Hartree-Fock Theory

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HF in brief I

For an N-electron Slater determinant wavefunction:

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

$$\equiv |\chi_i \chi_j \cdots \chi_k\rangle$$

we will show that the energy is written as:

$$\boxed{\langle \Psi | H | \Psi \rangle = \sum_i \langle i | h | i \rangle + \sum_{i>j} [\langle ij | ij \rangle - \langle ij | ji \rangle]}$$

HF in brief II

The Hartree–Fock approximation to the ground state energy is found by varying the spin-orbitals $\{\chi_i\}$ to minimize the energy:

$$E_0 \leq E^{\mathrm{HF}} = \min \langle \Psi | H | \Psi \rangle$$

subject to the conditions that the spin-orbitals are orthonormal. As before, but with many more steps, the variational principle leads to the following equations for the spin-orbitals

$$f(i)\chi(x_i) = \epsilon \chi(x_i)$$

where $f(i)$ is an effective operator called the *Fock operator*

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i)$$

HF in brief III

where $v^{\mathrm{HF}}(i)$ is the Hartree–Fock *effective* potential that depends on the solutions to the above equations. So we must solve these equations self-consistently: Make a guess for the solutions; construct the potential $v^{\mathrm{HF}}(i)$ from this guess; solve the Fock equations; get new solutions; and repeat till convergence.

Matrix Elements I

We will require a number of matrix elements for Hartree–Fock and post-HF methods. You have already seen these when we worked through the H_2 system. The rules for general N-electron matrix elements are very similar to those for the 2-electron case; the only complication is the added complication brought out by the algebric complexity of the N-electron Slater determinants.

Szabo & Ostlund describes the calculation of these matrix elements in some detail and I expect you to look through those derivations in case the ones presented here are not clear enough for you. A problem with the S&O derivations is that they are too long. More on this soon.

Matrix Elements II

We are after matrix elements of the form

$$\langle K|\mathcal{O}_1|L\rangle \quad \text{and} \quad \langle K|\mathcal{O}_2|L\rangle$$

where $|K/L\rangle$ are N-electron Slater determinant wavefunctions. In general, the N-electron determinant $|\Psi\rangle$ can be written as

$$|\Psi\rangle = \frac{1}{\sqrt{N!}}\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$

Here $\mathcal{P}_u$ is a permutation operator that can be expressed as a product of binary permutations:

$$\mathcal{P}_u = \mathcal{P}_{ij}\mathcal{P}_{kl}\cdots$$

and σ_u is phase factor that is $+1$ if $\mathcal{P}_u$ contains an even number of binary permutations and is -1 otherwise.

Matrix Elements III

Binary permutation operators swap electronic states:

$$\begin{aligned}\mathcal{P}_{ij}|\phi_i\phi_j\cdots\phi_q\rangle &\equiv \mathcal{P}_{ij}|ijkl\cdots q\rangle \\ &= -|{\color{blue}ji}kl\cdots q\rangle.\end{aligned}$$

In the Schrodinger picture this can be thought of as swapping the electronic labels 1 and 2. Here are some useful properties of these operators:

- Idempotent: $\mathcal{P}_{ij}\mathcal{P}_{ij} = \hat{I}$.
- Hermitian: ${\mathcal{P}_{ij}}^\dagger = \mathcal{P}_{ij}$.
- The permutation operators do not generally commute in a Hilbert space with more than two electrons.
- Commute with the Hamiltonian: $\mathcal{P}_{ij}\hat{H} = \hat{H}\mathcal{P}_{ij}$.

Matrix Elements IV

We now define the antisymmetrization operator $\mathcal{A}$ as

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u$$

Recall that the Hartree product (HP) is defined as $\Psi^{\mathrm{HP}} = \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$, so we will often write $|\Psi\rangle$ more compactly as

$$|\Psi\rangle = \mathcal{A}\Psi^{\mathrm{HP}}.$$

Matrix Elements V

The algebra of permutation operators is described in detail in *Quantum Mechanics*, Ch. XIV, Vol. 2, by Cohen-Tannoudji *et al.*. Read this before attempting the following.

Q: Show the following results:

- The operator $\mathcal{A}$ commutes with the Hamiltonian and any many-electron operator that is completely symmetric under exchange of indices.
- The operator $\mathcal{A}$ is Hermitian: $\mathcal{A} = \mathcal{A}^{\dagger}$
- $\mathcal{A}\mathcal{A} = \sqrt{N!}\mathcal{A}$.
- $\mathcal{A}\hat{H} = \hat{H}\mathcal{A}$.

Matrix Elements VI

These properties allow us to significantly simplify matrix element evaluation, for consider

$$\langle \Psi | H | \Psi \rangle = (N!)^{-1} \sum_{u=1}^{N!} \sigma_u \sum_{w=1}^{N!} \sigma_w \times \int dx_1 \cdots dx_N \\ \mathcal{P}_u \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}^* \; H \; \mathcal{P}_w \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$

Handling two permutation operators is tedious. S&O do it and you should see how these proofs go, but we will use the following theorem to make the proofs significantly easier.

