

# Notes on Matrix Factorization for Hartree-Fock Stability of HEG

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## I. ORBITAL HESSIAN FACTORIZATION

According to Seeger and Pople[1], (and many other sources) the molecular orbital Hessian has the form,

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}$$

Where the matrices denoted by  $\mathbf{A}$  and  $\mathbf{B}$  are given by,

$$\begin{aligned} A_{st} &= (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle \\ B_{st} &= \langle ab||ij \rangle \end{aligned}$$

The color is to help keep track of which portions of the matrices come from  $\mathbf{A}$  and  $\mathbf{B}$ . The integration is over spin and spatial coordinates. In the case of a stationary UHF solution, the matrices  $\mathbf{A}$  and  $\mathbf{B}$  have the following forms, after integrating over spin:

$$\begin{aligned} A_{st} &= (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \delta_{\sigma_i\sigma_a}\delta_{\sigma_j\sigma_b}\langle aj||ib \rangle - \delta_{\sigma_a\sigma_b}\delta_{\sigma_i\sigma_j}\langle aj||bi \rangle \\ B_{st} &= \delta_{\sigma_a\sigma_i}\delta_{\sigma_b\sigma_j}\langle ab||ij \rangle - \delta_{\sigma_a\sigma_b}\delta_{\sigma_i\sigma_j}\langle ab||ji \rangle \end{aligned}$$

In matrix form,

$$\mathbf{A} = \begin{matrix} & \begin{matrix} \alpha \rightarrow \alpha & \alpha \rightarrow \beta & \beta \rightarrow \alpha & \beta \rightarrow \beta \end{matrix} \\ \begin{matrix} \alpha \rightarrow \alpha \\ \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \\ \beta \rightarrow \beta \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle & 0 & 0 & \langle aj||ib \rangle \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj||bi \rangle & 0 & 0 \\ 0 & 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj||bi \rangle & 0 \\ \langle aj||ib \rangle & 0 & 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle \end{bmatrix} \end{matrix}$$

$$\mathbf{B} = \begin{matrix} & \begin{matrix} \alpha \rightarrow \alpha & \alpha \rightarrow \beta & \beta \rightarrow \alpha & \beta \rightarrow \beta \end{matrix} \\ \begin{matrix} \alpha \rightarrow \alpha \\ \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \\ \beta \rightarrow \beta \end{matrix} & \begin{bmatrix} \langle ab||ij \rangle & 0 & 0 & \langle ab||ij \rangle \\ 0 & 0 & -\langle ab||ji \rangle & 0 \\ 0 & -\langle ab||ji \rangle & 0 & 0 \\ \langle ab||ij \rangle & 0 & 0 & \langle ab||ij \rangle \end{bmatrix} \end{matrix}$$

These matrices factorize into “spin conserved” ( $\mathbf{A}'$ ,  $\mathbf{B}'$ ) and “spin-unconserved” ( $\mathbf{A}''$ ,  $\mathbf{B}''$ ) parts, to use the language of Seeger and Pople. The spin conserved matrices are given by

$$\mathbf{A}' = \begin{matrix} & \begin{matrix} \alpha \rightarrow \alpha & \beta \rightarrow \beta \end{matrix} \\ \begin{matrix} \alpha \rightarrow \alpha \\ \beta \rightarrow \beta \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle & \langle aj||ib \rangle \\ \langle aj||ib \rangle & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle \end{bmatrix} \end{matrix}$$

$$\mathbf{B}' = \begin{matrix} & \begin{matrix} \alpha \rightarrow \alpha & \beta \rightarrow \beta \end{matrix} \\ \begin{matrix} \alpha \rightarrow \alpha \\ \beta \rightarrow \beta \end{matrix} & \begin{bmatrix} \langle ab||ij \rangle & \langle ab||ij \rangle \\ \langle ab||ij \rangle & \langle ab||ij \rangle \end{bmatrix} \end{matrix}$$

while the spin-unconserved matrices are given by:

$$\mathbf{A}'' = \begin{matrix} & \begin{matrix} \alpha \rightarrow \beta & \beta \rightarrow \alpha \end{matrix} \\ \begin{matrix} \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj||bi \rangle & 0 \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj||bi \rangle \end{bmatrix} \end{matrix}$$

$$\mathbf{B}'' = \begin{matrix} & \begin{matrix} \alpha \rightarrow \beta & \beta \rightarrow \alpha \end{matrix} \\ \begin{matrix} \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \end{matrix} & \begin{bmatrix} 0 & -\langle ab||ji \rangle \\ -\langle ab||ji \rangle & 0 \end{bmatrix} \end{matrix}$$

