Chapter 2

CORRELATION METHODS IN ATOMIC THEORY

With respect to refining methods for recording atomic spectra, studying them near the threshold energies, and examining many-electron transitions and other anomalies, the development of effective, simple, and universal methods of accounting for the correlation between electrons is the most important problem in atomic physics, including the theory of electron and x-ray spectra. This chapter does not presume to be a systematic review of the various correlation methods. Methods of this type and variations of them have been proposed, but most of these are quite complex and are only used in practice for configurations containing either several electrons or closed electron shells. We will only describe the most widely used methods for describing electron and x-ray spectra — semiempirical and simple theoretical methods of accounting for correlations (Sec. 2.1), the many-configuration approximation and its variations, the method of configuration interaction (Sec. 2.2), stationary perturbation theory (Sec. 2.3), and the method that takes into account the interaction between a discrete state and a continuum, which is extremely important for highly excited states (Sec. 2.4). The various correlation methods in atomic theory have been thoroughly reviewed in the monographs [47, 45, 95, 96, etc.].

2.1. The Correlation Energy and the Simplest Methods of Accounting for It

According to Löwdin [97], the correlation energy is the difference between the exact nonrelativistic energy $E^r$, obtained approximately by subtracting the relativistic correction from the experimental energy, and the Hartree–Fock energy:

$$E^{cor} = E^r - E^{HF} \approx (E^{exp} - E^{rel}) - E^{HF}$$

(2.1)
Ordinarily, $E_{HF}$ is understood to be the energy calculated by the Hartree–Fock method for the average energy (HF-av.). Thus, we will call those methods that go beyond the scope of the HF-av. method correlation methods.

The Hartree–Fock method can be made more accurate by removing the constraint that all electrons in a shell have the same radial wave function. If we assume that this wave function also depends on the electron's direction of spin, we obtain the spin-polarized Hartree–Fock method [98–100]. However, when we fix the projections of the electron spins, the resulting spin angular momentum does not have an exact value. In addition dividing a shell into two subshells having upward and downward spins, just as in the relativistic theory, the configuration is divided into several subconfigurations that correspond to the different electron distributions in the subshells — these spin-polarized configurations mix via spin–orbit interaction. It is for these reasons that the spin-polarized method has not been widely adopted.

We can go even further in this direction and assume that the radial wave function is also dependent on the projection of the one-electron orbital angular momentum, i.e., that each electron is described by a different radial function. This corresponds to the unrestricted Hartree–Fock method [101]. A simpler version of this method is the extended method [102], in which a one-electron radial wave function does not belong to a specific spin-angular function: the wave function for a shell is presented as the product of an antisymmetrized spin-angular function and a symmetrized radial function as a permanent from the radial functions. All in all, the extended method is much more complex than the HF-av. method and allows us to calculate only a fraction of the correlation energy [45], i.e., only the radial correlations between equivalent electrons.

With the Hartree–Fock method we can also dispense with the condition that one-electron radial wave functions having the same $l$ be orthogonal [103]. This makes the wave functions and energy more precise for configurations containing two or more open shells that have the same $l$. Then, the energy calculated by using nonorthogonal wave functions is obtained exactly in the first and second terms of the expansion in powers of $Z$, whereas only the first term is exact when the condition given by Eq. (1.150) is taken into account [45]. However, when we dispense with the orthogonality condition the equations for the Hartree–Fock energy and potential become much more complex: additional terms containing overlap integrals and integrals $l(nl)$ appear in the expression for the potential.

A comparatively simple method of accounting for correlation methods, although it is neither very strict nor universal, is to use a potential function having one or more semiempirical parameters in the one-electron equation. Different semiempirical potentials are used most successfully to describe one, and less often, two outer electrons besides closed shells [57]. The Klapisch potential [104] is fairly effective for complex configurations.