Matrix Elements VII

Theorem

$$\langle \Psi | H | \Phi \rangle = \sqrt{N!} \langle \Psi^{HP} | H | \Phi \rangle .$$

Proof:

$$\begin{aligned} \langle \Psi | H | \Phi \rangle &= \langle \mathcal{A} \Psi^{\mathrm{HP}} | H | \mathcal{A} \Phi^{\mathrm{HP}} \rangle \\ &= \langle \Psi^{\mathrm{HP}} | H | \mathcal{A} \mathcal{A} \Phi^{\mathrm{HP}} \rangle \\ &= \langle \Psi^{\mathrm{HP}} | H | \sqrt{N!} \mathcal{A} \Phi^{\mathrm{HP}} \rangle \\ &= \sqrt{N!} \langle \Psi^{\mathrm{HP}} | H | \Phi \rangle \end{aligned}$$

Matrix Elements VIII

Using the above theorem we can write

$$\langle\Psi|H|\Psi\rangle = \sqrt{N!}\int dx_1\cdots dx_N$$
$$\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$
$$H\,\frac{1}{\sqrt{N!}}\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$

There is only one permutation operator to deal with here.
Now we will consider a series of cases with the operator being: C (a C-number), $\sum_i h(i)$, and $\sum_{i>j} r_{ij}^{-1}$. Additionally, we will consider matrix elements involving Ψ and singly and doubly excited determinants: Ψ_i^a and Ψ_{ij}^{ab}. We will not consider higher excitations as the rules for those follow from these.

Matrix Elements IX

C: C-number

$$\langle\Psi|C|\Psi\rangle =$$

$$C\langle\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}\rangle$$

- $\mathcal{P}_u = E$: we get $C\langle 1|1\rangle\langle 2|2\rangle\cdots = C$.
- $\mathcal{P}_u = \mathcal{P}_{12}$: we get $-C\langle 1|2\rangle\langle 1|2\rangle\langle 3|3\rangle\cdots = 0$.
- Similarly for other permutations.

Therefore, $\langle\Psi|C|\Psi\rangle = C$. Which also means that $|\Psi\rangle$ as defined is normalized!

Matrix Elements X

$\sum_{\mathbf{i}} \mathbf{h(i)}$: One-electron operator
Consider $h(i)$ only:

$\langle\Psi|h(i)|\Psi\rangle =$

$$\langle\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}|h(i)|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}\rangle$$

- $\mathcal{P}_u = E$: $\langle 1|1\rangle\cdots\langle i|h(i)|i\rangle\cdots = \langle i|h|i\rangle$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle\cdots\langle i|h(i)|j\rangle\cdots\langle j|i\rangle\cdots = 0$.
- Similarly, any other permutation gives a 0.

Therefore, $\langle\Psi|h(i)|\Psi\rangle = \langle i|h|i\rangle$, and

$$\langle\Psi|\sum_i h(i)|\Psi\rangle = \sum_i\langle i|h|i\rangle = \sum_i h_{ii}.$$

Matrix Elements XI

$\sum_{\mathbf{i>j}} \mathbf{r_{ij}^{-1}}$: two-electron operator
Consider r_{ij}^{-1} only:

$$\langle \Psi | r_{ij}^{-1} | \Psi \rangle =$$

$$\langle \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\} | r_{ij}^{-1} | \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\} \rangle$$

- $\mathcal{P}_u = E$: $\langle 1|1\rangle \cdots \langle i(i)j(j)|r_{ij}^{-1}|i(i)j(j)\rangle \cdots = \langle ij|ij\rangle = (ii|jj)$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle \cdots \langle i(i)j(j)|r_{ij}^{-1}|i(j)j(i)\rangle \cdots = -\langle ij|ji\rangle = -(ij|ji)$.
- Any other permutation gives a 0.

Matrix Elements XII

Therefore, $\langle\Psi|r_{ij}^{-1}|\Psi\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle$, and

$$\langle\Psi|\sum_{i>j} r_{ij}^{-1}|\Psi\rangle = \sum_{i>j}[\langle ij|ij\rangle - \langle ij|ji\rangle] = \sum_{i>j}\langle ij||ij\rangle.$$

Matrix Elements XIII

Putting these results together we can now write down the energy expression of any single-determinant wavefunction $|\Psi\rangle$:

$$\begin{aligned}\langle\Psi|H|\Psi\rangle &= \sum_i \langle i|h|i\rangle + \sum_{i>j}[\langle ij|ij\rangle - \langle ij|ji\rangle] \\ &= \sum_i \langle i|h|i\rangle + \sum_{i>j}[(ii|jj) - (ij|ji)]\end{aligned}$$

Matrix Elements XIV

Singly excited states: $\Psi_i^a = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}$

$$\langle \Psi_i^a | h | \Psi \rangle =$$

$$\langle \{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\} | h | \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1}\cdots\}\rangle$$

Contributions from $h = \sum_j h(j)$ must eliminate the zero overlap term $\langle \chi_a | \chi_i \rangle$. The only term that can do this is $h(i)$. Now consider the cases:

- $\mathcal{P}_u = E$: $\langle 1|1\rangle \cdots \langle a(i)|h(i)|i(i)\rangle \cdots = \langle a|h|i\rangle = h_{ai}$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle \cdots \langle a(i)|h(i)|j(i)\rangle \cdots \langle j(j)|i(j)\rangle \cdots = 0$.
- All other permutations result in a 0.

Therefore $\langle \Psi_i^a | h | \Psi \rangle = \langle a|h|i\rangle = h_{ai}$.

Matrix Elements XV

Singly excited states: $\Psi_i^a = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}$

$$\langle\Psi_i^a|\sum_{kl} r_{kl}^{-1}|\Psi\rangle =$$

$$\langle\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}|\sum_{kl} r_{kl}^{-1}|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1}\cdots\}\rangle$$

Once again, to eliminate the zero overlap term $\langle\chi_a|\chi_i\rangle$ we must have either $k = i$ or $l = i$. It doesn't matter which as these are dummy variables. So let us choose $k = i$ and $l = j$ (j goes over all electrons). We have effectively made the replacement: $\sum_{kl} r_{kl}^{-1} \to \sum_j r_{ij}^{-1}$.

