

Numerical treatment of many electron atoms

A Computer Exercise in Atomic Physics (1996) by Eva Lindroth

1 Introduction

For pure two-body systems, like the hydrogen atom, it is possible to solve the Schrödinger equation analytically. The other elements in the periodic table are, however, many-body systems where the motion of every electron is coupled to the motion of all the other electrons. To study such a system we have to rely on some approximation scheme. In this exercise you will meet one widely used approximation method called the Hartree-Fock method. It is based on the rather natural approximation that each electron moves in the *average* potential from the nucleus and the other electrons. This assumption leads to the *independent-particle model*, which essentially reduce the many-electron problem to the problem of solving a number of coupled single-particle equations. The single-particle equations are solved in an iterative way which will be described below. Hartree made the first calculation based on these ideas already 1928, but calculations of this type are of course best suited for computers. Today there are several computer codes available for anyone who are interested in atomic properties. You will work with one such code written by R. D. Cowan.

The Hartree-Fock approximation is a fast and reliable method for a wide range of atomic systems, but it is just a first approximation. Nowadays there are several calculation schemes developed which can produce much more accurate results. For very few electron systems, as helium, the “many-body problem” can be solved more or less exactly (at present the non-relativistic ground state energy of helium is known with fifteen significant figures). General many-electron systems cannot be treated with such a precision, but a large part of the *electron correlation*, i.e. effects beyond the independent particle model, can be accounted for with methods such as configuration interaction (CI) or perturbation theory. Here you will make a small CI calculation on helium and beryllium to get a feeling for the limitations of the independent particle model.

2 The Hartree-Fock method

As mentioned in the introduction the Hartree-Fock method is based on the independent particle approximation where each electron moves in an average potential created by the nucleus and the other electrons. . The approximative Hamiltonian can then be written as a sum of one-particle Hamiltonians

$$H_{approx.} = \sum_{i=1}^N h(i) \quad (1)$$

where N is the number of electrons in our system. The simplest form of an eigenfunction to $H_{approx.}$ will be a product function

$$\Psi = \psi_a(1)\psi_b(2)\psi_c(3)\psi_d(4)\dots \quad (2)$$

where a, b etc stand for the quantum numbers necessary to specify a single electron state. Any permutation of the single-particle functions, which we can call spin-orbitals, will also lead to an eigenfunction of $H_{approx.}$. However, in order to satisfy the Pauli exclusion principle the total wave function, Ψ , must be antisymmetric with respect to the interchange of any two of the electrons. We can form a wave function with this property by antisymmetrizing the product function above. We write this antisymmetrized wave function as

$$\Psi = \frac{1}{\sqrt{N!}} Det\{\psi_a(1)\psi_b(2)\psi_c(3)\psi_d(4)\dots\psi_x(N)\} \quad (3)$$

and it is called a Slater determinant. As a simple example consider an atom with two electrons, than the antisymmetrized wave function will be

$$\Psi = \frac{1}{\sqrt{2}}\{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)\}. \quad (4)$$

If we want the total wave function, Ψ , to consist of one Slater determinant, how do we chose the “best” one? The expectation value of the total energy for a state represented by the Slater determinant is given by the expectation value of the total Hamiltonian

$$H = \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} \right) + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}}. \quad (5)$$

The “best” determinant for the ground state should be the one which minimize the expectation value of H . We thus minimize the energy with respect to changes in the Slater determinant, Ψ . (For details see Lindgren, *Atomfysik* or Cowan, *Theory of Atomic Structure and Spectra*). This leads to the *Hartree-Fock equations*

$$\left(\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} \right) \psi_a(i) + \left[\sum_b^{occ} \int \psi_b(j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \psi_b(j) dV_j \right] \psi_a(i) - \left[\sum_b^{occ} \int \psi_b(j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \psi_a(j) dV_j \right] \psi_b(i) = \varepsilon_a \psi_a(i). \quad (6)$$

As before a and b denote the quantum numbers necessary to specify a single electron state. The sum over b runs over all occupied states. Although the expression looks complicated it is just an eigenvalue equation of the form

$$h(i)\psi_a(i) = \varepsilon_a \psi_a(i). \quad (7)$$

where h is

$$h(i) = \frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} + u_{HF}(i). \quad (8)$$

The last term, $u_{HF}(i)$ is called the Hartree-Fock potential. From Eq. 6 we see that its effect on $\psi_a(i)$ is

$$u_{HF}(i)\psi_a(i) = \left[\sum_b^{occ} \int \psi_b(j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \psi_b(j) dV_j \right] \psi_a(i) - \left[\sum_b^{occ} \int \psi_b(j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \psi_a(j) dV_j \right] \psi_b(i). \quad (9)$$

Due to the presence of the last term, the *exchange potential*, the potential is non-local. The exchange term is a consequence of the Pauli principle and the requirement of antisymmetric wave functions.

In the general case the Hartree-Fock equations given in Eq. 6, are hard to solve. In practice a few other restrictions are thus imposed on the spin-orbitals, ψ . The first restriction is the requirement that the spin-orbital can be separated into one spin and one orbital part. The second restriction is that we assume that the ψ 's are solutions to a spherical symmetric potential. This later restriction is called the *central field approximation* and it make possible a separation of the orbital part of the wave function into one radial and one angular part. For a closed shell system, where the total spin and angular momentum is zero, the system is indeed spherical symmetric and that restriction is automatically fulfilled. We can now write the spin-orbital as a product of the radial, the angular and the spin part

$$\psi(r, \theta, \phi, \sigma) = \frac{1}{r} P_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \chi_{m_s}(\sigma). \quad (10)$$

The $Y_{\ell m_\ell}$'s are spherical harmonics and the Hartree-Fock equation, Eq. /refeq:hf, can now be simplified to the *radial* Hartree-Fock equations

$$\left[\frac{\hbar^2}{2m} \left(-\frac{d^2}{dr_i^2} + \frac{\ell_a(\ell_a + 1)}{r_i^2} \right) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_i} \right] P_a(r_i) + \left[\sum_b^{occ} \int P_b(r_j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} P_b(r_j) dr_j \right] P_a(r_i) - \left[\sum_b^{occ} \int P_b(r_j) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} P_a(r_j) dr_j \right] P_b(r_i) = \varepsilon_a P_a(r_i) \quad (11)$$

which can be solved to obtain the radial functions, P .

As can be seen from Eq. 11 the equation for P_a depends on the radial functions for all the other electrons. Because of that one uses an iterative scheme. The starting point is an approximative description of the single particle functions, $P(r)$. It could be hydrogen-like functions, but usually some better approximation is used. With these starting functions the Hartree-Fock potential is constructed and the eigenvalue equation, Eq. 11, is solved. Then a new set of single-particle functions are obtained and a new Hartree-Fock potential is constructed and again the eigenvalue equation, Eq. 11, is solved. This is done over and over again until the radial functions as well as the energy eigenvalues are stable. We call this a *self-consistent* method.