Thus the spin conserved molecular orbital hessian,  $\mathbf{H}'$  is given by:

$$\mathbf{H}' = \begin{matrix} & \begin{matrix} \alpha \rightarrow \alpha & \beta \rightarrow \beta & \alpha \rightarrow \alpha & \beta \rightarrow \beta \end{matrix} \\ \begin{matrix} \alpha \rightarrow \alpha \\ \beta \rightarrow \beta \\ \alpha \rightarrow \alpha \\ \beta \rightarrow \beta \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle & \langle aj||ib \rangle & \langle ab||ij \rangle & \langle ab||ij \rangle \\ \langle aj||ib \rangle & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle & \langle ab||ij \rangle & \langle ab||ij \rangle \\ \langle ab||ij \rangle^* & \langle ab||ij \rangle^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle^* & \langle aj||ib \rangle^* \\ \langle ab||ij \rangle^* & \langle ab||ij \rangle^* & \langle aj||ib \rangle^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib \rangle^* \end{bmatrix} \end{matrix}$$

and the spin unconserved molecular orbital hessian,  $\mathbf{H}''$  is given by:

$$\mathbf{H}'' = \begin{matrix} & \alpha \rightarrow \beta & \beta \rightarrow \alpha & \alpha \rightarrow \beta & \beta \rightarrow \alpha \\ \begin{matrix} \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \\ \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & 0 & 0 & -(ab|ji) \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & -(ab|ji) & 0 \\ 0 & -(ab|ji)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* & 0 \\ -(ab|ji)^* & 0 & 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* \end{bmatrix} \end{matrix}$$

This matrix factorizes into two equivalent matrices,

$$\mathbf{H}'' = \begin{matrix} & \alpha \rightarrow \beta & \beta \rightarrow \alpha \\ \begin{matrix} \alpha \rightarrow \beta \\ \beta \rightarrow \alpha \end{matrix} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & -(ab|ji) \\ -(ab|ji)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* \end{bmatrix} \end{matrix}$$

And in this form it is entirely equivalent to the RHF-UHF stability matrix,  ${}^3\mathbf{H}'$  defined in equations 35 and 36 of Seeger/Pople[1]. This is where I suspect I've made a mistake.

## II. PROOF OF REAL-VALUED A AND B

In the case of the Homogeneous electron gas, the two electron integral is given by (eq. 12 of [2] and p. 16 of [3]):

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \stackrel{2D, 3D}{=} \begin{cases} \frac{\pi}{\Omega} \frac{2^{D-1}}{|\vec{k} - \vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' \text{ and } |\vec{k} - \vec{k}''| \neq 0 \\ 0 & \text{else} \end{cases} \quad (1a)$$

$$\langle k, k' | k'', k''' \rangle \stackrel{1D}{=} \begin{cases} e^{|k-k''|^2 a^2} \text{Ei}(-|k-k''|^2 a^2); & k''' = k + k' - k'' \text{ and } |k - k''| \neq 0 \\ 0; & \text{else} \end{cases} \quad (1b)$$

The two electron integrals are always real-valued. Therefore  $\mathbf{A} = \mathbf{A}^*$  and  $\mathbf{B} = \mathbf{B}^*$ . So far I have not used this to simplify anything, but it is true.

## III. REFERENCES

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- [1] R. Seeger and J. A. Pople, The Journal of Chemical Physics **66**, 3045 (1977), ISSN 00219606, URL <http://scitation.aip.org/content/aip/journal/jcp/66/7/10.1063/1.434318>.
  - [2] F. Delyon, M. Duneau, B. Bernu, and M. Holzmann, pp. 1–12 (2008), 0807.0770, URL <http://arxiv.org/abs/0807.0770>.
  - [3] G. Guilianì and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005), ISBN 978-0-521-82112-6.