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:

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

In matrix form,

$$\mathbf{A} = \begin{array}{c} \\ \alpha\to\alpha \\ \alpha\to\beta \\ \beta\to\alpha \\ \beta\to\beta \end{array} \begin{array}{c} \begin{array}{cccc} \alpha\to\alpha & \alpha\to\beta & \beta\to\alpha & \beta\to\beta \end{array} \\ \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) & 0 & 0 & (aj|ib) \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & 0 & 0 \\ 0 & 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & 0 \\ (aj|ib) & 0 & 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) \end{bmatrix} \end{array}$$

$$\mathbf{B} = \begin{array}{c} \\ \alpha\to\alpha \\ \alpha\to\beta \\ \beta\to\alpha \\ \beta\to\beta \end{array} \begin{array}{c} \begin{array}{cccc} \alpha\to\alpha & \alpha\to\beta & \beta\to\alpha & \beta\to\beta \end{array} \\ \begin{bmatrix} (ab||ij) & 0 & 0 & (ab|ij) \\ 0 & 0 & -(ab|ji) & 0 \\ 0 & -(ab|ji) & 0 & 0 \\ (ab|ij) & 0 & 0 & (ab||ij) \end{bmatrix} \end{array}$$

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

$$\mathbf{A}' = \begin{array}{c} \\ \alpha\to\alpha \\ \beta\to\beta \end{array} \begin{array}{c} \begin{array}{cc} \alpha\to\alpha & \beta\to\beta \end{array} \\ \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) & (aj|ib) \\ (aj|ib) & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) \end{bmatrix} \end{array}$$

$$\mathbf{B}' = \begin{array}{c} \\ \alpha\to\alpha \\ \beta\to\beta \end{array} \begin{array}{c} \begin{array}{cc} \alpha\to\alpha & \beta\to\beta \end{array} \\ \begin{bmatrix} (ab||ij) & (ab|ij) \\ (ab|ij) & (ab||ij) \end{bmatrix} \end{array}$$

while the spin-unconserved matrices are given by:

$$\mathbf{A}'' = \begin{array}{c} \\ \alpha\to\beta \\ \beta\to\alpha \end{array} \begin{array}{c} \begin{array}{cc} \alpha\to\beta & \beta\to\alpha \end{array} \\ \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & 0 \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) \end{bmatrix} \end{array}$$

$$\mathbf{B}'' = \begin{array}{c} \\ \alpha\to\beta \\ \beta\to\alpha \end{array} \begin{array}{c} \begin{array}{cc} \alpha\to\beta & \beta\to\alpha \end{array} \\ \begin{bmatrix} 0 & -(ab|ji) \\ -(ab|ji) & 0 \end{bmatrix} \end{array}$$

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

$$\mathbf{H}' = \begin{array}{c} \\ \alpha\to\alpha \\ \beta\to\beta \\ \alpha\to\alpha \\ \beta\to\beta \end{array} \begin{array}{c} \begin{array}{cccc} \alpha\to\alpha & \beta\to\beta & \alpha\to\alpha & \beta\to\beta \end{array} \\ \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) & (aj|ib) & (ab||ij) & (ab|ij) \\ (aj|ib) & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) & (ab|ij) & (ab||ij) \\ (ab||ij)^* & (ab|ij)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib)^* & (aj|ib)^* \\ (ab|ij)^* & (ab||ij)^* & (aj|ib)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib)^* \end{bmatrix} \end{array}$$

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

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

This matrix factorizes into to two equivalent matrices,

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

And in this form it is entirely equivalent to the RHF-UHF stability matrix, ${}^{\mathbf{3}}\mathbf{H}'$ 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]):

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

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

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

[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. Guiliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005), ISBN 978-0-521-82112-6.