Notes on Hartree-Fock Stability of HEG

Evan Curtin

November 3, 2016

Homogeneous Electron Gas

The Fermi level, k_f, is (p. 30 of [Guiliani and Vignale(2005)])

$$k_f = \begin{cases} (3\pi^2 n)^{\frac{1}{3}} = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s a_0} & 3D \\\\ (2\pi n)^{\frac{1}{2}} = \frac{\sqrt{2}}{r_s a_0} & 2D \\\\ \frac{\pi}{2} n = \frac{\pi}{4 r_s a_0} & 1D \end{cases} \qquad (1)$$

The two electron integral is given by (eq. 12 of [Delyon et al.(2008)Delyon, Duneau, Bernu, and Holzmann] and p. 16 of [Guiliani and Vignale(2005)])

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

(2a)

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

(2b)

where Ω is the direct lattice volume and D is the dimensionality of the system. $\text{Ei}(x)$ denotes the exponential integral function. The orbital energies are given by

0

$$
\epsilon_{\vec{k},\sigma} =
\begin{cases}
\dfrac{\hbar^2 \vec{k}^2}{2m} - \left(\dfrac{L}{2\pi}\right)^D \displaystyle\int\limits_{|\vec{k}'|<\vec{k}_f} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle \, d\vec{k}' & \text{continuous (eq. 23 of [Yamada a} \\[2ex]
\dfrac{\hbar^2 \vec{k}^2}{2m} - \displaystyle\sum_{\vec{k}}^{|\vec{k}|<k_f} n_{\vec{k}\sigma} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle & \text{discrete (p. 80 of [Guiliani and V}
\end{cases}
$$
(3)

Where $n_{\vec{k}\sigma}$ is the occupation number of the state with momentum $\vec{k}$ and spin σ. Here we have used the relationship to relate the discrete and continuous quantities, (p. 15 of [Guiliani and Vignale(2005)]). Note the factor of $\frac{1}{L^D}$ is not in the discrete equation; I have moved that to the definition of the two electron integral for consistency with other resources. Note also that $L^D = \Omega$.

$$
\sum_{\vec{k}} (...) \xrightarrow{dk \ll L} \left(\frac{L}{2\pi} \right)^D \int (...) d\vec{k}
$$
(4)

The analytic form of the exchange energy is known in the continuous case. Let $y = \frac{k}{k_{F\sigma}}$. Equations 5 through 7 are from p. 81-82 of

[Guiliani and Vignale(2005)]. In 2 or 3 dimensions the exchange energy is,

$$\epsilon_{k\sigma}^{(x)} = -\frac{2e^2 k_{F\sigma}}{\pi} f_{ND}\left(\frac{k}{k_{F\sigma}}\right), \tag{5}$$

where in 3D, the function f_{3D} is given by

$$f_{3D}\left(y\right) = \frac{1}{2} + \frac{1-y^2}{4y} \ln\left|\frac{1+y}{1-y}\right|, \tag{6}$$

and in 2D, it is

$$f_{2D}\left(y\right) = \begin{cases} \mathbf{E}\left(y\right), & y \leq 1, \\ y\left[\mathbf{E}\left(\frac{1}{y}\right) - \left(1 - \frac{1}{y^2}\right)\mathbf{K}\left(\frac{1}{y}\right)\right], & y \geq 1. \end{cases} \tag{7}$$

The functions $\mathbf{K}(y)$ and $\mathbf{E}(y)$ are complete elliptic integrals of the first and second kind, respectively. These are implemented in SciPy as *scipy.special.ellipk* and *scipy.special.ellipe*. After a significant struggle, I have found that the author of the textbook[Guiliani and Vignale(2005)] and scipy/wolfram use a different definition of the complete elliptic

integral. I was able to reproduce the graphs on pages 82 and 83 of [Guiliani and Vignale(2005)] properly with $\mathbf{K}(x) \to \mathbf{K}(x^2)$ and

