TCC Electronic Structure Module
L2: Hartree–Fock Theory

David P. Tew

February 7, 2021

Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

L1 Exact and inexact wavefunctions

L2 Hartree–Fock theory

L3 Configuration Interaction theory

L4 Møller–Plesset perturbation theory

L5 Coupled-cluster theory

L6 Properties and excited states

L7 Density Functional Theory

L8 Density Functional Approximations

Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

1 Hartree–Fock Theory

Molecular orbital theory is a powerful model for understanding molecular bonding, charge distribution, reaction mechanism and selectivity. HartreeFock (HF) theory is the application of molecular orbital theory to the full electronic Scrhödinger equation. The approximation to the n-electron wavefunction is that where the n electrons occupy n spin-orbitals $\varphi_i(\mathbf{x}_1)$. In Hartree–Fock theory the variational principle is used to find the best wavefunction of this form by optimising the orbitals to minimise the ground state energy.

1.1 The Hartree–Fock wavefunction

The Hartree–Fock wavefunction for closed-shell molecules is an antisymmetrised product of spin orbitals

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \sqrt{n!}\, \hat{A}\, \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)\cdots\varphi_n(\mathbf{x}_n) \tag{1}$$

$$|\Psi\rangle = \sqrt{n!}\, \hat{A}\, |\varphi_1\varphi_2\cdots\varphi_n\rangle \qquad \text{(Dirac notation)} \tag{2}$$

where the spin-orbitals are orthonormal $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$ and the wavefunction is normalised $\langle\Psi|\Psi\rangle = 1$. The antisymmetric projection operator $\hat{A}$ generates a linear combination of all $n!$ permutations of electrons in orbitals with either a plus or a minus depending on the parity p_μ of the permutation $\hat{\pi}_\mu$, such that Fermi antisymmetry is obeyed for interchange of any pair of electrons

$$\hat{A} = \frac{1}{n!}\sum_\mu (-1)^{p_\mu}\hat{\pi}_\mu \tag{3}$$

The Hartree–Fock wavefunction is an eigenfunction of both $\hat{S}^2$ and $\hat{S}_z$, with spin zero, if the set of β spin orbitals is restricted to be the same as the set of α spin orbitals, so that each spatial orbital is doubly occupied. Point group symmetry can be enforced by imposing the point group symmetry on the spin orbitals.

The antisymmetrised product is referred to as a Slater determinant because of the mathematical equivalence with the determinant of a matrix composed of rows of orbitals and columns of electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) & \cdots & \varphi_n(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{x}_n) & \varphi_2(\mathbf{x}_n) & \cdots & \varphi_n(\mathbf{x}_n) \end{vmatrix} \tag{4}$$

The Hartree–Fock wavefunction is invariant under unitary transformations among the occupied orbitals. This can most straightforwardly be seen in the determinental form: a determinant remains constant (within a phase) under unitary transformations: $|\mathbf{UA}| = |\mathbf{U}|\,|\mathbf{A}| = e^{i\theta}|\mathbf{A}|$. Hence the energy, and all other observable quantities, are invariant under such transformations.

For open-shell systems the Hartree–Fock wavefunction can be more complicated. The wavefunction for high-spin electronic states with extremal spin projection is a single Slater determinant, but the wavefunctions for fractionally occupied degenerate orbitals, low-spin open-shell states and non-extremal spin projection are linear combinations of Slater determinants such that the spins are appropriately coupled to be eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. These are referred to as configuration state functions. The Hartree–Fock method can be used to optimise the orbitals for some configuration state functions using the restricted open-shell Roothaan–Hall equations, but not in all cases.

1.2 The Hartree–Fock energy

The Hartree–Fock energy is the expectation value of the Hamiltonian for the Hartree–Fock wavefunction

$$E_{\mathrm{HF}} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{5}$$

The Hamiltonian decomposes into operators that act on one electron at a time and operators that act on two-electrons at a time

$$\hat{H} = \hat{h} + \hat{g} = \sum_i \hat{h}_i + \sum_{i<j} \hat{g}_{ij} \tag{6}$$

$$\hat{h}_i = \frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}} \tag{7}$$

$$\hat{g}_{ij} = \frac{1}{r_{ij}} \tag{8}$$

Let us consider each of the integrals $\langle\Psi|\Psi\rangle$, $\langle\Psi|\hat{h}|\Psi\rangle$ and $\langle\Psi|\hat{g}|\Psi\rangle$ separately. We will only deal with the case where Ψ is a single Slater determinant.

