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

## I. DEFINITIONS

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

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \tag{1}$$

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

$$A_{st} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib\rangle \tag{2}$$

$$B_{st} = \langle ab||ij\rangle \tag{3}$$

and the two electron integral used here is defined as,

$$\langle pq|rs\rangle = \int\int \chi_p^*(1)\chi_q^*(2)\frac{1}{r_{12}}\chi_r(1)\chi_s(2)d\tau d\sigma \tag{4}$$

$$\langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle \tag{5}$$

$$(pq|rs) = \int\int \chi_p^*(1)\chi_q^*(2)\frac{1}{r_{12}}\chi_r(1)\chi_s(2)d\tau \tag{6}$$

$$(pq||rs) = (pq|rs) - (pq|sr) \tag{7}$$

Where $\sigma$ is the spin coordinate and $d\tau$ is the volume element in all spatial coordinates. Additionally, the convention of $a, b$ being virtual states, $i, j$ being occupied states and $p, q, r, s$ being any state is followed.

The solution is said to be unstable when the lowest eigenvalue of $\mathbf{H}$ is strictly negative. The corresponding eigenvector points downhill in energy in the case of instability. Defining the eigenvector as $\mathbf{D}$, the eigenvalue problem can be written as

$$\mathbf{HD} = \lambda\mathbf{D} \tag{8}$$

## II. TRANSFORMING H DICTATES THE FORM OF D

In many cases, the matrix $\mathbf{H}$ factorizes into various components. The following form of a similarity transformed eigenvalue problem is useful to keep in mind:

$$\mathbf{S^{-1}HSS^{-1}D} = \lambda\mathbf{S^{-1}D} \tag{9}$$

$$\tilde{\mathbf{H}}\tilde{\mathbf{D}} = \lambda\tilde{\mathbf{D}} \tag{10}$$

Thus if the matrix $\mathbf{H}$ can be transformed via a similarity transformation defined by $\mathbf{S}$ into $\tilde{\mathbf{H}}$, then the corresponding eigenvector which satisfies the eigenvalue problem has the form $\tilde{\mathbf{D}} = \mathbf{S^{-1}D}$.

This approach is commonly used in the paper to transform into the basis that separates the real and complex contributions of the eigenvectors when $\mathbf{A}$ and $\mathbf{B}$ are real. Writing the eigenvalue problem in the form of Seeger & Pople (eq. 18 in [1]), we get

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}\begin{bmatrix} \mathbf{d} \\ \mathbf{d}^* \end{bmatrix} = 2E_2\begin{bmatrix} \mathbf{d} \\ \mathbf{d}^* \end{bmatrix} \tag{11}$$

We can now apply the similarity transform defined by the Unitary matrix

$$\mathbf{U} = \frac{1}{\sqrt{2}}\begin{bmatrix} \mathbf{I} & -\mathbf{I} \\ \mathbf{I} & \mathbf{I} \end{bmatrix} \tag{12}$$

after which the transformed eigenvalue problem has the form

$$\frac{1}{2}\begin{bmatrix} \mathbf{A}+\mathbf{B}+\mathbf{A}^*+\mathbf{B}^* & -\mathbf{A}+\mathbf{A}^*+\mathbf{B}-\mathbf{B}^* \\ -\mathbf{A}+\mathbf{A}^*-\mathbf{B}+\mathbf{B}^* & \mathbf{A}^*+\mathbf{A}-\mathbf{B}-\mathbf{B}^* \end{bmatrix}\begin{bmatrix} \mathbf{d}+\mathbf{d}^* \\ \mathbf{d}-\mathbf{d}^* \end{bmatrix} = 2E_2\begin{bmatrix} \mathbf{d}+\mathbf{d}^* \\ -\mathbf{d}+\mathbf{d}^* \end{bmatrix} \tag{13}$$

$$= 2E_2\begin{bmatrix} \mathbf{Re(d)} \\ \mathbf{Im(d)} \end{bmatrix} \tag{14}$$

If $\mathbf{A}$ and $\mathbf{B}$ are both real, $\mathbf{A} = \mathbf{A}^*$ and $\mathbf{B} = \mathbf{B}^*$ and the above simplifies to

$$\begin{bmatrix} \mathbf{A}+\mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}-\mathbf{B} \end{bmatrix}\begin{bmatrix} \mathbf{Re(d)} \\ \mathbf{Im(d)} \end{bmatrix} = 2E_2\begin{bmatrix} \mathbf{Re(d)} \\ \mathbf{Im(d)} \end{bmatrix} \tag{15}$$

Clearly, the matrix factorizes into $\mathbf{A}+\mathbf{B}$ and $\mathbf{A}-\mathbf{B}$. The eigenvectors factorize into the real and imaginary displacements of the orbitals, respectively. This is equivalent to the condition derived in and around eq. 20 in Seeger/Pople for internal and external instabilities of real GHF solutions [1], however this approach applies to any matrix with the same form as equation 1.

