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,

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

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:

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

(columns: $\alpha\to\alpha$, $\alpha\to\beta$, $\beta\to\alpha$, $\beta\to\beta$)

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

(columns: $\alpha\to\alpha$, $\alpha\to\beta$, $\beta\to\alpha$, $\beta\to\beta$)

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

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

(columns: $\alpha\to\alpha$, $\beta\to\beta$)

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

(columns: $\alpha\to\alpha$, $\beta\to\beta$)

while the spin-unconserved matrices are given by:

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

(columns: $\alpha\to\beta$, $\beta\to\alpha$)

$$
\mathbf{B} =
\begin{array}{c}
\alpha\to\beta \\ \beta\to\alpha
\end{array}
\begin{bmatrix}
0 & -\langle ab|ji\rangle \\
-\langle ab|ji\rangle & 0
\end{bmatrix}
$$

(columns: $\alpha\to\beta$, $\beta\to\alpha$)

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

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

(columns: $\alpha\to\alpha$, $\beta\to\beta$, $\alpha\to\alpha$, $\beta\to\beta$)

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

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

This matrix factorizes into to two equivalent matrices,

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

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

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

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

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, J. Chem. Phys. **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.