1.2.1 Overlap

We begin by showing that the wavefunction is normalised, i.e. that $\langle\Psi|\Psi\rangle = 1$. Substituting in the wavefunction we have

$$\langle\Psi|\Psi\rangle = n!\langle\varphi_1\varphi_2\cdots\varphi_n|\hat{A}^\dagger\hat{A}|\varphi_1\varphi_2\cdots\varphi_n\rangle \tag{9}$$

Now the antisymmetriser $\hat{A}$ is hermitian and also idempotent (see box below), so $\hat{A}^\dagger\hat{A} = \hat{A}^2 = \hat{A}$. Hence we have

$$\langle\Psi|\Psi\rangle = n!\langle\varphi_1\varphi_2\cdots\varphi_n|\hat{A}|\varphi_1\varphi_2\cdots\varphi_n\rangle \tag{10}$$

A note about projection operators

It is noted above that the antisymmetriser is a projection operator and is hermitian and idempotent. The first means that $\hat{A}^\dagger = \hat{A}$ and the second that $\hat{A}^2 = \hat{A}$. The latter property is a consequence of how projection operators work: projecting a function (or vector or anything else) onto some subspace twice is the same as doing so once.

Substituting the antisymmetriser (equation (3)) into equation (10) we have

$$\langle\Psi|\Psi\rangle = \sum_\mu (-1)^{p_\mu}\langle\varphi_1\varphi_2\cdots\varphi_n|\hat{\pi}_\mu|\varphi_1\varphi_2\cdots\varphi_n\rangle \tag{11}$$

Since the orbitals are orthogonal, the only permutation that gives a non-zero integral is the identity so that

$$\langle\Psi|\Psi\rangle = \langle\varphi_1|\varphi_1\rangle\langle\varphi_2|\varphi_2\rangle\cdots\langle\varphi_n|\varphi_n\rangle = 1 \tag{12}$$

because the orbitals are normalised.

1.2.2 One-electron operators

The integral for the one-electron Hamiltonian component is

$$\langle \Psi | \hat{h} | \Psi \rangle = n! \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{A}^\dagger \hat{h} \hat{A} | \varphi_1 \varphi_2 \cdots \varphi_n \rangle \tag{13}$$

Since $\hat{h}$ is symmetric under particle interchange $[\hat{A}, \hat{h}] = 0$. This, together with the properties of $\hat{A}$, allows us to simplify the integral to

$$\langle \Psi | \hat{h} | \Psi \rangle = n! \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{h} \hat{A} | \varphi_1 \varphi_2 \cdots \varphi_n \rangle = \sum_\mu (-1)^{p_\mu} \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{h} \hat{\pi}_\mu | \varphi_1 \varphi_2 \cdots \varphi_n \rangle \tag{14}$$

Just as for the overlap, the only permutation that gives a non-zero integral is the identity, because of orthogonality among the orbitals. Examining first the integral over the operator h_1, we find

$$\langle \Psi | \hat{h}_1 | \Psi \rangle = \langle \varphi_1 | \hat{h}_1 | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle \cdots \langle \varphi_n | \varphi_n \rangle = \langle \varphi_1 | \hat{h}_1 | \varphi_1 \rangle \tag{15}$$

Thus the integral over all the one-electron operators is

$$\langle \Psi | \hat{h} | \Psi \rangle = \sum_i \langle \varphi_i | \hat{h}_1 | \varphi_i \rangle \tag{16}$$

Note that the 1 in h_1 refers to the electronic coordinate, which is integrated over and is therefore a dummy index in this final equation.

1.2.3 Two-electron operators

The integral for the two-electron Hamiltonian component is

$$\langle \Psi | \hat{g} | \Psi \rangle = n! \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{A}^\dagger \hat{g} \hat{A} | \varphi_1 \varphi_2 \cdots \varphi_n \rangle \tag{17}$$

Since $\hat{g}$ is symmetric under particle interchange $[\hat{A}, \hat{g}] = 0$ and we have

$$\langle \Psi | \hat{g} | \Psi \rangle = n! \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{g} \hat{A} | \varphi_1 \varphi_2 \cdots \varphi_n \rangle = \sum_\mu (-1)^{p_\mu} \langle \varphi_1 \varphi_2 \cdots \varphi_n | \hat{g} \hat{\pi}_\mu | \varphi_1 \varphi_2 \cdots \varphi_n \rangle \tag{18}$$

