# Generalized Hartree-Fock and Self-Consistent Field

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## 1  Formulating Hartree-Fock without Fock Orbitals

Standard Hartree-Fock is usually described in a first-quantization picture. While normally phrased in terms of $n$ occupied orbitals mixed from a set of $N$ available, this (unnecessarily) imposes a basis on the space of filled orbitals. When the product wavefunction is antisymmetrized by the Slater determinant, it actually loses uniqueness of what the 'factor' orbitals are. In the Hilbert space spanned by the available orbitals, there is an occupied subspace and a vacant subspace.

With this in mind, we will show the problem can be equivalently described by a density matrix $D$. Suppose we are given a set of $n$ molecular orbitals $|\psi_i\rangle$, each written as a sum of atomic orbitals $|\phi_j\rangle$:

$$|\psi_i\rangle = \sum_{j \leq N} U_{ij} |\phi_j\rangle$$

This gives us an $n \times N$ matrix $U$. The orthonormality of the $|\psi_i\rangle$ means we require that $U$ be unitary. This might seem awkward since $U$ isn't square, but it means that its rows are orthonormal. We can write down the density matrix as:

$$D_{ij} = \sum_{k \leq n} U^{\dagger}_{ik} U_{kj} = \sum_{k \leq n} |\psi_k\rangle \langle \psi_k|$$

The matrix $D$ is Hermitian with trace $n$, where the only eigenvalues are 0 (corresponding unoccupied states) or 1 (occupied). If we are given a Hamiltonian

$$H = \sum_{i,j \leq N} t_{ij}\, c^{\dagger}_i c_j + \sum_{i,j,k,\ell \leq N} u_{ijk\ell}\, c^{\dagger}_i c^{\dagger}_j c_k c_\ell$$

and we want to compute the energy of a state $|\psi\rangle$, we can actually do so purely in terms of $D$. Note that $u$ obeys 3 symmetries, $u_{ijkl} = u_{jikl} = u_{ijlk} = u_{klij}$. The first two arise because of symmetry in $c$'s, the last one arises because $H$ must be Hermitian. We can show that

$$\langle \psi|H|\psi\rangle = \sum_{ij} t_{ij} D_{ij} + \sum_{ijk\ell} u_{ijk\ell} \left( D_{i\ell} D_{jk} - D_{ik} D_{j\ell} \right)$$

by expanding $|\psi\rangle$ into $|\psi_i\rangle$ and then $|\phi_j\rangle$, and repeatedly applying $c_i |\phi_j\rangle = \delta_{ij} |\phi_j\rangle$ and contracting. Since we've now phrased things entirely in terms of $D_{ij}$, we see how the particulars of our $|\psi_i\rangle$ basis don't matter. If we changed mixed our occupied orbitals with an $n \times n$ unitary $M$:

$$|\psi'_i\rangle = M_{ij} |\psi_j\rangle = U'_{ij} |\phi_j\rangle$$

$$\implies D'_{ij} = \sum_{k \leq n} U'^{\dagger}_{ik} U'_{kj} = \sum_{k \leq n} (U^{\dagger}_{ik} M^{\dagger}_{ij})(M_{ij} U_{kj}) = \sum_{k \leq n} U^{\dagger}_{ik} U_{kj} = D_{ij}$$

so that our new density matrix $D'$ would be equal to our old density matrix $D$, and thus our Hartree-Fock energy unchanged. In this setting, we are optimizing $D$ over the space of Hermitian operators with $n$ eigenvalues of 1, and $(N - n)$ eigenvalues of zero.