## III. FORMS OF EQUATIONS WITH UHF SOLUTION

In the case of a stationary UHF solution, the elements of matrices **A** and **B** have the following forms, after integrating over spin:

$$A_{i\to a,j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \delta_{\sigma_i\sigma_a}\delta_{\sigma_j\sigma_b}(aj|ib) - \delta_{\sigma_a\sigma_b}\delta_{\sigma_i\sigma_j}(aj|bi) \tag{16}$$
$$B_{i\to a,j\to b} = \delta_{\sigma_a\sigma_i}\delta_{\sigma_b\sigma_j}(ab|ij) - \delta_{\sigma_a\sigma_j}\delta_{\sigma_b\sigma_i}(ab|ji) \tag{17}$$

Writing down the matrices, where the row index corresponds to $i \to a$ excitations and the column index corresponds to $j \to b$ excitations:

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

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

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. Similarly, $\mathbf{H}$ factorizes, with no approximations, into $\mathbf{H}'$ and $\mathbf{H}''$

$$\mathbf{H}' = \begin{bmatrix} \mathbf{A}' & \mathbf{B}' \\ \mathbf{B}'^{*} & \mathbf{A}'^{*} \end{bmatrix} \tag{18}$$

$$\mathbf{H}'' = \begin{bmatrix} \mathbf{A}'' & \mathbf{B}'' \\ \mathbf{B}''^{*} & \mathbf{A}''^{*} \end{bmatrix} \tag{19}$$

The spin conserved matrices are given by

$$\mathbf{A}' = \begin{array}{cc} & \begin{array}{cc} \alpha\to\alpha & \beta\to\beta \end{array} \\ \begin{array}{c} \alpha\to\alpha \\ \beta\to\beta \end{array} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) & (aj|ib) \\ (aj|ib) & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (aj||ib) \end{bmatrix} \end{array} \tag{20}$$

$$\mathbf{B}' = \begin{array}{cc} & \begin{array}{cc} \alpha\to\alpha & \beta\to\beta \end{array} \\ \begin{array}{c} \alpha\to\alpha \\ \beta\to\beta \end{array} & \begin{bmatrix} (ab||ij) & (ab|ij) \\ (ab|ij) & (ab||ij) \end{bmatrix} \end{array} \tag{21}$$

while the spin-unconserved matrices are given by:

$$\mathbf{A}'' = \begin{array}{cc} & \begin{array}{cc} \alpha\to\beta & \beta\to\alpha \end{array} \\ \begin{array}{c} \alpha\to\beta \\ \beta\to\alpha \end{array} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & 0 \\ 0 & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) \end{bmatrix} \end{array} \tag{22}$$

$$\mathbf{B}'' = \begin{array}{cc} & \begin{array}{cc} \alpha\to\beta & \beta\to\alpha \end{array} \\ \begin{array}{c} \alpha\to\beta \\ \beta\to\alpha \end{array} & \begin{bmatrix} 0 & -(ab|ji) \\ -(ab|ji) & 0 \end{bmatrix} \end{array} \tag{23}$$

Thus the spin conserved molecular orbital hessian, is given by

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

and the spin unconserved molecular orbital hessian, is given by:

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

The eigenvalue equation defining $\mathbf{D}'$ is,

$$\mathbf{H}'\mathbf{D}' = \mathbf{H}' \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} \\ \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} \\ \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} \\ \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} \\ \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} \tag{24}$$

Applying the transformation defined by the unitary matrix,

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mathbf{1} & -\mathbf{1} & 0 & 0 \\ \mathbf{1} & \mathbf{1} & 0 & 0 \\ 0 & 0 & \mathbf{1} & -\mathbf{1} \\ 0 & 0 & \mathbf{1} & \mathbf{1} \end{bmatrix} \tag{25}$$