Focusing on the first term in $\hat{g}$, we find that two permutations survive: the identity and $\hat{\pi}_{12}$, with all other permutations giving vanishing integrals due to orthogonality among the orbitals

$$\sum_\mu (-1)^{p_\mu} \langle \varphi_1 \varphi_2 \cdots \varphi_n | r_{12}^{-1} \hat{\pi}_\mu | \varphi_1 \varphi_2 \cdots \varphi_n \rangle = \langle \varphi_1 \varphi_2 | r_{12}^{-1} (1 - \hat{\pi}_{12}) | \varphi_1 \varphi_2 \rangle \langle \varphi_3 | \varphi_3 \rangle \cdots \langle \varphi_n | \varphi_n \rangle \tag{19}$$

Thus the integral over all the two-electron operators is

$$\langle \Psi | \hat{g} | \Psi \rangle = \sum_{i<j} \langle \varphi_i \varphi_j | r_{12}^{-1} (1 - \hat{\pi}_{12}) | \varphi_i \varphi_j \rangle \ . \tag{20}$$

Note that the 1 and 2 refer to the electronic coordinates, which are integrated over and are therefore dummy indices. Thus the two-electron energy contains two terms,

$$\langle \Psi | \hat{g} | \Psi \rangle = \sum_{i<j} \langle \varphi_i \varphi_j | r_{12}^{-1} | \varphi_i \varphi_j \rangle - \sum_{i<j} \langle \varphi_i \varphi_j | r_{12}^{-1} | \varphi_j \varphi_i \rangle \tag{21}$$

respectively called the *Coulomb energy* and the *exchange energy*. For later manipulations it is actually more convenient to move from summing over all pairs $i < j$ to all i and all j, introducing a factor of one half to avoid double counting:

$$\langle\Psi|\hat{g}|\Psi\rangle = \frac{1}{2}\sum_{ij}\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_i\varphi_j\rangle - \frac{1}{2}\sum_{ij}\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_j\varphi_i\rangle\ , \tag{22}$$

and noting that the $i = j$ terms in the exchange energy cancel exactly with the corresponding terms in Coulomb.[1]

Putting it all together, the Hartree–Fock energy is

$$E_{\mathrm{HF}} = \sum_i\langle\varphi_i|\hat{h}_1|\varphi_i\rangle + \frac{1}{2}\sum_{ij}\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_i\varphi_j\rangle - \frac{1}{2}\sum_{ij}\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_j\varphi_i\rangle \tag{23}$$

1.3 The Fock equation

Having obtained an expression for the Hartree–Fock energy, we can now use calculus of variations to minimise the energy functional with respect to the orbitals. The Hartree–Fock energy expression is valid for orthonormal orbitals, so we must impose a constraint on the orbital variations to maintain orthonormality, which is achieved through the technique of Lagrange multipliers. The appropriate Lagrangian is

$$L[\varphi] = E_{\mathrm{HF}}[\varphi] - \sum_{ij}\epsilon_{ij}(\langle\varphi_i|\varphi_j\rangle - \delta_{ij}) \tag{24}$$

Requiring stationarity of L with respect to change of each orbital φ_k yields the equation

$$\delta L = \langle\delta\varphi_k|\hat{h}_1|\varphi_k\rangle + \sum_j(\langle\delta\varphi_k\varphi_j|r_{12}^{-1}|\varphi_k\varphi_j\rangle - \langle\delta\varphi_k\varphi_j|r_{12}^{-1}|\varphi_j\varphi_k\rangle) - \sum_j\epsilon_{kj}\langle\delta\varphi_k|\varphi_j\rangle + \text{h.c.} = 0 \tag{25}$$

which is written concisely as

$$\langle\delta\varphi_k|\hat{f}_1|\varphi_k\rangle + \text{h.c.} = \sum_j\epsilon_{kj}\langle\delta\varphi_k|\varphi_j\rangle + \text{h.c.} \tag{26}$$

where $\hat{f}_1$ is the one-electron Fock operator

$$\hat{f}_1 = \hat{h}_1 + \sum_j\int d\mathbf{x}_2\,\varphi_j(\mathbf{x_2})(1-\hat{\pi}_{12})r_{12}^{-1}\varphi_j(\mathbf{x}_2) \tag{27}$$

Since all the integrals are hermitian, the matrix of Lagrange multipliers must also be hermitian and we can bring the multipliers into canonical form by rotating the occupied orbitals among themselves to diagonalise expression

$$\hat{f}_1\varphi_k(\mathbf{x_1}) = \varepsilon_k\varphi_k(\mathbf{x_1}) \tag{28}$$

The set of optimal Hartree–Fock orbitals can be obtained by finding eigenfunctions of the Fock operator. The Fock operator itself depends on the orbitals, so this is a self-consistent set of equations and their solution requires an iterative procedure. Moreover, locating the minimum energy is a global search problem and all possible ways of selecting which orbitals to occupy should be sampled.