## 2 Enforcing the constraints on $U$

We ultimately want the H-F state with 0 variation in the expectation of the energy, or

$$\delta \langle \boldsymbol{\psi}|H|\boldsymbol{\psi}\rangle = 0$$

but this needs to happen while respecting the constraints. Constraints are enforced via Lagrange multipliers $\lambda$, which we add to create a new optimization functional, $F$. The standard approach is to formulate the problem in terms of $U$, where the constraint is then unitarity. This leads to the following optimization problem:

$$0 = \delta F = \delta(\langle \boldsymbol{\psi}|H|\boldsymbol{\psi}\rangle + \delta \sum_{ij} \lambda_{ij}(\langle \psi_i|\psi_j\rangle - \mathbb{1}_{ij})$$

To put this in a usable form, distribute the $\delta$s, and then factor out a single $\langle\,\delta\psi|$:

$$\delta \langle \psi|H|\boldsymbol{\psi}\rangle + \sum_{ij} \lambda_{ij}(\langle\,\delta\psi_i|\psi_j\rangle + \langle \psi_i|\,\delta\psi_j\rangle)$$

$$= \delta \langle \psi|H|\boldsymbol{\psi}\rangle + \sum_{ij} \lambda_{ij} \langle\,\delta\psi_i|\psi_j\rangle + \lambda_{ij} \langle\,\delta\psi_j|\psi_i\rangle^*$$

$$= \delta \langle \psi|H|\boldsymbol{\psi}\rangle + \sum_{ij} \lambda_{ij} \langle\,\delta\psi_i|\psi_j\rangle + \lambda_{ji} \langle\,\delta\psi_i|\psi_j\rangle^*$$

Then expanding the variation of $H$:

$$\delta \langle \psi|H|\boldsymbol{\psi}\rangle = \delta\left(\sum_{ij} t_{ij}D_{ij} + \sum_{ijk\ell} u_{ijk\ell}\left(D_{i\ell}D_{jk} - D_{ik}D_{j\ell}\right)\right)$$

$$= \sum_{ij} t_{ij}\,\delta D_{ij} + \sum_{ijk\ell} u_{ijk\ell}\left(\,\delta D_{i\ell}D_{jk} + D_{i\ell}\,\delta D_{jk} - \delta D_{ik}D_{j\ell} - D_{ik}\,\delta D_{j\ell}\right)$$

We'd like to write this in the form $M_{ij}\,\delta D_{ij}$, so distribute and relabel indices in the $u$ term. We can also use the symmetry in $u$ and $D$ to further arrange indices.

$$\delta \langle \psi|H|\psi\rangle = \sum_{ij} t_{ij}\,\delta D_{ij} + \sum_{ijk\ell} u_{ijk\ell}\,\delta D_{i\ell}D_{jk} + u_{ijk\ell}D_{i\ell}\,\delta D_{jk} - u_{ijk\ell}\,\delta D_{ik}D_{j\ell} - u_{ijk\ell}D_{ik}\,\delta D_{j\ell}$$

$$= \sum_{ij} t_{ij}\,\delta D_{ij} + \sum_{ijk\ell} u_{i\ell kj}\,\delta D_{ij}D_{\ell k} + u_{kji\ell}D_{k\ell}\,\delta D_{ij} - u_{ikj\ell}\,\delta D_{ij}D_{k\ell} - u_{\ell jki}D_{\ell k}\,\delta D_{ij}$$

$$= \sum_{ij}\left(t_{ij} + \sum_{k\ell} u_{i\ell jk}D_{k\ell} + u_{i\ell jk}D_{k\ell} - u_{ikj\ell}D_{k\ell} - u_{ikj\ell}D_{k\ell}\right)\delta D_{ij}$$

$$= \sum_{ij}\left(t_{ij} + 2\sum_{k\ell}(u_{i\ell jk} - u_{ikj\ell})D_{k\ell}\right)\delta D_{ij}$$

Then:

$$\delta D = \delta\left(\sum_{i\leq n}|\psi_i\rangle\langle\psi_i|\right) = \sum_{i\leq n}|\,\delta\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\,\delta\psi_i|$$