Matrix Elements XVI

- $\mathcal{P}_u = E$:

$$\langle\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1} \cdots \chi_j \cdots\}|\sum_j \frac{1}{r_{ij}}|\{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1} \cdots \chi_j \cdots\}\rangle$$

$$= \sum_j \langle \chi_a(i)\chi_j(j)|r_{ij}^{-1}|\chi_i(i)\chi_j(j)\rangle \equiv \sum_j \langle aj|ij\rangle = \sum_j (ai|jj)$$

- $\mathcal{P}_u = \mathcal{P}_{ij}$:

$$-\langle\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1} \cdots \chi_j \cdots\}|\sum_j \frac{1}{r_{ij}}|\{\chi_1 \cdots \chi_{i-1}\chi_j\chi_{i+1} \cdots \chi_i \cdots$$

$$= -\sum_j \langle \chi_a(i)\chi_j(j)|r_{ij}^{-1}|\chi_j(i)\chi_i(j)\rangle \equiv -\sum_j \langle aj|ji\rangle = -\sum_j (aj|ji)$$

Matrix Elements XVII

- All other permutations — those that do not involve i — will result in a 0. Show it!

So we have the result:

$$\boxed{\begin{aligned}\langle \Psi_i^a | \sum_{kl} \frac{1}{r_{kl}} | \Psi \rangle &= \sum_j [\langle aj | ij \rangle - \langle aj | ji \rangle] \\ &= \sum_j [(ai | jj) - (aj | ji)]\end{aligned}}$$

And, including the one-electron terms, we have:

Matrix Elements XVIII

$$
\begin{aligned}
\langle \Psi_i^a | H | \Psi \rangle &= \langle a|h|i\rangle + \sum_j [\langle aj|ij\rangle - \langle aj|ji\rangle] \\
&= \langle a|h|i\rangle + \sum_j [(ai|jj) - (aj|ji)]
\end{aligned}
$$

Matrix Elements XIX

Doubly excited states:

$$\Psi_{ij}^{ab} = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\chi_{j-1}\chi_b\chi_{j+1}\cdots\}$$

Q: Show that

- There are no contributions from the one-electron operator $h = \sum_i h(i)$.
- The two-electron operator $\sum_{kl}\frac{1}{r_{kl}}$ results in single contribution: $(ai|bj) - (aj|bi)$. No summations here.

Consequently,

$$\boxed{\langle\Psi_{ij}^{ab}|\sum_{kl}\frac{1}{r_{kl}}|\Psi\rangle = \langle ab|ij\rangle - \langle ab|ji\rangle = (ai|bj) - (aj|bi)}$$

Matrix Elements XX

This time there is no contribution from the one-electron part, so

$$\boxed{\begin{aligned}\langle\Psi_{ij}^{ab}|H|\Psi\rangle &= \langle ab|ij\rangle - \langle ab|ji\rangle\\ &= (ai|bj) - (aj|bi)\end{aligned}}$$

Introduction I

We now know that the energy of a single determinant $|\Psi\rangle$ can be written as

$$\begin{aligned}\langle\Psi|H|\Psi\rangle &= \sum_i \langle i|h|i\rangle + \sum_{i>j}[\langle ij|ij\rangle - \langle ij|ji\rangle] \\ &= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij}[\langle ij|ij\rangle - \langle ij|ji\rangle]\end{aligned}$$

The problem here is that we still do not know what the spin-orbitals (SOs) χ_i are or how to calculate them.
Here, the variational principle comes to our aid and allows us to re-cast this optimization problem as an eigenvalue equation. More

Introduction II

importantly, it will turn out to be a *one-electron* eigenvalue equation of the form

$$\hat{f}|\chi_m\rangle = \epsilon_m|\chi_m\rangle.$$

We will show that the one-electron Fock operator $\hat{f}$ is defined as

$$f(1) = h(1) + v^{\mathrm{HF}}(1),$$

where $h(1)$ is the usual one-electon Hamiltonian and v^{HF} is the Hartree–Fock effective potential that is defined as follows:

$$v^{\mathrm{HF}}(1) = \sum_i [\mathcal{J}_i(1) - \mathcal{K}_i(1)],$$

Introduction III

where the Coulomb and exchange operators are defined as

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right]\chi_m(1)$$

$$\mathcal{K}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right]\chi_i(1)$$

Introduction IV

Have a look at the form of the Coulomb operator:

$$\mathcal{J}_i(1) = \int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}} = \int dx_2 \frac{\rho_i(2)}{r_12}.$$

This is the Coulomb potential of the electron in orbital χ_i. So in the expression

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right] \chi_m(1)$$

electron 1 in orbital χ_i does not see the potential from a point electron at 2, but rather, interacts with this electron via the classical Coulomb potential arising from the electronic density.

Introduction V

Of course, this is a quantum system, so we also have an exchange interaction. Unlike the Coulomb interaction, this one has a complex form: the exchange operator includes the orbital on which it is operating.

$$\begin{aligned}\mathcal{K}_i(1)\chi_m(1) &= \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right]\chi_i(1)\\ &= \left[\int dx_2 \frac{\chi_i^*(2)\ \mathcal{P}_{12}\ \chi_i(2)}{r_{12}}\right]\chi_m(1)\end{aligned}$$

where, in the second form, we have used the permutation operator $\mathcal{P}_{12}$ to perform the exchange. This also allows us to write the operator $\mathcal{K}_i$ in more conventional form.

Introduction VI

Because the electrons do not interact directly with other electrons, but rather, see the average potential (Coulomb and exchange) from other electrons, Hartree–Fock theory is called a *mean-field theory*. Here is the Fock Hamiltonian again:

$$\boxed{f(1) = h(1) + \sum_i \int dx_2 \frac{\chi_i^*(2)\ (1 - \mathcal{P}_{12})\ \chi_i(2)}{r_{12}}}$$

We will now prove this and demonstrate the the SOs χ_a are eigenstates of this Fock operator. (They are not eigenstates of the Hamiltonian $\mathcal{H}$!)