---

[1] For later reference, this exact cancellation of the self-interacting Coulombic contribution is important in the context of density functional theory, where the approximate treatment of the exchange energy leads to imperfect cancellation of self-interaction, which in turn is at the heart of many of the cases where DFT fails badly.

1.4 Koopman's Theorems

Consider the cationic system generated by removing an electron from canonical orbital φ_i of the neutral systems and keeping all the other orbitals frozen (not allowing them to relax due to the modified field). The energy of ionisation is

$$E^+ - E = -\langle\varphi_i|\hat{h}_1|\varphi_i\rangle - \sum_j \langle\varphi_i\varphi_j|(1-\hat{\pi}_{12})r_{12}^{-1}|\varphi_i\varphi_j\rangle = -\varepsilon_i \tag{29}$$

This provides a physical interpretation of the eigenvalues ε_i for the occuied orbitals: they are approximately equal to the energy required to remove an electron from orbital φ_i.

Consider the anionic system generated by adding an electron into a vacant canonical orbital φ_a of the neutral system and keeping all other orbitals frozen (not allowing them to relax due to the modified field). The electron affinity is

$$E^- - E = \langle\varphi_a|\hat{h}_1|\varphi_a\rangle + \sum_j \langle\varphi_a\varphi_j|(1-\hat{\pi}_{12})r_{12}^{-1}|\varphi_a\varphi_j\rangle = \varepsilon_a \tag{30}$$

This provides a physical interpretation of the eigenvalues ε_a for the vacant orbitals: they are approximately equal to the energy change when adding an electron into orbital φ_a.

Koopman's theorems provide the justification for selecting the lowest energy orbitals to be occupied when searching for the minimum energy (applying the aufbau principle based on eigenvalues of the Fock operator). However, if orbital relaxation is strong when changing occupancy, this approach may fail to find the minimum, particularly if the initial orbital guess is chosen poorly.

Excercise 1: Prove Koopman's Theorems. Hint, the $i = j$ and $a = j$ terms cancel in the sum.

1.5 The Roothaan–Hall equations

We now turn to a practical method for solving the Hartree–Fock equations numerically. The widely adopted strategy for expanding the unkown orbitals in a basis of known functions is to express the molecular orbitals as a linear combination of atomic basis functions

$$|\varphi_i\rangle = \sum_\mu |\eta_\mu\rangle C_{\mu i} \tag{31}$$

$C_{\mu i}$ are referred to as the molecular-orbital coefficients.[2] The atomic functions $|\eta_\mu\rangle$ are chosen to be products of Gaussian radial functions and spherical harmonics, since a) the functions mimic the hydrogenic orbitals

---

[2] My choice of notation already betrays a peculiarity of the way electronic structure theory is written down. We keep certain sets of letters for certain kinds of objects. Thus it is very common in modern literature to use i, j, k, l for occupied orbitals; a, b, c, d for virtual or unoccupied orbitals; p, q, r, s for any molecular orbital; and $\mu, \nu, \kappa, \lambda$ for atomic orbitals. One quite often sees $\alpha, \beta, \gamma, \delta$ for atomic orbitals too, but I here I want to use Greek letters $\mu, \nu, \ldots$ to avoid any confusion with spin functions. Irritatingly a key book in this area (by Szabo and Ostlund) uses a nonstandard convention, but is far too good to ignore on those grounds alone.

b) the expansion is complete for an atom (overcomplete for a molecule) and c) all integrals can be evaluated analytically. The parameters for the atomic functions now be taken from libraries of pre-optimised basis sets designed to deliver consistent accuracy across all elements of the periodic table.

