Optimització de gradient en VQMC: cas del trió confinat

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1 Introducció

La funció d'ona variacional del trió confinat assumim que és:

$$\Psi(r_e, \sigma_e, r_{h1}, \sigma_{h1}, r_{h2}, \sigma_{h2}) = \Phi(r_{h1}, r_{h2})[\alpha(\sigma_{h1})\beta(\sigma_{h2}) - \beta(\sigma_{h1})\alpha(\sigma_{h2})]\ \phi(r_e)\Sigma(\sigma_e) \tag{1}$$

amb,

$$\begin{aligned}
\Phi(r_{h1}, r_{h2}) &= \phi(z_{h1}, z_{h2})\ \Psi(x_{h1}, x_{h2}, y_{h1}, y_{h2}) \\
\phi(z_{h1}, z_{h2}) &= N_z \cos k_z z_{h1} \cos k_z z_{h2} \\
\Psi(x_{h1}, x_{h2}, y_{h1}, y_{h2}) &= N_\perp \cos k_x x_{h1} \cos k_x x_{h2} \cos k_y y_{h1} \cos k_y x_{h2}\, e^{-Z r_1}\ e^{-Z r_2}\, e^{\frac{\beta r_{12}}{1+\alpha\, r_{12}}} \\
\phi(r_e) &= N_e \cos k_x x_e \cos k_y y_e \cos k_z z_e \\
r_{12} &= \sqrt{(x_{h1} - x_{h2})^2 + (y_{h1} - y_{h2})^2} \\
r_1 &= \sqrt{(x_{h1} - x_e)^2 + (y_{h1} - y_e)^2} \\
r_2 &= \sqrt{(x_{h2} - x_e)^2 + (y_{h2} - y_e)^2}
\end{aligned} \tag{2}$$

i $[\alpha(\sigma_{h1})\beta(\sigma_{h2}) - \beta(\sigma_{h1})\alpha(\sigma_{h2})]$ la funció d'espín singulet dels dos forats i $\Sigma(\sigma_e)$ la funció d'espín doblet de l'electró (α o β). Amb tot açò, la part orbital de la funció d'ona queda:

$$\begin{aligned}
\Psi &= N \cos k_x x_e \cos k_x x_1 \cos k_x x_2 \cos k_y y_e \cos k_y y_1 \cos k_y y_2 \cos k_z z_e \cos k_z z_1 \cos k_z z_2\ F(r_{ij}) \\
F(r_{ij}) &= e^{-Z r_{1e}} e^{-Z r_{2e}} e^{\beta r_{12}/(1+\alpha r_{12})}
\end{aligned}$$

La funció Energia té tres variables $E(Z, \beta, \alpha) = E(|p\rangle)$. Per tant, trobar el mínim de la funció $E(|p\rangle)$ equival a trobar el zero de la seua derivada $|g(Z, \beta, \alpha)\rangle$. Anomenem $H_{i,j} = \partial E/\partial i \partial j$ al Hessià. En sèrie Taylor fins el terme lineal tenim (Mètode de Newton) $|p\rangle \approx |p_0\rangle - H_0^{-1}|g_0\rangle$.

Les primeres i segones derivades de l'energia variacional, anomenant Ψ' a la derivada logarítmica de Ψ:

$$\mathbb{E}'_\alpha = 2\left[\langle E_L \Psi' \rangle - \langle E_L \rangle \langle \Psi' \rangle\right] \tag{3}$$

$$\begin{aligned}
\mathbb{E}''_{\alpha,\beta} = {} & 2\left[\langle E_L \Psi''_{\alpha,\beta} \rangle - \langle E_L \rangle \langle \Psi''_{\alpha,\beta} \rangle + 2\left[\langle E_L \Psi'_\alpha \Psi'_\beta \rangle - \langle E_L \rangle \langle \Psi'_\alpha \Psi'_\beta \rangle\right] - \langle \Psi'_\alpha \rangle\, E'_\beta - \langle \Psi'_\beta \rangle\, E'_\alpha\right] + \\
& \langle \Psi'_\beta \frac{\partial E_L}{\partial \alpha} \rangle - \langle \Psi'_\beta \rangle \langle \frac{\partial E_L}{\partial \alpha} \rangle + \langle \Psi'_\alpha \frac{\partial E_L}{\partial \beta} \rangle - \langle \Psi'_\alpha \rangle \langle \frac{\partial E_L}{\partial \beta} \rangle
\end{aligned} \tag{4}$$