$\mathbf{E}(x) \to \mathbf{E}(x^2).$

Hartree-Fock Stability

The HF stability conditions (to my knowledge) were presented by Thouless [Thouless(1972)] (1st Ed. 1960). More general conditions were presented by Adams[Adams(1962)]. The stability condition is that the eigenvalues (λ) given by (p. 41 of [Thouless(1972)])

$$(\epsilon_a - \epsilon_i)C_{ai} + \sum_{j}^{occ} \sum_{b}^{vir} (\langle aj|ib \rangle - \langle aj|bi \rangle)C_{bj} + (\langle ab|ij \rangle - \langle ab|ji \rangle)C_{bj}^* = \lambda C_{ai}$$

(8)

$$(\epsilon_a - \epsilon_i)C_{ai}^* + \sum_{j}^{occ} \sum_{b}^{vir} (\langle ij|ab \rangle - \langle ij|ba \rangle)C_{bj} + (\langle ib|aj \rangle - \langle ib|ja \rangle)C_{bj}^* = \lambda C_{ai}^*,$$

(9)

are nonnegative. This is equivalent to the RPA oscillation frequencies being all real (p. 115 of [Thouless(1972)]). The RPA is a linearized approximation to Time-Dependent Hartree-Fock theory. These can be

written[Dunning(1967)][Seeger and Pople(1977)] in the following form:

$$^{1,3}\mathbf{H}' = \begin{bmatrix} ^{1,3}\mathbf{A}' & ^{1,3}\mathbf{B}' \\ \left(^{1,3}\mathbf{B}'\right)^* & \left(^{1,3}\mathbf{A}'\right)^* \end{bmatrix} \tag{10}$$

Where the $1, 3$ denote singlet and triplet states, respectively. $\mathbf{A}$, $\mathbf{B}$ have dimension $N_{occ} \times N_{vir}$ and are defined as follows:

$$^1A'_{i \to a, j \to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2\langle aj|ib \rangle - \langle aj|bi \rangle \tag{11a}$$

$$^3A'_{i \to a, j \to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj|bi \rangle \tag{11b}$$

$$^1B'_{i \to a, j \to b} = 2\langle ab|ij \rangle - \langle ab|ji \rangle \tag{11c}$$

$$^3B'_{i \to a, j \to b} = -\langle ab|ji \rangle \tag{11d}$$

The matrix given in Equation 10 represents the case of complex RHF stability in the space of complex RHF space ($^1\mathbf{H}$ - internal instability) and in the space of complex UHF space ($^3\mathbf{H}$ - triplet instability). Seeger and Pople [Seeger and Pople(1977)] give both more general formulae, and simplifications in special cases. Figure 1 is a reproduction of the stability conditions they developed, and more details can be found in the paper.

0

TABLE I. Matrices required to have positive semidefinite character as a necessary condition for stability of self-consistent solution of type X in the space of type Y.

X \ Y	Real RHF[a]	Complex RHF	Real UHF	Complex UHF	Real GHF	Complex GHF
Real RHF[a]	$^1\mathbf{A'}+{}^1\mathbf{B'}$	$^1\mathbf{A'}-{}^1\mathbf{B'}$	$^3\mathbf{A'}+{}^3\mathbf{B'}$			
Complex RHF		$^1\mathbf{H'}$		$^3\mathbf{H'}$		
Real UHF			$\mathbf{A'}+\mathbf{B'}$	$\mathbf{A'}-\mathbf{B'}$	$\mathbf{A''}+\mathbf{B''}$	
Complex UHF				$\mathbf{H'}$		$\mathbf{H''}$
Real GHF					$\mathbf{A}+\mathbf{B}$	$\mathbf{A}-\mathbf{B}$
Complex GHF						$\mathbf{H}$

[a]Singlet closed shell case ($n_\alpha = n_\beta$) only.