With no further assumptions, this transformation doesn't do much. However, if the spatial orbitals corresponding to $\alpha$ and $\beta$ are assumed equivalent, the transformed $\mathbf{H}'$ is

$$\mathbf{U^{-1}H'U} = \begin{bmatrix} (\epsilon_a - \epsilon_i) + (aj||ib) + (aj|ib) & 0 & (ab||ij) + (ab|ij) & 0 \\ 0 & (\epsilon_a - \epsilon_i) + (aj||ib) - (aj|ib) & 0 & (ab||ij) - (ab|ij) \\ (ab||ij)^* + (ab|ij)^* & 0 & (\epsilon_a - \epsilon_i) + (aj||ib)^* + (aj|ib)^* & 0 \\ 0 & (ab||ij)^* - (ab|ij)^* & 0 & (\epsilon_a - \epsilon_i) + (aj||ib)^* - (aj|ib)^* \end{bmatrix}$$

while the corresponding eigenvectors are

$$\mathbf{U^{-1}D'} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} + \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}_{\alpha\to\alpha} - \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} + \mathbf{d}^*_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} - \mathbf{d}^*_{\beta\to\beta} \end{bmatrix}$$

In this basis the equations clearly factorize into the following sets of eigenvalue equations:

$$\begin{bmatrix} (\epsilon_a - \epsilon_i) + (aj||ib) + (aj|ib) & (ab||ij) + (ab|ij) \\ (ab||ij)^* + (ab|ij)^* & (\epsilon_a - \epsilon_i) + (aj||ib)^* + (aj|ib)^* \end{bmatrix} \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} + \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} + \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} + \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} + \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} \tag{26}$$

$$\begin{bmatrix} (\epsilon_a - \epsilon_i) + (aj||ib) - (aj|ib) & (ab||ij) - (ab|ij) \\ (ab||ij)^* - (ab|ij)^* & (\epsilon_a - \epsilon_i) + (aj||ib)^* - (aj|ib)^* \end{bmatrix} \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} - \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} - \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} - \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} - \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} \tag{27}$$

Equation 27 defines the matrix ${}^3\mathbf{H}'$, the triplet instability matrix, while 26 defines the matrix ${}^1\mathbf{H}'$, which defines instabilities that mix singlet states. The only assumption made until this point in the analysis of $\mathbf{H}'$ was that the original solution was a complex RHF solution. No assumption was made about the outside space towards which the eigenvector points. Even still, the eigenvectors can be shown to have the form given in equations 26 and 27. Thus, the space in which the eigenvectors of $\mathbf{H}'$ point can only be that of UHF solutions.

Now, the other part of the general form of the stability matrix is $\mathbf{H}''$. The eigenvalue equation defining $\mathbf{D}''$ is,

$$\mathbf{H}''\mathbf{D}'' = \mathbf{H}'' \begin{bmatrix} \mathbf{d}_{\alpha\to\beta} \\ \mathbf{d}_{\beta\to\alpha} \\ \mathbf{d}^*_{\alpha\to\beta} \\ \mathbf{d}^*_{\beta\to\alpha} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\alpha\to\beta} \\ \mathbf{d}_{\beta\to\alpha} \\ \mathbf{d}^*_{\alpha\to\beta} \\ \mathbf{d}^*_{\beta\to\alpha} \end{bmatrix} \tag{28}$$

Equation 28 clearly factors into the following two eigenvalue equations:

$$\begin{array}{cc} & \begin{array}{cc} \beta\to\alpha & \alpha\to\beta \end{array} \\ \begin{array}{c} \beta\to\alpha \\ \alpha\to\beta \end{array} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & -(ab|ji) \\ -(ab|ji)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* \end{bmatrix} \end{array} \begin{bmatrix} \mathbf{d}_{\beta\to\alpha} \\ \mathbf{d}^*_{\alpha\to\beta} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\beta\to\alpha} \\ \mathbf{d}^*_{\alpha\to\beta} \end{bmatrix} \tag{29}$$

$$\begin{array}{cc} & \begin{array}{cc} \alpha\to\beta & \beta\to\alpha \end{array} \\ \begin{array}{c} \alpha\to\beta \\ \beta\to\alpha \end{array} & \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & -(ab|ji) \\ -(ab|ji)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* \end{bmatrix} \end{array} \begin{bmatrix} \mathbf{d}_{\alpha\to\beta} \\ \mathbf{d}^*_{\beta\to\alpha} \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d}_{\alpha\to\beta} \\ \mathbf{d}^*_{\beta\to\alpha} \end{bmatrix} \tag{30}$$