Functionals I

Revision of functionals and functional derivatives.
See Appendix B in Ullrich's *Time-Dependent Density-Functional Theory* for an overview of this topic. Or else, a mathematical physics book such as the one by Arfken.
Definition of the functional derivative:

$$\boxed{\frac{\delta F[\phi]}{\delta \phi(y)} = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \{ F[\phi(x) + \epsilon \delta(x-y)] - F[\phi(x)] \}.}$$

Functionals II

Alternative definition:
If $F[y]$ is a functional of $y(x)$, and if $\delta y(x)$ is some arbitrary variation in y, then we may define $dF = F[y + \delta y] - F[y]$. The functional derivative of $F[y]$ w.r.t. $y(x)$ is then defined via

$$dF = \int dx \frac{\delta F[y]}{\delta y(x)} \delta y(x).$$

The latter definition is often more useful than the first, though the first is the one we should fall back on in case of doubt.

Functionals III

$$F[y] = \int y(x)^2 dx.$$

Q: Show that

$$\frac{\delta F[y]}{\delta y(x)} = 2y(x).$$

Use both definitions to do this.

Functionals IV

Useful results:

- $F[\phi] = g(\phi(x))$

$$\frac{\delta F[\phi]}{\delta \phi(y)} = \frac{\delta g(\phi(x))}{\delta \phi(y)} = g'(\phi(x))\delta(x-y).$$

- $F[\phi] = \int g(\phi(x))dx$

$$\frac{\delta F[\phi]}{\delta \phi(y)} = g'(\phi(y)).$$

- $F[\phi] = \int g(\nabla\phi(x))dx$

$$\frac{\delta F[\phi]}{\delta \phi(y)} = -\nabla g'(\nabla\phi(y)).$$

The last result follows using integration by parts. Using the above you can derive the Euler–Lagrange equations for the functional $F[x, y(x), y'(x)]$. Try it.

Functionals V

Product Rule:

$$\boxed{\frac{\delta F[\phi]G[\phi]}{\delta\phi(y)} = F[\phi]\frac{\delta G[\phi]}{\delta\phi(y)} + \frac{\delta F[\phi]}{\delta\phi(y)}G[\phi].}$$

Chain Rule:

$$\boxed{\frac{\delta F[\gamma[\phi]]}{\delta\phi(y)} = \int dy'\,\frac{\delta F[\gamma]}{\delta\gamma(y')}\frac{\delta\gamma(y')}{\delta\phi(y)}.}$$

Functionals VI

When we write the energy in terms of the spin-orbitals we will end up with expressions that involve both χ_i and its complex conjugate χ_i^*. Mathematically these are independent functions. One way of looking at this is to consider that the real and imaginary parts of the spin-orbitals can be varied independently.

A consequence of this is that the energy functional can be thought of as being a functional of both χ_i and χ_i^*. So the variation can be carried out w.r.t. either, or both. But as the Hamiltonian is Hermitian, only one need be considered, and it is usually more convenient to conduct the variation w.r.t. χ_i^*.

HF: Derivation I

We need to minimize:

$$E_0[\{\chi_i\}] = \langle\Psi|H|\Psi\rangle = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}[\langle ij|ij\rangle - \langle ij|ji\rangle]$$

w.r.t. the $\{\chi_i\}$ subject to the conditions $\langle\chi_i|\chi_j\rangle = \delta_{ij}$. The orthonormality condition can be included using the method of Lagrange multipliers, i.e., we minimize the functional

$$\mathcal{L}[\{\chi_i\}] = E_0[\{\chi_i\}] - \sum_{ij}^{N} \epsilon_{ji}\left(\langle\chi_i|\chi_j\rangle - \delta_{ij}\right)$$

HF: Derivation II

First a result we will need:

Q: We will impose the condition that $\mathcal{L}$ is real. This is reasonable as the energy is real. Show that this condition implies $\epsilon_{ji} = \epsilon_{ij}^*$, i.e., the Lagrange multiplier matrix is Hermitian.

Hint: Set $s_{ij} = \langle \chi_i | \chi_j \rangle - \delta_{ij}$ and consider the real sum $\sum_{ij} \epsilon_{ji} s_{ij}$. Use the fact that $s_{ij} = s_{ji}^*$ to show the required result.

HF: Derivation III

$$\mathcal{L}[\{\chi_i\}] = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}[\langle ij|ij\rangle - \langle ij|ji\rangle] - \sum_{ij}^{N} \epsilon_{ji}\left(\langle \chi_i|\chi_j\rangle - \delta_{ij}\right)$$

$$\begin{aligned}
0 &= \frac{\delta \mathcal{L}}{\delta\langle k|} \\
&= h|k\rangle + \frac{1}{2}\sum_j \langle j|\frac{1}{r_{12}}|j\rangle|k\rangle + \frac{1}{2}\sum_i \langle i|\frac{1}{r_{12}}|i\rangle|k\rangle \\
&- \frac{1}{2}\sum_j \langle j|\frac{1}{r_{12}}|k\rangle|j\rangle - \frac{1}{2}\sum_i \langle i|\frac{1}{r_{12}}|k\rangle|i\rangle - \sum_j \epsilon_{jk}|j\rangle \\
&= h|k\rangle + \sum_i \langle i|\frac{1}{r_{12}}|i\rangle|k\rangle - \sum_i \langle i|\frac{1}{r_{12}}|k\rangle|i\rangle - \sum_i \epsilon_{ik}|i\rangle
\end{aligned}$$