Figure 1: Hartree-Fock Stability conditions reproduced from Seeger & Pople [Seeger and Pople(1977)]

Davidson's Algorithm

Oftentimes we're interested only in the lowest or highest few eigenvalues of a large, symmetric matrix. Matrix eigenvalue problem operation counts scale as $\sim O(N^3)$ for an $N \times N$ matrix, while the memory requirement scales quadratically. Iterative subspace methods based off the Rayleigh-Ritz method are popular ways of dealing with this issue. The most famous are the Lanczos (hermitian) and Arnoldi (non-hermitian) algorithms, which build as their subspace a Krylov space. A more involved algorithm was proposed by Davidson[Davidson(1975)] and involves building a subspace with correction vectors to be described momentarily. But first, a few definitions are introduced to define the notation to be used.

We are interested in the lowest (or highest) k ($0 < k \leq N$) eigenvalue(s) of the $N \times N$ hermitian matrix, A,

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x} \tag{12}$$

We begin by guessing M ($M \geq k$) vectors, **v** which approximately span the space of the actual eigenvectors. Let **V** be the $N \times M$ matrix whose

columns are the approximate eigenvectors,

$$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}] \tag{13}$$

where care must be taken to ensure columns of $\mathbf{V}$ form an orthogonal set. We then transform our matrix into the subspace as follows,

$$\tilde{\mathbf{A}} = \mathbf{V}^\dagger \mathbf{A} \mathbf{V} \tag{14}$$

where the ~ will be used to denote entities in the subspace. $\tilde{\mathbf{A}}$ is an $M \times M$ matrix where $M \ll N$, and therefore we can use standard diagonalization routines to calculate the eigenvalues and eigenvectors in the subspace,

$$\tilde{\mathbf{A}}\tilde{\mathbf{x}} = \tilde{\lambda}\tilde{\mathbf{x}} \tag{15}$$

The subspace eigenpair $(\tilde{\lambda}_i, \tilde{\mathbf{x}}_i)$ is then used to create the *Ritz pair*, $(\lambda_i^R, \mathbf{x}_i^R)$. The ritz pair is the approximation to the exact eigenpair of the matrix, and is determined by

$$\mathbf{x_i} \approx \mathbf{x}_i^R = \mathbf{V}\tilde{\mathbf{x}}_i \tag{16a}$$

$$\lambda_i \approx \lambda_i^R = \tilde{\lambda}_i \tag{16b}$$

At any time, the quality of the approximation can be determined by calculating the norm of the *residue*,

$$\mathbf{r}_i = (\mathbf{A} - \lambda_i \mathbf{I}) \mathbf{x}_i^R \tag{17}$$

when $||\mathbf{r}_i||$ is smaller than a given tolerance for the desired k eigenpairs, the algorithm is finished and the current Ritz pairs are taken to be the eigenpairs. If this condition is not met, the subspace needs to be expanded. This is done by computing correction vectors, δ_i,

$$\delta_i = c_i \mathbf{r}_i \tag{18}$$

for $i = 0...l$ where l is the number of desired ritz pairs with $||\mathbf{r}_i||$ greater than the given tolerance. Corrections are only calculated for these Ritz pairs. The coefficient, c_i is a preconditioner. The original choice of c_i introduced by Davidson[Davidson(1975)] was diagonal preconditioning,

$$c_i = \frac{1}{\lambda_i \mathbf{I} - \mathbf{D}} \tag{19}$$

where $\mathbf{D}$ is the $N \times N$ diagonal matrix consisting of the diagonal elements of $\mathbf{A}$, and $\mathbf{I}$ is the identity matrix of the same size. It may help

convergence to use a modified version of this approach,

$$c_i = \frac{1}{\rho_i \mathbf{I} - \mathbf{D}} \tag{20}$$

where ρ_i is the *rayleigh quotient*, defined by

$$\rho_i = \frac{\mathbf{x}_i^{R\dagger} \mathbf{A} \mathbf{x}_i^R}{||\mathbf{x}_i^R||} \tag{21}$$

The rayleigh quotient from a physicist's perspective is $\rho_i = \langle \mathbf{x}_i^R | \mathbf{A} | \mathbf{x}_i^R \rangle$, which looks like the expectation value of $\mathbf{A}$ in the state $\mathbf{x}_i^R$. As $\mathbf{x}_i^R$ approaches the actual eigenstate of the system, the rayleigh quotient approaches the eigenvalue.