Equations 29 and 30 are complex conjugates in the general case. If however, the solution is an RHF solution, the spatial orbitals for $\alpha$ and $\beta$ spins are identical by definition. In this case, the matrices in both equation 29 and equation 30 are equivalent to the triplet instability matrix defined by Seeger and Pople:

$$\mathbf{^3H} = \begin{bmatrix} (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi) & -(ab|ji) \\ -(ab|ji)^* & (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - (aj|bi)^* \end{bmatrix} \tag{31}$$

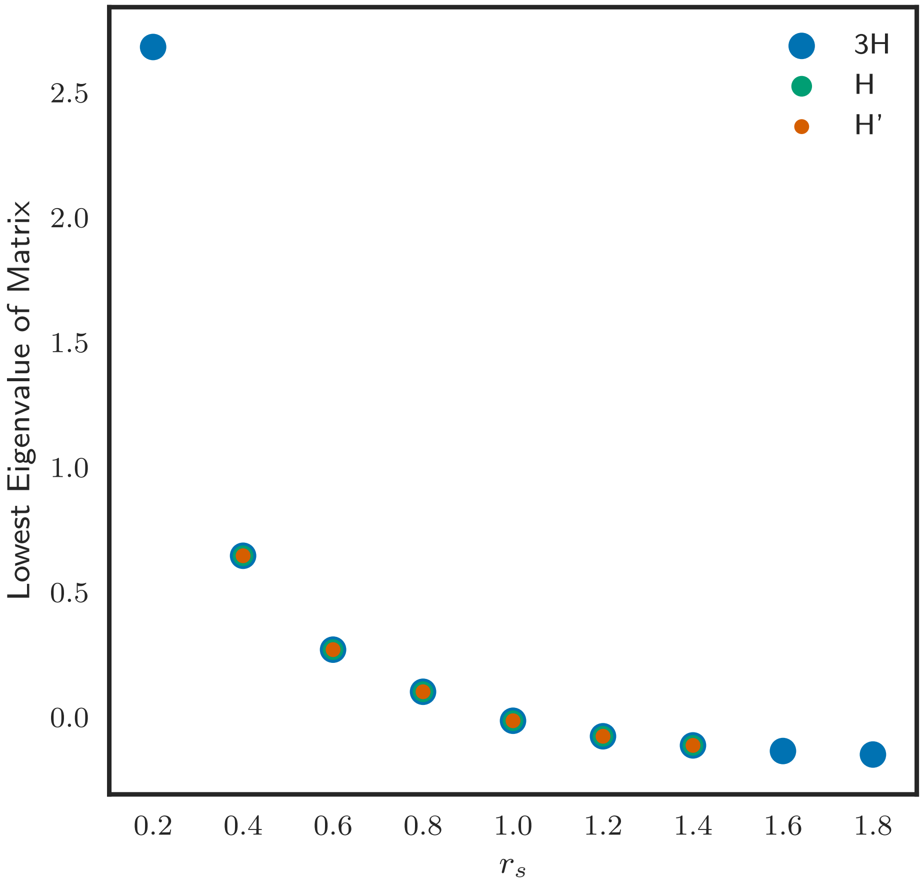
The implication of equations 29, 30 and 27 is that the following sets of eigenvectors comprise a degenerate manifold when the solution is an RHF wavefunction.

$$\begin{bmatrix} \mathbf{d}_{\beta\to\alpha} \\ \mathbf{d}^*_{\alpha\to\beta} \end{bmatrix}, \begin{bmatrix} \mathbf{d}_{\alpha\to\beta} \\ \mathbf{d}^*_{\beta\to\alpha} \end{bmatrix}, \begin{bmatrix} \mathbf{d}_{\alpha\to\alpha} - \mathbf{d}_{\beta\to\beta} \\ \mathbf{d}^*_{\alpha\to\alpha} - \mathbf{d}^*_{\beta\to\beta} \end{bmatrix} \tag{32}$$

As such, the RHF-GHF instability eigenvectors can always be transformed into eigenvectors having the form of the RHF-UHF instability. On the other hand, if the solution is not an RHF solution, this is not the case and the eigenvalues/vectors and corresponding instabilities are distinct.

## IV. NUMERICAL RESULT

To verify numerically, the diagonalization of the matrices $\mathbf{H}, \mathbf{H}'$ and $^3\mathbf{H}'$ were implemented independently of one another. No factorizations or simplifications were performed. The lowest eigenvalue of each is shown below for a constant number of K-points and a varying density. The results are equivalent within the convergence criteria of Davidson's Algorithm.




## V. 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`.

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