Leaving the equation

$$\sum_{ij}\left(t_{ij} + 2\sum_{k\ell}(u_{i\ell jk} - u_{ikj\ell})D_{k\ell}\right)\left(\sum_{k\leq n}|\,\delta\psi_k\rangle\langle\psi_k| + |\psi_k\rangle\langle\,\delta\psi_k|\right)_{ij} + \sum_{ij}\lambda_{ij}\langle\,\delta\psi_i|\psi_j\rangle + \lambda_{ji}\langle\,\delta\psi_i|\psi_j\rangle^* = 0$$

Terms arising from $|\delta\psi_k\rangle$ are conjugate-linear to $\langle\delta\psi_k|$, and so they can be treated as two separate equations. Taking only the linear part leaves

$$\sum_{k\le n}\langle\delta\psi_k|_i\,|\psi_k\rangle_j+\sum_{ij}\lambda_{ij}\,\langle\delta\psi_i|\psi_j\rangle=0$$

We can simplify notation by treating the part in the middle as an operator:

$$F=\sum_{ij}\left(t_{ij}+2\sum_{k\ell}(u_{i\ell jk}-u_{ikj\ell})D_{k\ell}\right)$$

$$\sum_{k\le n}\langle\delta\psi_k|\,F\,|\psi_k\rangle+\sum_{ij}\lambda_{ij}\,\langle\delta\psi_i|\psi_j\rangle=0$$

This equation is satisfied (among many possibilities) by taking $|\psi_j\rangle$ to be eigenvectors of $F$, so that $\lambda$ is diagonal. So repeatedly diagonalizing $F$ and recomputing $F$ leads to the self-consistent field approach.

# 3   Enforcing the constraints on $D$

As we saw, however, we don't actually need to solve for $U$ (or equivalently, the $|\psi_k\rangle$): we can optimize directly on $D$. Now our constraints on $D$ can be written as

$$D^2-D=0$$

(All eigenvalues 0/1. Matrix equation, so $n^2/2$ constraints bc Hermitian.)

$$\mathrm{Tr}[D]-n=0$$

($n$ orbitals filled. 1 equation.)

We add Lagrange multipliers $\lambda_{ij}$ and $\Lambda$ for these two. The former leads to variation of

$$\sum_{ij}\delta(\lambda_{ij}D_{ik}D_{kj}-D_{ij})=\sum_{ij}\lambda_{ij}D_{ik}\,\delta D_{kj}+\lambda_{ij}D_{kj}\,\delta D_{ik}-\lambda_{ij}\,\delta D_{ij}$$

$$=\sum_{ij}\lambda_{jk}D_{ik}\,\delta D_{ij}+\lambda_{ik}D_{jk}\,\delta D_{ij}-\lambda_{ij}\,\delta D_{ij}=\sum_{ij}\left(\lambda_{jk}D_{ik}+\lambda_{ik}D_{jk}-\lambda_{ij}\right)\delta D_{ij}$$

Neglecting the $\Lambda\,\mathrm{Tr}[\delta D]$ for now, this leaves

$$0=\sum_{ij}F_{ij}\,\delta D_{ij}+\sum_{ij}\left(\lambda_{jk}D_{ik}+\lambda_{ik}D_{jk}-\lambda_{ij}\right)\delta D_{ij}$$

$$\implies\forall_{i,j},\quad 0=F_{ij}+D_{ik}\lambda_{kj}+\lambda_{ik}D_{kj}-\lambda_{ij}$$

Or with implicit matrix multiplication,

$$F+D\lambda+\lambda D-\lambda=0$$

By multiplying only on the left by $D$ and using $D^2=D$, we get

$$0=DF+D\lambda+D\lambda D-D\lambda=DF+D\lambda D$$

By multiplying only on the right:

$$0=FD+D\lambda D+\lambda D-\lambda D=FD+D\lambda D$$

$$\implies FD = -D\lambda D = DF$$

So that $D$ and $F$ commute. This shows us that $D$ must be diagonalized in a common basis as $F$. Thus, $\lambda$ can be as well. In the 0-eigenspace of $D$, we have $\lambda = F$, and in the 1-eigenspace, we have $\lambda = -F$. At this point it's clear that to satisfy the constraints, while minimizing energy, and keeping $D$ and $F$ commuting: diagonalize $F$, and build $D$ with $n$ eigenvectors that minimize the total energy.