The correction vector is then added to $\mathbf{V}$ and the process is repeated. The correction vector must be normalized and orthogonalized to the columns of $\mathbf{V}$. The subspace size is therefore increased by l.

$$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}, \delta_1, \delta_2, ..., \delta_l] \tag{22a}$$

$$\mathbf{V} = orthonormalized(\mathbf{V}) \tag{22b}$$

$$M = M + l \tag{22c}$$

[H] [1] create $\mathbf{V}$ $i = 0$, *max iterations* $\tilde{\mathbf{A}} = \mathbf{V}^\dagger \mathbf{A} \mathbf{V}$ $\tilde{\lambda}, \tilde{\mathbf{x}} = \textit{eigensystem}(\tilde{\mathbf{A}})$ **sort** $\tilde{\lambda}, \tilde{\mathbf{x}}$ $i >$ **stringlen false** $j \leftarrow$ **patlen string**$(i) =$ **path**(j) $j \leftarrow j - 1$. $i \leftarrow i - 1$. **goto loop. close;** $i \leftarrow i + \max(\mathbf{delta}_1(\mathbf{string}(i)), \mathbf{delta}_2(j))$.

Code Layout

Hartree-Fock Stability of Homogeneous Electron Gas

Define Parameters
rs - Wigner-Seitz Radius
ndim - number of dimensoins
Nk - number of k-points per dim

Calc. Resulting Parameters
V, kf, a = 2kf
kgrid = linspace(-2kf,2kf,Nk)

Determine which kpoints are occupied and virtual, store indices in arrays occ, vir

Calculate energy of states store in e_state array

Determine Nocc, Nvir

Determine all excitations

Make k array
each row corresponds to state #
[kx, ky, kz]

For each excitation, difference in eigenvalue?

Find array of indices that sorts exc_energy in ascending order

Sort excitations

sort exc_energy

Map excitation index into occ and vir index

Indices of lowest exc_energy

Guess vectors

two_electron()
likely one version for each dimensionality
global const = pi/omega*2^D-1
takes: k1, k3
return: const/|k3-k1|^D-1

0

Figure 2: Layout of code implementation. Red boxes are python, blue are C++ and purple dotted lines require cython. Green are likely to be removed for speed

References

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

F. Delyon, M. Duneau, B. Bernu, and M. Holzmann, pp. 1–12 (2008), 0807.0770, URL http://arxiv.org/abs/0807.0770.

T. Yamada and S. Hirata, J. Chem. Phys. **143**, 114112 (2015), ISSN 0021-9606, URL http://dx.doi.org/10.1063/1.4929354http://scitation.aip.org/content/aip/journal/jcp/143/11/10.1063/1.4929354.

D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Dover, Mineola, NY, 1972), 2nd ed., ISBN 978-0-486-49357-2.

W. H. Adams, Phys. Rev. **127**, 1650 (1962), ISSN 0031-899X, URL http://link.aps.org/doi/10.1103/PhysRev.127.1650.

T. H. Dunning, J. Chem. Phys. **47**, 1735 (1967), ISSN 00219606, URL http://scitation.aip.org/content/aip/journal/jcp/47/5/10.1063/1.1712158.

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`.

E. R. Davidson, J. Comput. Phys. **17**, 87 (1975), ISSN 00219991, URL `http://linkinghub.elsevier.com/retrieve/pii/0021999175900650`.