Àtom d'heli: minimitzacio de la variància

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L'hamiltonià:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{1}$$

La funció variacional:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-Zr_1}\, e^{-Zr_2}\, e^{\frac{\beta r_{12}}{1+\alpha\, r_{12}}} \tag{2}$$

L'energia local:

$$\begin{aligned} E_L(\mathbf{r}_1, \mathbf{r}_2) &= -Z^2 + \frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{r_{12}}\left[1 - \frac{2\,\beta}{(1+\alpha r_{12})^2}\right] \\ &\quad + \frac{2\alpha\beta}{(1+\alpha r_{12})^3} - \frac{\beta^2}{(1+\alpha r_{12})^4} + \frac{Z\beta}{(1+\alpha\, r_{12})^2}\,\frac{r_1+r_2}{r_{12}}\left(1 - \frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1 r_2}\right) \end{aligned} \tag{3}$$

Les derivades logarítmiques de la funció d'ona:

$$\Psi'_{\ln,\alpha} = -\frac{\beta\, r_{12}^2}{(1+\alpha\, r_{12})^2} \tag{4}$$

$$\Psi'_{\ln,\beta} = \frac{r_{12}}{1+\alpha\, r_{12}} \tag{5}$$

Les primeres derivades de l'energia local:

$$\frac{\partial E_L}{\partial \alpha} = \frac{2\beta\left(-3\alpha r_{12}(1+\alpha r_{12}) + 3(1+\alpha r_{12})^2 - Z(r_1+r_2)(1+\alpha r_{12})^2\left(1 - \frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1 r_2}\right) + 2\beta r_{12}\right)}{(1+\alpha r_{12})^5} \tag{6}$$

$$\frac{\partial E_L}{\partial \beta} = \frac{2\alpha(1+\alpha r_{12})r_{12} + Z(r_1+r_2)(1+\alpha r_{12})^2\left(1 - \frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1 r_2}\right) - 2(1+\alpha r_{12})^2 - 2\beta r_{12}}{r_{12}(1+\alpha r_{12})^4} \tag{7}$$

La inversa d'una matriu 2×2:

$$M = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \rightarrow M^{-1} = \frac{1}{a\,c - b^2}\begin{pmatrix} c & -b \\ -b & a \end{pmatrix} \tag{8}$$

Les derivades primeres i segones aproximades de la variància:[1]

$$V'_\alpha = 2\langle\left(E^L - E\right)\left(E'^L_\alpha - E'_\alpha\right)\rangle \tag{9}$$

$$V''_{\alpha,\beta} = 2\langle\left(E'^L_\beta - E'_\beta\right)\left(E'^L_\alpha - E'_\alpha\right)\rangle \tag{10}$$

Reescrivim més explícitament la primera derivada:

$$V'_\alpha = 2\left\langle\left[(E_L)_i - \langle(E_L)_i\rangle\right]\left[\left(\frac{\partial E_L}{\partial\alpha}\right)_i - \langle(E_L)_i\left(\frac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle + \langle(E_L)_i\rangle\cdot\langle\left(\frac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle\right]\right\rangle \tag{11}$$

Si anomenem a, b, c, d, p, q als diferents termes de l'equació anterior, efectuem els productes:

$$V' = 2(a-b)(c-d+p\cdot q) = 2\left(a\cdot c - b\cdot c - a\cdot d + b\cdot d + a\cdot p\cdot q - b\cdot p\cdot q\right)$$

i escrivim els termes resultants, tenim:

$$\begin{aligned}
a\cdot c &= \langle(E_L)_i\left(\tfrac{\partial E_L}{\partial\alpha}\right)_i\rangle \\
b\cdot c &= \langle(E_L)_i\rangle\cdot\langle\left(\tfrac{\partial E_L}{\partial\alpha}\right)_i\rangle \\
a\cdot d &= \langle(E_L)_i\rangle\cdot\langle(E_L)_i\left(\tfrac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle \\
b\cdot d &= \langle(E_L)_i\rangle\cdot\langle(E_L)_i\left(\tfrac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle \\
a\cdot p\cdot q &= \langle(E_L)_i\rangle^2\cdot\langle\left(\tfrac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle \\
b\cdot p\cdot q &= \langle(E_L)_i\rangle^2\cdot\langle\left(\tfrac{\partial \ln\Psi}{\partial\alpha}\right)_i\rangle
\end{aligned} \tag{12}$$

Observem que $a\cdot d = b\cdot d$ i que $a\cdot p\cdot q = b\cdot p\cdot q$, amb la qual cosa $V' = a\cdot c - b\cdot c$, és a dir:

$$V'_\alpha = 2\left[\left\langle(E_L)_i\left(\frac{\partial E_L}{\partial\alpha}\right)_i\right\rangle - \langle(E_L)_i\rangle\cdot\left\langle\left(\frac{\partial E_L}{\partial\alpha}\right)_i\right\rangle\right] \tag{13}$$

