_{ki}}$$

For the Padé-Jastrow form we set $g_{ij} \equiv g(r_{ij}) = e^{f(r_{ij})} = e^{f_{ij}}$ and

$$\frac{\partial g_{ij}}{\partial r_{ij}} = g_{ij} \frac{\partial f_{ij}}{\partial r_{ij}}$$

and arrive at

$$\frac{1}{\Psi_C} \frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1} \frac{\mathbf{r_{ik}}}{r_{ik}} \frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N} \frac{\mathbf{r_{ki}}}{r_{ki}} \frac{\partial f_{ki}}{\partial r_{ki}}$$

where we have the relative vectorial distance

$$\mathbf{r}_{ij} = |\mathbf{r}_j - \mathbf{r}_i| = (x_j - x_i)\mathbf{e}_1 + (y_j - y_i)\mathbf{e}_2 + (z_j - z_i)\mathbf{e}_3$$

With a linear Padé-Jastrow we set

$$f_{ij} = \frac{ar_{ij}}{(1 + \beta r_{ij})}$$

with the corresponding closed form expression

$$\frac{\partial f_{ij}}{\partial r_{ij}} = \frac{a}{(1 + \beta r_{ij})^2}$$

1.1.9 The $\nabla^2\Psi_C/\Psi_C$ ratio

For the kinetic energy we also need the second derivative of the Jastrow factor divided by the Jastrow factor. We start with this

$$\left[\frac{\nabla^2\Psi_C}{\Psi_C}\right]_x = 2\sum_{k=1}^{N}\sum_{i=1}^{k-1}\frac{\partial^2 g_{ik}}{\partial x_k^2} + \sum_{k=1}^{N}\left(\sum_{i=1}^{k-1}\frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N}\frac{\partial g_{ki}}{\partial x_i}\right)^2$$

But we have another, simpler form for the function

$$\Psi_C = \prod_{i<j}\exp f(r_{ij}) = \exp\left\{\sum_{i<j}\frac{ar_{ij}}{1 + \beta r_{ij}}\right\}$$

and for particle k we have

$$\frac{\nabla_k^2\Psi_C}{\Psi_C} = \sum_{ij\neq k}\frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ki}r_{kj}}f'(r_{ki})f'(r_{kj}) + \sum_{j\neq k}\left(f''(r_{kj}) + \frac{2}{r_{kj}}f'(r_{kj})\right)$$

We use

$$f(r_{ij}) = \frac{ar_{ij}}{1 + \beta r_{ij}}$$

and with

$$g'(r_{kj}) = dg(r_{kj})/dr_{kj} \qquad \text{and} \qquad g''(r_{kj}) = d^2g(r_{kj})/dr_{kj}^2$$

we find that for particle k we have

$$\frac{\nabla_k^2\Psi_C}{\Psi_C} = \sum_{ij\neq k}\frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ki}r_{kj}}\frac{a}{(1 + \beta r_{ki})^2}\frac{a}{(1 + \beta r_{kj})^2} + \sum_{j\neq k}\left(\frac{2a}{r_{kj}(1 + \beta r_{kj})^2} - \frac{2a\beta}{(1 + \beta r_{kj})^3}\right)$$

And for the linear Padé-Jastrow we get the closed form result

$$\frac{\partial^2 f_{ij}}{\partial r_{ij}^2} = -\frac{2a_{ij}\beta_{ij}}{(1 + \beta_{ij}r_{ij})^3}$$