We can substitute the orbital in equation (31) into the Lagrangian to obtain

$$L = \sum_{i\mu\nu} C^*_{\mu i} C_{\nu i} \langle \eta_\mu | \hat{h} | \eta_\nu \rangle + \frac{1}{2} \sum_{ij\mu\nu\kappa\lambda} C^*_{\mu i} C^*_{\nu j} C_{\kappa i} C_{\lambda j} \left[\langle \eta_\mu \eta_\nu | r_{12}^{-1} | \eta_\kappa \eta_\lambda \rangle - \langle \eta_\mu \eta_\nu | r_{12}^{-1} | \eta_\lambda \eta_\kappa \rangle \right] \\ - \sum_{ij} \epsilon_{ij} (\sum_{\mu\nu} C^*_{\mu i} C_{\nu j} \langle \eta_\mu | \eta_\nu \rangle - \delta_{ij}) \tag{32}$$

Now we do a bit of notational compression by writing $S_{\mu\nu} \equiv \langle \eta_\mu | \eta_\nu \rangle$, $H_{\mu\nu} \equiv \langle \eta_\mu | \hat{h} | \eta_\nu \rangle$, $\langle \mu\nu | r_{12}^{-1} | \kappa\lambda \rangle \equiv \langle \eta_\mu \eta_\nu | r_{12}^{-1} | \eta_\kappa \eta_\lambda \rangle$ and $\langle \mu\nu || \kappa\lambda \rangle \equiv \langle \mu\nu | r_{12}^{-1} | \kappa\lambda \rangle - \langle \mu\nu | r_{12}^{-1} | \lambda\kappa \rangle$. We also identify that the 1-particle reduced density matrix appears in several places

$$D_{\mu\nu} = \sum_i C^*_{i\mu} C_{i\nu}, \tag{33}$$

The energy expression has a very compact form in this notation

$$E = \sum_{\mu\nu} D_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\kappa\lambda} D_{\mu\kappa} D_{\nu\lambda} \langle \mu\nu || \kappa\lambda \rangle \tag{34}$$

We require that the derivative of the Lagrangian with respect to each orbital coefficient $C_{\mu k}$ is zero, which yeilds

$$\sum_\nu H_{\mu\nu} C_{\nu k} + \sum_{\nu j} \langle \mu j || \nu j \rangle C_{\nu k} - \sum_{\nu j} S_{\mu\nu} C_{\nu j} \epsilon_{jk} + \text{h.c.} = 0 \tag{35}$$

The Fock matrix is

$$F_{\mu\nu} = H_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu} = H_{\mu\nu} + \sum_j \langle \mu j | \nu j \rangle - \sum_j \langle \mu j | j \nu \rangle \tag{36}$$

and the set of optimal Hartree–Fock molecular orbital coefficients can be obtained from the generalised eigenvalue problem

$$\sum_\nu F_{\mu\nu} C_{\nu k} = \sum_\nu S_{\mu\nu} C_{\nu k} \epsilon_k \tag{37}$$

These are the Roothaan–Hall equations, the matrix representation of the Fock equations. Since the Fock matrix, $\mathbf{F}$, is itself a function of the orbital coefficients $\mathbf{C}$ (*via* the density matrix $\mathbf{D}$), the equation is non-linear and has to be solved iteratively. The basic algorithm is:

1. Guess the molecular orbital coefficients $\mathbf{C}$
2. Form the density matrix $\mathbf{D}$
3. Form the Fock matrix $\mathbf{F}$
4. Solve the Roothaan–Hall eigenvalue problem to form new $\mathbf{C}$
5. Iterate until convergence.

This is called self-consistent field theory (SCF). It is prone to oscillatory behaviour, so real Hartree–Fock programs always use more advanced techniques to assist convergence.

2 Further Exercises

1. Show that the wavefunction $\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)$ does not obey the Pauli principle, and show that the form $(1-\hat{\pi}_{12})\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)$ does.
2. For closed-shell systems the occupied α orbitals are the same as the occupied β orbitals so that the product becomes $\varphi_1\alpha\ldots\varphi_n\alpha\varphi_1\beta\ldots\varphi_n\beta$ with n being the number of occupied orbitals rather than the number of electrons. The sum over spin orbitals $\sum_j$ in Eq. (23) can be replaced by a double sum over space orbitals and spin $\sum_\sigma\sum_j$. Show that the energy expression Eq. (23) reduces to

$$E_{\mathrm{HF}} = 2\sum_i \langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{ij}\Big(2\langle\phi_i\phi_j|r_{12}^{-1}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|r_{12}^{-1}|\phi_j\phi_i\rangle\Big)\,. \tag{38}$$

3. Write an RHF code in Python. Calculate the ionisation energy of helium and the energy and orbitals of beryllium.
4. (Optionally) extend the code to work for UHF. Calculate the singlet-triplet splitting of helium and the ionisation energy of lithium.