Anàlogament, explicitant l'equació (10) tenim:

$$\begin{aligned}
V''_{\alpha,\beta} = 2\Bigg\langle&\left[\left(\frac{\partial E_L}{\partial\beta}\right)_i - \left\langle(E_L)_i\left(\frac{\partial \ln\Psi}{\partial\beta}\right)_i\right\rangle + \langle(E_L)_i\rangle\cdot\left\langle\left(\frac{\partial \ln\Psi}{\partial\beta}\right)_i\right\rangle\right]\cdot \\
&\cdot\left[\left(\frac{\partial E_L}{\partial\alpha}\right)_i - \left\langle(E_L)_i\left(\frac{\partial \ln\Psi}{\partial\alpha}\right)_i\right\rangle + \langle(E_L)_i\rangle\cdot\left\langle\left(\frac{\partial \ln\Psi}{\partial\alpha}\right)_i\right\rangle\right]\Bigg\rangle
\end{aligned} \tag{14}$$

Si anomenem a, b, c, d, p, q, r, s als diferents termes de l'equació anterior, efectuem els productes:

$$\begin{aligned}
V''_{\alpha,\beta} &= 2(a-b+c\cdot d)(p-q+r\cdot s) \\
&= 2\left(a\cdot p - b\cdot p + c\cdot d\cdot p - a\cdot q + b\cdot q - c\cdot d\cdot q + a\cdot r\cdot s - b\cdot r\cdot s + c\cdot d\cdot r\cdot s\right)
\end{aligned}$$

i escrivim els termes resultants, tenim:

$$
\begin{aligned}
a \cdot p &= \langle \left(\frac{\partial E_L}{\partial \beta}\right)_i \left(\frac{\partial E_L}{\partial \alpha}\right)_i \rangle \\
b \cdot p &= \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle \left(\frac{\partial E_L}{\partial \alpha}\right)_i \rangle \\
c \cdot d \cdot p &= \langle (E_L)_i \rangle \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle \left(\frac{\partial E_L}{\partial \alpha}\right)_i \rangle \\
a \cdot q &= \langle \left(\frac{\partial E_L}{\partial \beta}\right)_i \rangle \cdot \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle \\
b \cdot q &= \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle \qquad (15) \\
c \cdot d \cdot q &= \langle (E_L)_i \rangle \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle \\
a \cdot r \cdot s &= \langle \left(\frac{\partial E_L}{\partial \beta}\right)_i \rangle \cdot \langle (E_L)_i \rangle \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle \\
b \cdot r \cdot s &= \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle (E_L)_i \rangle \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle \\
c \cdot d \cdot r \cdot s &= \langle (E_L)_i \rangle^2 \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \cdot \langle \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle
\end{aligned}
$$

En aquest cas no hi ha cancel·lacions (no hi ha dos termes iguals). Els elements diagonals del Hessià $V''_{\alpha,\alpha}$, $V''_{\beta,\beta}$ són idèntics, excepte que cal fer que els dos paràmetres siguen el mateix.

Les llistes que cal construir:

$$
\begin{array}{llll}
E = \langle (E_L)_i \rangle & & & \\
Ea = \langle \left(\frac{\partial E_L}{\partial \alpha}\right)_i \rangle & Eb = \langle \left(\frac{\partial E_L}{\partial \beta}\right)_i \rangle & Fa = \langle \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle & Fb = \langle \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \\
EEa = \langle (E_L)_i \left(\frac{\partial E_L}{\partial \alpha}\right)_i \rangle & EEb = \langle (E_L)_i \left(\frac{\partial E_L}{\partial \beta}\right)_i \rangle & EFa = \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \alpha}\right)_i \rangle & EFb = \langle (E_L)_i \left(\frac{\partial \ln \Psi}{\partial \beta}\right)_i \rangle \\
EaEb = \langle \left(\frac{\partial E_L}{\partial \alpha}\right)_i \left(\frac{\partial E_L}{\partial \beta}\right)_i \rangle & Ea2 = \langle \left(\frac{\partial E_L}{\partial \alpha}\right)_i^2 \rangle & Eb2 = \langle \left(\frac{\partial E_L}{\partial \beta}\right)_i^2 \rangle &
\end{array}
\qquad (16)
$$

Les fórmules per a la primera derivada:

$$
\begin{aligned}
V(1) &= 2.d0 * (EEa - E * Ea) \\
V(2) &= 2.d0 * (EEb - E * Eb)
\end{aligned}
\qquad (17)
$$

Les fórmules per a la segon derivada:

$$
\begin{aligned}
H(1,2) &= 2.d0 * (EaEb - EFb * Ea + E * Fb * Ea - Eb * EFa + EFb * EFa \\
&\quad - E * Fb * EFa + Eb * E * Fa - EFb * E * Fa + E^2 * Fb * Fa) \qquad (18) \\
H(1,1) &= 2.d0 * (Ea2 - EFa * Ea + E * Fa * Ea - Ea * EFa + EFa^2 \\
&\quad - E * Fa * EFa + Ea * E * Fa - EFa * E * Fa + E^2 * Fa^2)
\end{aligned}
$$

El terme $H(2,2)$ és com $H(1,1)$ canviant a per b.

Si anomenem $det = Det[H] = H(1,1) * H(2,2) - H(1,2) * H(2,1)$, els elements de la inversa G del Hessià resulten:

$$\begin{aligned} G(1,1) &= H(2,2)/det \\ G(1,2) = G(2,1) &= -H(1,2)/det \\ G(2,2) &= H(1,1)/det \end{aligned} \tag{19}$$

Finalment,

$$|x_s\rangle \approx |x_0\rangle - G|V\rangle \tag{20}$$

References

[1] C. J. Umrigar and C. Filippi, *Phys. Rev. Lett*, 94 (2005) 150201.