HF: Derivation IV

We can write this as

$$
\begin{aligned}
\sum_i \epsilon_{ik}|i\rangle &= h|k\rangle + \sum_i \langle i|\frac{1}{r_{12}}|i\rangle|k\rangle - \sum_i \langle i|\frac{1}{r_{12}}|k\rangle|i\rangle \\
&= h|k\rangle + \sum_i \langle i|\frac{1}{r_{12}}(1-\mathcal{P}_{ik})|i\rangle|k\rangle \\
&= \left(h + \sum_i \langle i|\frac{1}{r_{12}}(1-\mathcal{P}_{ik})|i\rangle\right)|k\rangle \\
&= f|k\rangle
\end{aligned}
$$

where $\mathcal{P}_{ik}$ is the permutation operator that permutes the states i and k, and the last step defines the Fock operator.

HF: Derivation V

We now have the Fock equations, but they are in an unusual form:

$$f|k\rangle = \sum_i \epsilon_{ik}|i\rangle,$$

or

$$\langle i|f|k\rangle = \epsilon_{ik}.$$

What we'd like to do is re-cast these equations in their *canonical form* in which $\epsilon_{ik} = \epsilon_k \delta_{ik}$. How can we do this?

HF: Derivation VI

Before moving on let us analyse the Fock operator f:

$$f = h + \sum_i \langle i | \frac{1}{r_{12}} (1 - \mathcal{P}_{ik}) | i \rangle .$$

This can be written as

$$\begin{aligned} f(1) &= h(1) + \sum_i \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}} - \int dx_2 \frac{\chi_i^*(2)\ \mathcal{P}_{12}\ \chi_i(2)}{r_{12}} \right] \\ &= h(1) + \sum_i \left[\mathcal{J}_i(1) - \mathcal{K}_i(1) \right] \\ &= h(1) + v^{\mathrm{HF}}(1), \end{aligned}$$

HF: Derivation VII

where $h(1)$ is the usual one-electron Hamiltonian and v^{HF} is the Hartree–Fock effective potential that is defined as follows:

$$v^{\mathrm{HF}}(1) = \sum_i \left[\mathcal{J}_i(1) - \mathcal{K}_i(1)\right],$$

and the Coulomb and exchange operators are defined as

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right]\chi_m(1)$$
$$\mathcal{K}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right]\chi_i(1).$$

HF: Derivation VIII

Have a look at the form of the Coulomb operator:

$$\mathcal{J}_i(1) = \int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}} = \int dx_2 \frac{\rho_i(x_2)}{r_1 2},$$

where $\rho_i = \chi_i * \chi_i$ is the density associated with spin-orbital i. This is the Coulomb potential of the electron in orbital χ_i, so in the expression

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right] \chi_m(1)$$

electron 1 in orbital χ_m does not see the $1/r_{12}$ potential from a point electron at r_2, but rather, interacts with this electron in an average manner through the Coulomb potential $\mathcal{J}_i$.

HF: Derivation IX

The exchange operator is given in a similar way:

$$\begin{aligned}\mathcal{K}_i(1)\chi_m(1) &= \left[\int dx_2 \frac{\chi_i^*(2)\ \mathcal{P}_{12}\ \chi_i(2)}{r_{12}}\right]\chi_m(1) \\ &= \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right]\chi_i(1).\end{aligned}$$

Only this time we need to include the permutation operator. Note that this operator can operate either on the electron labels or on the spin-orbital indices.

HF: Derivation X

Because the electrons do not interact directly with other electrons, but rather, see the average potential (Coulomb and exchange) from other electrons, Hartree–Fock theory is called a *mean-field theory*. Here is the Fock operator again:

$$f(1) = h(1) + \sum_i \int dx_2 \frac{\chi_i^*(2)\ (1-\mathcal{P}_{12})\ \chi_i(2)}{r_{12}}$$

In the Dirac formalism we will use

$$f = h + \sum_i \langle i|\frac{1}{r_{12}}(1-\mathcal{P}_{ik})|i\rangle.$$

HF: Derivation XI

Once we have the spin-orbitals, the Hartree–Fock energy is given by

$$\boxed{\begin{aligned}\langle \Psi | H | \Psi \rangle &= \sum_i \langle i|h|i\rangle + \sum_{i>j} \left[\langle ij|ij\rangle - \langle ij|ji\rangle\right] \\ &= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij} \langle ij||ij\rangle .\end{aligned}}$$

HF: Derivation XII

Q: What does the sum over i go over in the Fock operator? All spin-orbitals? Only some sub-set of them?

Q: In the Dirac notation we have the permutation operator $\mathcal{P}_{ik}$. What is k here?

Q: In what sense is the permutation operator $\mathcal{P}_{ik}$ that acts on spin-orbital labels equivalent to the operator $\mathcal{P}_{12}$ that exchanges electron labels?

Q: How many solutions to the Fock equation are there? I.e., what is the dimension of the energy matrix ϵ?