It's worth noting that these $n$ should actually be the vectors $|\psi\rangle$ with the lowest total energy; perhaps a better estimate would be the vectors with the lowest $\langle\psi|H_{\text{eff}}|\psi\rangle$, as opposed to the vectors with the lowest $\langle\psi|F|\psi\rangle$. In practice, this will often be the same; picking the true minimal set of vectors is known to be NP-Hard, unfortunately.

# 4  Generalized Hartree-Fock

For the generalized, variable number case, we replace the density matrix $D$ with the anti-symmetric covariance matrix,

$$\Gamma_{k\ell} = \langle \frac{i}{2}[c_k, c_\ell]\rangle$$

where $c_{2k} = a_k^\dagger + a_k$ and $c_{2k+1} = -i(a_k^\dagger - a_k)$. The basis of the $c_k$ is more convenient to work with here, because it introduces more symmetry between otherwise disparate creation and annihilation operators. To highlight the differences from $D$, $\Gamma$ is twice the size now, at $2N \times 2N$. Instead of being real symmetric, $\Gamma$ is real anti-symmetric. And to correspond to a pure state, instead of $D(1 - D) = 0$, we require

$$\Gamma^2 + 1 = 0$$

forcing the eigenvalues to come in $\pm i$ pairs. In a similar way to how $D$ can be written as

$$D = UU^\dagger$$

where $U$ is an $n \times N$ unitary matrix, a $\Gamma$ can always be written as

$$\Gamma = OJO^T$$

where $O$ is an orthogonal matrix and $J = \oplus_{i \leq N} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$, the symplectic form. Our Hamiltonian is largely the same as before, but now written in terms of $c_k$. We allow $aa$ and $a^\dagger ca\dagger$ terms (and similar quartic terms), lifting our earlier restriction of number conservation. This means $t$ and $u$ now also have length $2N$ in each index. Evaluating the Hamiltonian in terms of $\Gamma$ proceeds similarly to before, but with a third quadratic term. Due to the extra symmetries from working $c_k$ instead of $a_k$, and the symmetries available in $u$, all three terms end up being identical.

$$\langle\boldsymbol{\psi}|H|\boldsymbol{\psi}\rangle = \sum_{ij} t_{ij}\Gamma_{ij} + 3\sum_{ijk\ell} u_{ijk\ell}\Gamma_{\ell k}\Gamma_{ij}$$

Expanding the variation leads to a generalized Fock matrix,

$$\delta\langle H\rangle = \sum_{ij} t_{ij}\,\delta\Gamma_{ij} + 3\sum_{ijk\ell} u_{ijk\ell}\,\delta\Gamma_{\ell k}\Gamma_{ij} + 3\sum_{ijk\ell} u_{ijk\ell}\Gamma_{\ell k}\,\delta\Gamma_{ij}$$

$$= \sum_{ij} t_{ij}\,\delta\Gamma_{ij} + 3\sum_{ijk\ell} u_{\ell kji}\,\delta\Gamma_{ij}\Gamma_{\ell k} + +3\sum_{ijk\ell} u_{ijk\ell}\Gamma_{\ell k}\,\delta\Gamma_{ij}$$

$$= \left(\sum_{ij} t_{ij} + 3\sum_{ijk\ell} u_{ijkl}\Gamma_{\ell k} + 3\sum_{ijk\ell} u_{ijk\ell}\Gamma_{\ell k}\right)\delta\Gamma_{ij}$$

$$= \left( \sum_{ij} t_{ij} + 6 \sum_{ijk\ell} u_{ijkl}\Gamma_{\ell k} \right) \delta\Gamma_{ij}$$