Que particularitzem:

$$\frac{1}{2}\,\mathbb{E}'_Z = \langle E_L \Psi'_Z\rangle - \langle E_L\rangle\langle\Psi'_Z\rangle \quad (5)$$
$$\frac{1}{2}\,\mathbb{E}'_\beta = \langle E_L \Psi'_\beta\rangle - \langle E_L\rangle\langle\Psi'_\beta\rangle \quad (6)$$
$$\frac{1}{2}\,\mathbb{E}'_\alpha = \langle E_L \Psi'_\alpha\rangle - \langle E_L\rangle\langle\Psi'_\alpha\rangle \quad (7)$$

$$\frac{1}{2}\,\mathbb{E}''_{Z,Z} = 2\left[\langle E_L(\Psi'_Z)^2\rangle - \langle E_L\rangle\langle(\Psi'_Z)^2\rangle\right] - 2\langle\Psi'_Z\rangle\,\mathbb{E}'_Z + \langle\frac{\partial E_L}{\partial Z}\,\Psi'_Z\rangle \quad (8)$$
$$\frac{1}{2}\,\mathbb{E}''_{\beta,\beta} = 2\left[\langle E_L(\Psi'_\beta)^2\rangle - \langle E_L\rangle\langle(\Psi'_\beta)^2\rangle\right] - 2\langle\Psi'_\beta\rangle\,\mathbb{E}'_\beta + \langle\frac{\partial E_L}{\partial \beta}\,\Psi'_\beta\rangle \quad (9)$$
$$\frac{1}{2}\,\mathbb{E}''_{\alpha,\alpha} = \langle E_L\Psi''_{\alpha,\alpha}\rangle - \langle E_L\rangle\langle\Psi''_{\alpha,\alpha}\rangle + 2\left[\langle E_L(\Psi'_\alpha)^2\rangle - \langle E_L\rangle\langle(\Psi'_\alpha)^2\rangle\right] - 2\langle\Psi'_\alpha\rangle\,\mathbb{E}'_\alpha + \langle\frac{\partial E_L}{\partial \alpha}\,\Psi'_\alpha\rangle \quad (10)$$
$$\frac{1}{2}\,\mathbb{E}''_{Z,\beta} = 2\left[\langle E_L\Psi'_Z\Psi'_\beta\rangle - \langle E_L\rangle\langle\Psi'_Z\Psi'_\beta\rangle\right] - \langle\Psi'_Z\rangle\,\mathbb{E}'_\beta - \langle\Psi'_\beta\rangle\,\mathbb{E}'_Z + \langle\frac{\partial E_L}{\partial \beta}\,\Psi'_Z\rangle - \langle\frac{\partial E_L}{\partial \beta}\rangle\langle\Psi'_Z\rangle + \langle\frac{\partial E_L}{\partial Z}\,\Psi'_\beta\rangle - \langle\frac{\partial E_L}{\partial Z}\rangle\langle\Psi'_\beta\rangle \quad (11)$$
$$\frac{1}{2}\,\mathbb{E}''_{Z,\alpha} = 2\left[\langle E_L\Psi'_Z\Psi'_\alpha\rangle - \langle E_L\rangle\langle\Psi'_Z\Psi'_\alpha\rangle\right] - \langle\Psi'_Z\rangle\,\mathbb{E}'_\alpha - \langle\Psi'_\alpha\rangle\,\mathbb{E}'_Z + \langle\frac{\partial E_L}{\partial \alpha}\,\Psi'_Z\rangle - \langle\frac{\partial E_L}{\partial \alpha}\rangle\langle\Psi'_Z\rangle + \langle\frac{\partial E_L}{\partial Z}\,\Psi'_\alpha\rangle - \langle\frac{\partial E_L}{\partial Z}\rangle\langle\Psi'_\alpha\rangle \quad (12)$$
$$\frac{1}{2}\,\mathbb{E}''_{\alpha,\beta} = \langle E_L\Psi''_{\alpha,\beta}\rangle - \langle E_L\rangle\langle\Psi''_{\alpha,\beta}\rangle + 2\left[\langle E_L\Psi'_\alpha\Psi'_\beta\rangle - \langle E_L\rangle\langle\Psi'_\alpha\Psi'_\beta\rangle\right] - \langle\Psi'_\alpha\rangle\,\mathbb{E}'_\beta - \langle\Psi'_\beta\rangle\,\mathbb{E}'_\alpha + \langle\frac{\partial E_L}{\partial \beta}\,\Psi'_\alpha\rangle - \langle\frac{\partial E_L}{\partial \beta}\rangle\langle\Psi'_\alpha\rangle + \langle\frac{\partial E_L}{\partial \alpha}\,\Psi'_\beta\rangle - \langle\frac{\partial E_L}{\partial \alpha}\rangle\langle\Psi'_\beta\rangle \quad (13)$$

L'aparent falta de simetria en les equacions de segones derivades s'origina del fet que algunes de les derivades logarítmiques de la funció d'ona són zero, cosa que elimina el càlcul d'alguns termes. En particular trobem que: $\Psi''_{Z,Z} = \Psi''_{\beta,\beta} = \Psi''_{Z,\alpha} = \Psi''_{Z,\beta} = 0$.