Canonical form I

The Fock equations in their *non-canonical form* are given by

$$f|i\rangle = \sum_{i} \epsilon_{ji}|j\rangle.$$

This implies that we can define the energy matrix:

$$\epsilon_{ij} = \langle i|f|j\rangle.$$

We have shown that ϵ is an Hermitian matrix, so we can always find a Unitary matrix, **U** that diagonalises it giving the diagonal matrix ϵ'. That is

$$\epsilon' = \mathbf{U}^{\dagger}\epsilon\mathbf{U},$$

Canonical form II

where $\mathbf{U}^\dagger\mathbf{U} = \mathbf{I}$. In index notation we have

$$\begin{aligned} \epsilon'_{ij} = \epsilon'_i\delta_{ij} &= U^*_{ki}\epsilon_{kl}U_{lj} \\ &= U^*_{ki}\langle k|f|l\rangle U_{lj} \\ &= \langle i'|f|j'\rangle, \end{aligned}$$

where, in the last step we have defined a new set of spin-orbitals:

$$|i'\rangle \equiv \chi'_i = \sum_j \chi_j U_{ji}.$$

Canonical form III

In this basis of what are called the *canonical orbitals*, the energy matrix is diagonal so the Fock equations become

$$\begin{aligned} f|i'\rangle &= \sum_i \epsilon'_{ji}|j'\rangle \\ &= \sum_i \epsilon'_i\delta_{ij}|j'\rangle \\ &= \epsilon'_i|i'\rangle. \end{aligned}$$

Equivalently we can write this as

$$f\chi'_i = \epsilon'_i\chi'_i.$$

This is the usual form of an eigenvalue equation. When codes like NWChem present the spin-orbitals they present them in this, *canonical*, form.

Canonical form IV

There is one complication with the previous derivation: the Fock operator is defined in terms of the spin orbitals $\{\chi_i\}$, so when we transform to the canonical orbitals $\{\chi_i'\}$ we will have also changed $\hat{f}$ to $\hat{f}'$. This would seem to imply that we have made a fundamental change to the problem we were trying to solve. However, as we will now show, the form of the Fock operator implies that it remains invariant under a unitary transformation.

$$f(1) = h(1) + \sum_i \int dx_2 \frac{\chi_i^*(2)\ (1 - \mathcal{P}_{12})\ \chi_i(2)}{r_{12}}$$

The one-electron Hamiltonian $h(1)$ does not depend on the spin-orbitals so the unitary transformation has no effect on this term.

Canonical form V

Consider the Coulomb operator:

$$\begin{aligned}\sum_i \mathcal{J}'_i(1) &= \sum_i \int dx_2 \frac{\chi'^*_i(2)\ \chi'_i(2)}{r_{12}} \\ &= \sum_{kl} \sum_i [U^*_{ki} U_{li}] \int dx_2 \frac{\chi^*_k(2)\ \chi_l(2)}{r_{12}} \\ &= \sum_{kl} [\delta_{kl}] \int dx_2 \frac{\chi^*_k(2)\ \chi_l(2)}{r_{12}} \\ &= \sum_{k} \int dx_2 \frac{\chi^*_k(2)\ \chi_k(2)}{r_{12}} \\ &= \sum_i \mathcal{J}_i(2) \quad \text{change of dummy index.}\end{aligned}$$

Here, the indices i, k, l all go over occupied orbitals only.

Canonical form VI

Q: Show that the exchange operator is also unchanged under a unitary transformation of the occupied orbitals. I.e. show that $\sum_i \mathcal{K}'_i = \sum_i \mathcal{K}_i$.

Hence we get our result: $f'(1) = f(1)$: the Fock operator is invariant under a unitary transformation of the occupied spin-orbitals. Henceforth we always deal with canonical spin-orbitals and drop the primes to write:

$$f\chi_i = \epsilon_i \chi_i.$$

Canonical form VII

Pause here: Why does the unitary transformation apply to the occupied spin-orbitals only? Better yet, what do we mean by *occupied*?

- The Fock operator yields an infinite number of solutions.
- The ground-state is usually obtained by placing the electron in the lowest energy spin-orbitals. These will be the *occupied* orbitals.
- The remaining will be the *un-occupied* or *virtual* orbitals.
- The Fock operator itself contains only the occupied orbitals.

Q: What is meant by the last statement?

Canonical form VIII

Q: Can you think of a scenario in which we may not place the electrons in the lowest energy orbitals?

Index Notation:

- Occupied orbitals: i, j, k, l
  (S&O use a, b, c, d)
- Un-occupied/virtual orbitals: a, b, c, d
  (S&O use r, s, t, u)
- General orbitals: m, n, o, p

Remember that the Fock operator is defined in terms of the *occupied* orbitals but can *operate on* all orbitals.

Canonical form IX

Notes:

- The canonical spin orbitals are generally delocalised.
- Like the non-canonical SOs, they are orthonormal.
- We have proved that we can obtain a set of canonical SOs for the occupied orbitals. It turns out that this can be done for the virtual (un-occupied) SOs too.

Orbital Energies I

What do the spin orbitals and orbitals energies mean? When we solve the Fock equations we formally obtain an infinity of solutions (any partial differential equation has an infinity of solutions). We place the N electrons in the N lowest energy SOs. These are our occupied orbitals. The others, the un-occupied ones, are called the virtual SOs. There are an infinity of these (formally!). We will now try to understand what these orbitals mean. But first, something to think about

Q: Why have we assumed (as we will) that the putting the electrons in the N lowest energy SOs is the correct thing to do? After all, our goal is to minimize the energy E_0 which, as we will soon see, is not the same as the sum of the energies of the occupied SOs.

Orbital Energies II

What are the orbital energies?

$$\begin{aligned}\epsilon_i = \langle \chi_i | f | \chi_i \rangle &= \langle \chi_i | h + \sum_j (\mathcal{J}_j - \mathcal{K}_j) | \chi_i \rangle \\ &= \langle \chi_i | h | \chi_i \rangle + \sum_j [\langle \chi_i | \mathcal{J}_j | \chi_i \rangle - \langle \chi_i | \mathcal{K}_j | \chi_i \rangle] \\ &= \langle i | h | i \rangle + \sum_j [\langle ij | ij \rangle - \langle ij | ji \rangle] \\ &= \langle i | h | i \rangle + \sum_j \langle ij || ij \rangle\end{aligned}$$

Orbital Energies III

Now let's look at the energies of an occupied and a virtual orbital:

- **Occupied orbital**

$$\epsilon_i = \langle i|h|i\rangle + \sum_j \langle ij||ij\rangle = \langle i|h|i\rangle + \sum_{j\neq i} \langle ij||ij\rangle$$

We could eliminate the $j = i$ case in the sum as $\langle ii||ii\rangle = 0$. These is the way self-interaction is removed in Hartree–Fock theory. Notice that the sum now includes Coulomb and exchange interactions with $N - 1$ electrons.

