FYS-4411: Computational Physics II
Project 1

Gullik Vetvik Killie
Håkon Sebastian Bakke Mørk
Jose Emilio Ruiz Navarro

April 16, 2015

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	$\frac{\partial \psi_i}{\partial r_i}$	$\frac{\partial^2 \psi_i}{\partial r_i^2}$
ψ_{1S}	$e^{-\alpha ri}$	$-\frac{\alpha}{r_i}\left(x_i + y_i + z_i\right) e^{-\alpha r_i}$	$\frac{\alpha}{r_i}\left(\alpha r_i - 2\right) e^{-\alpha r_i}$
ψ_{2S}	$\left(-\frac{\alpha r_i}{2} + 1\right) e^{-\frac{\alpha r_i}{2}}$	$\frac{\alpha e^{-\frac{\alpha r_i}{2}}}{4 r_i}\left(\alpha r_i - 4\right)\left(x_i + y_i + z_i\right)$	$-\frac{\alpha e^{-\frac{\alpha r_i}{2}}}{8 r_i}\left(\alpha^2 r_i^2 - 10 \alpha r_i + 16\right)$
ψ_{2P}	$\alpha x_i e^{-\frac{\alpha r_i}{2}}$	$-\frac{\alpha e^{-\frac{\alpha r_i}{2}}}{2 r_i}\left(\alpha x_i^2 + \alpha x_i y_i + \alpha x_i z_i - 2 r_i\right)$	$\frac{\alpha^2 x_i}{4 r_i}\left(\alpha r_i - 8\right) e^{-\frac{\alpha r_i}{2}}$

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.

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