Les mitjanes a calcular són:

$$
\begin{array}{llllll}
\langle E_L \rangle & & & & & \\
\langle \Psi'_Z \rangle & \langle E_L\, \Psi'_Z \rangle & \langle E_L\, (\Psi'_Z)^2 \rangle & \langle \frac{\partial E_L}{\partial Z}\, \Psi'_Z \rangle & \langle E_L\, \Psi''_{\alpha,\alpha} \rangle & \langle \frac{\partial E_L}{\partial Z} \rangle \\
\langle \Psi'_\beta \rangle & \langle E_L\, \Psi'_\beta \rangle & \langle E_L\, (\Psi'_\beta)^2 \rangle & \langle \frac{\partial E_L}{\partial \beta}\, \Psi'_\beta \rangle & \langle E_L\, \Psi''_{\alpha,\beta} \rangle & \langle \frac{\partial E_L}{\partial \beta} \rangle \\
\langle \Psi'_\alpha \rangle & \langle E_L\, \Psi'_\alpha \rangle & \langle E_L\, (\Psi'_\alpha)^2 \rangle & \langle \frac{\partial E_L}{\partial \alpha}\, \Psi'_\alpha \rangle & & \langle \frac{\partial E_L}{\partial \alpha} \rangle \\
\langle (\Psi'_Z)^2 \rangle & & \langle E_L\, \Psi'_Z\, \Psi'_\beta \rangle & \langle \frac{\partial E_L}{\partial \beta}\, \Psi'_Z \rangle & & \\
\langle (\Psi'_\beta)^2 \rangle & & \langle E_L\, \Psi'_Z\, \Psi'_\alpha \rangle & \langle \frac{\partial E_L}{\partial Z}\, \Psi'_\beta \rangle & & \\
\langle \Psi''_{\alpha,\alpha} \rangle & & \langle E_L\, \Psi'_\alpha\, \Psi'_\beta \rangle & \langle \frac{\partial E_L}{\partial \alpha}\, \Psi'_Z \rangle & & \\
\langle (\Psi'_\alpha)^2 \rangle & & & \langle \frac{\partial E_L}{\partial Z}\, \Psi'_\alpha \rangle & & \\
\langle \Psi'_Z \Psi'_\beta \rangle & & & \langle \frac{\partial E_L}{\partial \beta}\, \Psi'_\alpha \rangle & & \\
\langle \Psi'_Z \Psi'_\alpha \rangle & & & \langle \frac{\partial E_L}{\partial \alpha}\, \Psi'_\beta \rangle & & \\
\langle \Psi''_{\alpha,\beta} \rangle & & & & & \\
\langle \Psi'_\alpha \Psi'_\beta \rangle & & & & &
\end{array}
\tag{14}
$$

La nomenclatura de les variables en el programa són:

$$
\begin{array}{llllll}
energ & & & & & \\
FZ & ElFZ & ElFZ2 & dElZFZ & ElF2alp & dElZ \\
Fbet & ElFbet & ElFbet2 & dElbetFbet & ElF2alpbet & dElbet \\
Falp & ElFalp & ElFalp2 & dElalpFalp & & dElalp \\
FZ2 & & ElFZFbet & dElbetFZ & & \\
Fbet2 & & ElFZFalp & dElZFbet & & \\
F2alp & & ElFalpFbet & dElalpFZ & & \\
Falp2 & & & dElZFalp & & \\
FZFbet & & & dElbetFalp & & \\
FZFalp & & & dElalpFbet & & \\
F2alpbet & & & & & \\
FalpFbet & & & & &
\end{array}
\tag{15}
$$

Amb aquesta nomenclatura, les derivades a calcular són:

$$derZ = 2*(ElFZ - energ*FZ) \tag{16}$$

$$derbet = 2*(ElFbet - energ*Fbet) \tag{17}$$

$$deralp = 2*(ElFalp - energ*Falp) \tag{18}$$

$$der2ZZ = 2*(2*(ElFZ2 - energ*FZ2) - 2*FZ*derZ + dElZFZ) \tag{19}$$

$$der2betbet = 2*(2*(ElFbet2 - energ*Fbet2) - 2*Fbet*derbet + dElbetFbet) \tag{20}$$

$$der2alpalp = 2*(ElF2alp - energ*F2alp + 2*(ElFalp2 - energ*Falp2) - 2*Falp*deralp + dElalpFalp) \tag{21}$$

$$der2Zbet = 2*(2*(ElFZFbet - energ*FZFbet) - FZ*derbet - Fbet*derZ + dElbetFZ - FZ*dElbet + dElZFbet - Fbet*dElZ) \tag{22}$$

$$der2Zalp = 2*(2*(ElFZFalp - energ*FZFalp) - FZ*deralp - Falp*derZ + dElalpFZ - FZ*dElalp + dElZFalp - Falp*dElZ) \tag{23}$$

$$\begin{aligned} der2alpbet &= 2*(ElF2alpbet - energ*F2alpbet + 2*(ElFalpFbet - energ*FalpFbet) - Falp*derbet - Fbet*deralp \\ &\quad + dElbetFalp - Falp*dElbet + dElalpFbet - Fbet*dElalp) \end{aligned} \tag{24}$$