$$\implies F_{ij} = t_{ij} + 6 \sum_{k\ell} u_{ijkl}\Gamma_{\ell k}$$

The constraint that $\Gamma^2 + 1 = 0$ enters as

$$0 = \delta \left( \sum_{ij} \lambda_{ij}\Gamma_{ik}\Gamma_{kj} + \lambda_{ij} \right) = \sum_{ij} \lambda_{ij}\, \delta\Gamma_{ik}\Gamma_{kj} + \sum_{ij} \lambda_{ij}\Gamma_{ik}\, \delta\Gamma_{kj}$$

$$= \sum_{ij} \lambda_{ik}\, \delta\Gamma_{ij}\Gamma_{jk} + \sum_{ij} \lambda_{kj}\Gamma_{ki}\, \delta\Gamma_{ij} = \sum_{ij} \left( -\Gamma_{ik}\lambda_{kj} - \lambda_{ik}\Gamma_{kj} \right) \delta\Gamma_{ij}$$

The zero-variation equations thus reduce to

$$F + \Gamma\lambda + \lambda\Gamma = 0$$

To solve, use similar tricks as before. Multiply by $\Gamma$ on the left, and use $\Gamma^2 = -1$:

$$\Gamma F - \lambda + \Gamma\lambda\Gamma = 0$$

And when we multiply on the right:

$$F\Gamma + \Gamma\lambda\Gamma - \lambda = 0$$

$$\implies F\Gamma = \Gamma F$$

leading us again to conclude that our matrix (before $D$, now $\Gamma$) can be commonly diagonalized with $F$. Before, we were choosing $n$ eigenvectors to give eigenvalue 1, and the remaining $N-n$ to give 0. Now, the eigenvectors of $F$ are naturally paired up into complex conjugates, and we have to choose which in each pair will get an eigenvalue of $i$ in $\Gamma$, and which gets an eigenvalue of $-i$. Instead of having a single real Fock energy, we have two conjugate purely imaginary eigenvalues, $\pm i\epsilon$. Now the analog of choosing $n$ orbitals based on their Fock energies, is choosing to assign $+i$ to the vector with positive imaginary eigenvalue, and vice versa, so that

$$\mathrm{Tr}[F\Gamma] = \sum (+i)(+i\epsilon) + (-i)(-i\epsilon) = \sum -2\epsilon$$

is as small as possible. If instead we would like to choose based on energies of $H$, we use $H = (T+F)/2$, optionally flipping the sign on eigenvector $v$ if $ivTv^* > \epsilon$. So, the corresponding procedure for self-consistent field in the gHF form:

1. Transform from the $a$, $a^\dagger$ basis into $c$, building appropriate $t$ and $u$.

2. Choose an initial $\Gamma$

3. Compute $F = t_{ij} + 6 \sum_{k\ell} u_{ijkl}\Gamma_{\ell k}$

4. Diagonalize $F$

5. Replace an eigenvalue $\pm i\epsilon$ with $\pm i$

6. The resulting matrix is the new $\Gamma$, proceed to step 3.

In practice, diagonalizing $F$ directly with a generic eigenvector library will waste time, since it has the anti-symmetric structure, and so a 2x redundancy in the eigenvectors and eigenvalues. Unless your linear algebra library has direct support for anti-symmetric matrices, it might be faster to diagonalize $iF$, which will be Hermitian (although, complex).

# 5 Recovering the energy

Once we have $\Gamma$ from the above, the energy is computed as

$$F = t_{ij} + 6 \sum_{k\ell} u_{ijkl} \Gamma_{\ell k}$$

$$E_{final} = E_0 + \frac{1}{4} \operatorname{Tr}[\Gamma(t + F)]$$

where $E_0$ is the constant term in the Hamiltonian. The factor of $\frac{1}{4}$ is there (as compared to the $\frac{1}{2}$ before) because we've doubled the number of modes when we went to the Majorana basis. If are we given $U$ and $T$ in the creation/annihilation basis, then when we switch to Majorana modes and antisymmetrize, $U$ will contribute to $t$ (the 'diagonal terms'), and both $U$ and $T$ will contribute to $E_0$.