Orbital Energies IV

- **Virtual orbital**

$$\epsilon_a = \langle a|h|a\rangle + \sum_j \langle aj||aj\rangle$$

Since $j \in$ occ, we cannot make the same reduction in the sum and see that ϵ_a is the energy of an electron in the virtual orbital a and this electron interacts with N electrons in the occupied orbitals.

Orbital Energies V

Q: Do the orbital energies add up to the total energy?

$$\sum_{i}^{N} \epsilon_i = \sum_{i} \langle i|h|i\rangle + \sum_{ij} \langle ij||ij\rangle$$
$$= E_0 + \frac{1}{2}\sum_{ij} \langle ij||ij\rangle$$

So $E_0 \neq \sum_i^N \epsilon_i$! The reason for this difference is that, as we have just seen, ϵ_i includes the Coulomb and exchange interactions (in the average, mean-field sense) with the other $N-1$ electrons. So by summing over all ϵ_i we double count and hence to get E_0 we need to remove half these interactions.

Koopman's Theorem I

To find out exactly what these Hartree–Fock orbital energies mean we evaluate the Ionization Potential (IP) and Electron Affinity (EA) while keeping all orbitals frozen (no relaxation allowed). The IP is defined as the energy taken to remove an electron. We will remove the electron from orbital k. This creates the $N-1$ electron state

$$|\Psi_k(N-1)\rangle = a_k|\Psi_0\rangle$$

And

$$\mathrm{IP} = E_k(N-1) - E_0(N)$$

where

$$\begin{aligned} E_0(N) &= \langle\Psi_0(N)|H|\Psi_0(N)\rangle \\ E_k(N-1) &= \langle\Psi_k(N-1)|H|\Psi_k(N-1)\rangle. \end{aligned}$$

Koopman's Theorem II

We already know that

$$E_0(N) = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

To evaluate $E_k(N-1)$ we use a similar expression but eliminate all instances of orbital k:

$$E_k(N-1) = \sum_{i\neq k}\langle i|h|i\rangle + \frac{1}{2}\sum_{i\neq k, j\neq k}\langle ij||ij\rangle$$

Koopman's Theorem III

So the IP is

$$\begin{aligned}
\mathrm{IP} &= E_k(N-1) - E_0(N) \\
&= -\langle k|h|k\rangle - \frac{1}{2}\sum_i \langle ik||ik\rangle - \frac{1}{2}\sum_j \langle kj||kj\rangle \\
&= -\langle k|h|k\rangle - \sum_i \langle ik||ik\rangle \\
&= -\epsilon_k
\end{aligned}$$

So the orbital energy ϵ_k of occupied orbital k is negative of the energy required to remove the electron from the orbital while keeping all orbitals fixed.

Koopman's Theorem IV

Now consider the process of adding an electron to a virtual orbital a of the system to generate $|\Psi^a(N+1)\rangle = a_a^\dagger|\Psi_0\rangle$. The electron affinity is defined as

$$\mathrm{EA} = E_0(N) - E^a(N+1).$$

Q: Show that

$$\mathrm{EA} = E_0(N) - E^a(N+1) = -\epsilon_a$$

That is, the energy of a virtual orbital is the negative of the electron affinity for adding an electron to that orbital.

Koopman's Theorem V

This now explains why an electron in a virtual orbital has an energies that is consistent with it interacting with N other electrons. From the above we see that this is so because the energy of a virtual orbital is (minus) the energy required to create an $N+1$ state.

Koopman's Theorem VI

Koopmans' Theorem

Given an N-electron Hartree–Fock single determinant with occupied and virtual spin orbital energues ϵ_i and ϵ_a, the ionization potential to produce an $N-1$-electron state with all orbitals frozen and the electron removed from orbital i is $-\epsilon_i$, and the electron affinity to produce a $N+1$-electron state with an additional electron in virtual orbital a is $-\epsilon_a$.

Brillioun's Theorem I

Brillioun's theorem deals with the *stability* of the Hartree–Fock solution w.r.t. first-order changes to the wavefunction (the Fock single-determinant).

We have derived the Fock equations using the variational principle, so, the solutions to the Fock equations should be stable in the variational sense, that is, the Hartree–Fock energy should not change (to first order) with small changes to the wavefunction.

What Brillioun's Theorem tells us is that this is indeed true if by *small changes* we mean *single excitations*: that is, single excitations will not change the Hartree–Fock energy.

