

# Quantum Chemistry

## Lecture 15

### Hartree-Fock Theory

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# Introduction

An approximate method for many-electron atoms was first proposed by Hartree. In this method the atomic wave function is a product of one-electron wave functions. This is an extension of what we have seen for helium.

$$\Psi(r_1, r_2, r_3 \dots r_N) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3) \dots \phi_N(r_N)$$

In this equation the  $r_i$  are the positional coordinates and a spin coordinate for each electron  $r_i = (x_i, y_i, z_i, m_i)$ . As we have seen for the hydrogen atom, spherical polar coordinates work better than Cartesian coordinates. The spin coordinate can be spin up  $\alpha$  or spin down  $\beta$ .

# Limitations of the Hartree approximation

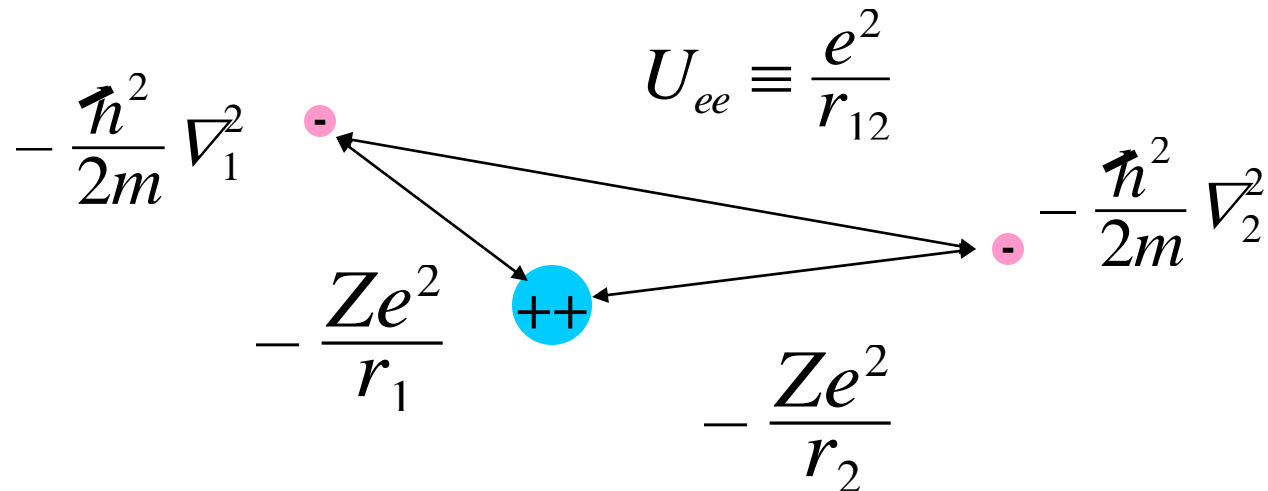
The Hartree approximation works well for atoms. However, the form of the wave function is not correct and the method fails for molecules. One property of the wave function is that it must change sign when any two electrons are interchanged. Around 1930 both Fock and Slater proposed to fix the problem with Hartree model by introducing a wave function that is anti-symmetric with respect to electron exchange

$$\Psi(q_1, q_2, q_3, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(q_1) & \phi_2(q_1) & \phi_3(q_1) & \dots & \phi_N(q_1) \\ \phi_1(q_2) & \phi_2(q_2) & \phi_3(q_2) & \dots & \phi_N(q_2) \\ \phi_1(q_3) & \phi_2(q_3) & \phi_3(q_3) & \dots & \phi_N(q_3) \\ \dots & \dots & \dots & \dots & \dots \\ \phi_1(q_N) & \phi_2(q_N) & \phi_3(q_N) & \dots & \phi_N(q_N) \end{vmatrix}$$

The wave function is the determinant of the matrix.

# The atomic electronic hamiltonian

We reintroduce the hamiltonian for He to introduce commonly used abbreviations.



$$T_e = - \sum_i \frac{\hbar^2}{2m} \nabla_i^2$$

$$V_{ext} = - \sum_i \frac{Ze^2}{r_i}$$

The kinetic energy operator is the sum of the kinetic terms for all of the electrons. The external potential is the field of nuclei (Coulomb attraction) felt by the electrons.

# The nuclear hamiltonian

The Born-Oppenheimer approximation states that electronic and nuclear motion can be separated because of the large difference in mass (1 proton has 1836 times the mass of an electron). Thus, the nuclear kinetic energy and repulsion terms are not included. However, it is important to understand that the nuclear terms are used for translational, rotational and vibrational motion. Vibrations are of particular relevance since the quantum chemical calculation of vibrational frequencies is the basis for parameterization of classical molecular force fields.

$$T_{nucl} = - \sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 \quad \text{Kinetic energy term}$$

$$U_{nucl} = \sum_j \frac{Z_j e^2}{R_j} \quad \text{Nuclear repulsion energy}$$

# The effective hamiltonian

Using these approximations we can write the hamiltonian of an atom as

$$H_{el} = T_e + V_{ext} + U_{ee}$$

The first two terms alone comprise a set of N hydrogen atom calculations which can be solved exactly.

$$T_e + V_{ext} = - \sum_i \left( \frac{\hbar^2}{2m} \nabla_i^2 + \frac{Ze^2}{r_i} \right) = \sum_i h_i$$

The total hamiltonian in this nomenclature is:

$$H_{el} = \sum_i h_i + U_{ee}$$

Note that the inclusion of the electron-electron repulsion term  $U_{ee}$  makes it impossible to solve the Schrödinger equation using this hamiltonian.