Brillioun's Theorem II

Brillioun's theorem states that a singly-excited determinant Ψ_i^a does not connect to the HF solution Ψ_0 via the Hamiltonian. I.e.,

$$\langle \Psi_i^a | H | \Psi_0 \rangle = 0.$$

To demonstrate this we need a couple of results:

$$\begin{aligned} \langle \Psi_i^a | H | \Psi_0 \rangle &= \langle a | h | i \rangle + \sum_j [\langle aj | ij \rangle - \langle aj | ji \rangle] \\ &= \langle a | h | i \rangle + \sum_j \langle aj || ij \rangle \end{aligned}$$

Brillioun's Theorem III

and we need the general form of matrix elements of the Fock operator:

$$
\begin{aligned}
f_{mn} = \langle \chi_m | f | \chi_n \rangle &= \langle \chi_m | h + \sum_j (\mathcal{J}_j - \mathcal{K}_j) | \chi_n \rangle \\
&= \langle \chi_m | h | \chi_n \rangle + \sum_j [\langle \chi_m | \mathcal{J}_j | \chi_n \rangle - \langle \chi_m | \mathcal{K}_j | \chi_n \rangle] \\
&= \langle m | h | n \rangle + \sum_j [\langle mj | nj \rangle - \langle mj | jn \rangle] \\
&= \langle m | h | n \rangle + \sum_j \langle mj || nj \rangle
\end{aligned}
$$

Since the SOs χ_m are eigenstates of the Fock operator, we have

$$f_{mn} = \langle \chi_m | f | \chi_n \rangle = \epsilon_n \langle \chi_m | \chi_n \rangle = \epsilon_n \delta_{mn}.$$

Brillioun's Theorem IV

From the second result we see that

$$\begin{aligned}\langle\Psi_i^a|H|\Psi_0\rangle &= \langle a|h|i\rangle + \sum_j \langle aj||ij\rangle \\ &= \langle\chi_a|f|\chi_i\rangle \\ &= \epsilon_i\delta_{ai} = 0 \quad \text{since} \quad a \neq i\end{aligned}$$

That is, the singly excited determinant Ψ_i^a does not (directly) connect with the Hartree–Fock ground state Ψ_0.
This means that we cannot improve the HF solution by mixing in contributions from the virtual space. Or, in other words, the HF solution is *stable* to first-order changes to the HF solution.
To see the significance of this result, let us consider a CI expansion to *improve* the Hartree–Fock wavefunction and energy.

Brillioun's Theorem V

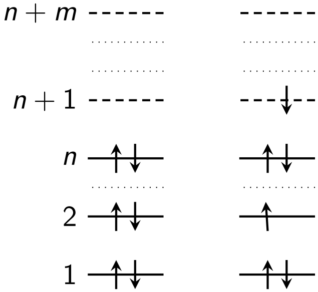

Figure: Left: HF ground state configuration. Right: An example of an excited state configuration. If there are n occupied levels (2 electrons each, so $N = 2n$) and m virtual (un-occupied) levels, in how many ways can we form excited states? Each of these states will correspond to a Slater determinant.

Brillioun's Theorem VI

We generate the full CI (FCI) wavefunction by including all kinds of single determinants in a linear expansion:

$$\begin{aligned}|\Psi\rangle &= c_0|\Psi_0\rangle + \sum_{ia} c_i^a|\Psi_i^a\rangle + \sum_{ij,ab} c_{ij}^{ab}|\Psi_{ij}^{ab}\rangle + \cdots \\ &= c_0|\Psi_0\rangle + c_S|S\rangle + c_D|D\rangle + \cdots\end{aligned}$$

where electrons are excited from the *occupied* orbitals $i, j, k, \cdots$ to the *virtual* orbitals $a, b, c, \cdots$.
We may think that the simplest way to improve the HF solution $|\Psi_0\rangle$ is to include the single excitations $|S\rangle$. This is a reasonable assumption that proves to be wrong because of Brillouin's theorem. To see this, consider the simple case where we have only

Brillioun's Theorem VII

one singly excited determinant $|\Psi_i^a\rangle$. So the CI — call it CIS for configuration interaction with single excitations — expansion is

$$|\Psi\rangle = |\Psi_0\rangle + c_i^a|\Psi_i^a\rangle$$

Using the usual variational methods we have discussed before to determine the coefficients c_0 and c_{ij}^{ab} we convert this problem into the set of linear equations

$$\begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_0|H|\Psi_i^a\rangle \\ \langle\Psi_i^a|H|\Psi_0\rangle & \langle\Psi_i^a|H|\Psi_i^a\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix} = \mathcal{E} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix}$$

From Brillouin's theorem $\langle\Psi_i^a|H|\Psi_0\rangle = 0$ and $\langle\Psi_0|H|\Psi_0\rangle = E_0$, therefore we get

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle\Psi_i^a|H|\Psi_i^a\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix} = \mathcal{E} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix}$$

Brillioun's Theorem VIII

The ground-state solution is simply $\mathcal{E} = E_0$ with $c_0 = 1$ and $c_i^a = 0$. I.e., the ground-state of the CIS variational expansion is the Hartree–Fock solution. That is, singly excited determinants (on their own) cannot improve the Hartree–Fock solution. I.e., Hartree–Fock is *stable* to perturbations that take the form of single excitations.

This does not mean that single excitation can never contribute. They can if we also include double excitations. Can you see how?

Brillioun's Theorem IX

An elaboration on the above:
If we have a wavefunction Ψ_0 and wish to add a small change $\delta\Psi$ to it, what are the allowed kinds of $\delta\Psi$? Not all choices will be physically valid as the following conditions must be satisfied:

- $\delta\Psi$ must be anti-symmetric in an *N*-electron Hilbert space.
- It must be integrable.
- It should be orthogonal to Ψ_0 for it to be a *change* to Ψ_0.

The easiest way to satisfy these conditions is to construct $\delta\Psi$ out of Slater determinants, and these are going to be the determinants formed by single-excitations, double-excitations, etc. formed by starting from the HF wavefunction Ψ_0. That is

$$|\delta\Psi\rangle = \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{ij,ab} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \cdots$$

Brillioun's Theorem X

What Brillioun's theorem implies is that if we construct the simplest change $\delta\Psi = \sum_{ia} c_i^a |\Psi_i^a\rangle$ formed only of single excitations from the HF wavefunction, then there will be no change to the ground-state energy.