# The Hartree approximation

The method is to solve the Schrödinger equation for each individual electron in the field of all of the other electrons. If we assume that we know the individual wave functions  $\phi_i(r)$  for each electron we can calculate the electron density according to:

$$\rho_i = |\phi_i(q)|^2$$

The total electron density is:

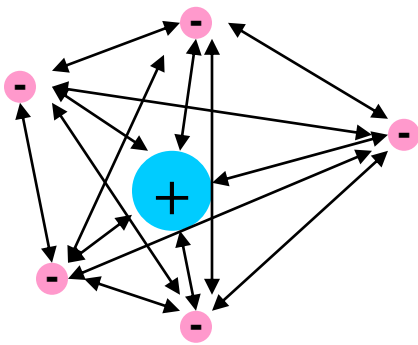
$$\rho_{tot} = \sum_i \rho_i = \sum_i |\phi_i(q)|^2$$

However, the  $k$ th electron does not interact with itself so must subtract the density of  $\rho_k$  from the total.

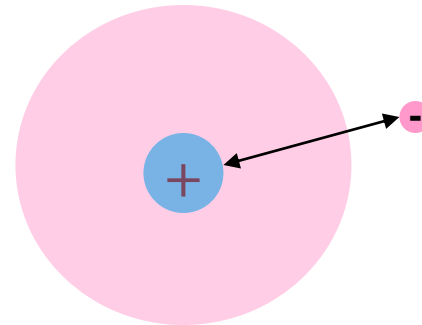
$$\rho^{(k)} = \rho_{tot} - \rho_k = \sum_i \rho_i - |\phi_k(q)|^2 = \sum_{i \neq k} |\phi_i(q)|^2$$

# Overview of the Hartree method

The  $k$ th electron is now treated as a point charge in the field of all of the other electrons. This procedure takes the many-electron problem and simplifies it to many one electron problems.



Many-electron system  
All electron-electron repulsion  
is included explicitly.



One-electron system  
with remaining electrons  
represented by an average  
charge density.  
Mean field approach



# The Hartree procedure

The interaction of the point charge with the electron density is

$$g_k(q) = \int \rho^{(k)}(q') \frac{1}{q - q'} dq'$$

Making this approximation we can write

$$U_{ee} \approx \sum_i g_i(q)$$

and the hamiltonian  $H_{el}$  now consists of one-electron operators:

$$H_{el} = \sum_i (h_i + g_i)$$

The many-electron Schrödinger equation can now be Solved as N one-electron Schrödinger equations

$$\sum_i (h_i + g_i)\phi_i = E \sum_i \phi_i$$

# The Coulomb integral

The set of one-electron Schrödinger equations can be solved iteratively to find the best energy. According to the variational principle the true energy will always be lower than the energy calculated using this method.

However, this method counts the interaction between each pair of electrons twice. Therefore, we cannot simply add the individual one-electron energies  $\varepsilon_i$  to obtain the total energy  $E$ . We correct for this using the Coulomb integral between each pair of electrons  $J_{ij}$

$$J_{ij} = \int \int \frac{\rho_i(r_1)\rho_j(r_2)}{|r_2 - r_1|} dr_1 dr_2$$

# The exchange integral

The determinantal wave function adds a new term to the Hartree energy, the exchange term  $K_{ij}$ .

$$E = \sum_{i=1}^N \varepsilon_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( J_{ij} - K_{ij} \right)$$

We compare the Coulomb and exchange integrals below.

$$J_{ij} = \int \int \phi_i^*(q_1) \phi_i(q_1) \frac{1}{q_2 - q_1} \phi_j^*(q_2) \phi_j(q_2) dq_1 dq_2$$

$$K_{ij} = \int \int \phi_i^*(q_1) \phi_j(q_1) \frac{1}{q_2 - q_1} \phi_j^*(q_2) \phi_i(q_2) dq_1 dq_2$$

Notice that the difference is a rather subtle swap of the indices  $i$  and  $j$ . This small change has a profound effect on the contribution calculated by the integral.

# The Fock equations

The procedure leads to the Fock equations.

$$f_i(q_1)\phi_i(q_1) = \varepsilon_i\phi_i(q_1)$$

The Fock operator is a one-electron operator

$$f_i(q_1) = h_i(q_1) + \sum_a (j_a(q_1) - k_a(q_1))$$

The choice of electron 1 is arbitrary. These equations can be written for all of the electrons. The Coulomb and exchange terms are

$$j_a(q_1)\phi_b^*(q_1) = \phi_b^*(q_1) \int |\phi_a(q_2)|^2 \frac{1}{q_2 - q_1} dq_2$$

$$k_a(q_1)\phi_b^*(q_1) = \phi_b^*(q_1) \int \phi_a^*(q_2)\phi_b^*(q_2) \frac{1}{q_2 - q_1} dq_2$$