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Volker Schmidt

Excerpt

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Part A

Background and basic principles

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Introduction

1.1 Theoretical background and general aims

In the non-relativistic limit, the electronic structure of an atom is determined by the Coulomb interaction between the electrons and the nucleus and the Coulomb interaction between the electrons themselves. In the relativistic case, other interactions have to be added, of which the spin-orbit interaction represents the largest contribution. The complete and exact description of these forces in the atom follows from quantum electrodynamics which is nowadays a well-established theory. Therefore, structure studies in atoms as compared to other systems (nuclei or elementary particles) have the advantage of involving forces which are known exactly. However, even for an ideal case it is extremely difficult accurately to calculate the atomic parameters for a many-electron system. As an example the structure of the helium atom in its ground state wavefunction will be discussed, first within the model of independent particles and then for two types of wavefunction which take into account electron correlations, i.e., the correlated motions of the electrons. The fundamental features demonstrated for this relatively simple case can then also be applied to the more complicated dynamical process of photoionization. Here the observed effects of electron-electron interactions and their theoretical treatment brought a renaissance of atomic physics with exciting new insight into the structure and dynamics of atoms interacting with photons, and this aspect will appear in many places throughout the book.

1.1.1 Atomic structure

In order to understand atomic structure, some results from quantum mechanics have to be recalled. For simplicity, it is sufficient to consider the non-relativistic case; however, the existence of the electron spin must be taken into account. The Hamiltonian H for an atom with Z electrons is given by (using atomic units which are defined in Section 6.1)

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - Z \sum_i \frac{1}{r_i} + \sum_{i < j} \frac{1}{r_{ij}}. \quad (1.1)$$

The electronic structure of the ground state follows from the properties of the ground state wavefunction $\tilde{\Psi}$ which is the solution of the stationary Schrödinger equation

$$H\tilde{\Psi} = E\tilde{\Psi}, \quad (1.2)$$

where E is the ground state energy (minimum energy value). The tilde on the wavefunction $\tilde{\Psi}$ indicates that the wavefunction must be antisymmetric with respect to the interchange of any two electrons because electrons are fermions, with spin $1/2$. (Fermions are named after E. Fermi who studied their properties in great detail.)

Approximating the Coulomb interaction between the electrons by a mean spherical potential $V(r)$, it follows that

$$H \approx H^0 = \sum_i h_i \quad (1.3a)$$

with

$$h_i = -\frac{1}{2}\nabla_i^2 - Z\frac{1}{r_i} + V(r_i), \quad (1.3b)$$

and the Schrödinger equation can easily be solved. First, one solves the single-particle Schrödinger equation with the operator h_i for electron i , which is just the Hamiltonian operator for the hydrogen atom (examples of the solution are given in Section 7.1)

$$h_i\varphi_i = \varepsilon_i\varphi_i. \quad (1.4)$$

Second, one solves the approximate Hamiltonian H^0 for the Z -electron problem

$$H^0\tilde{\Psi}^0 = E^0\tilde{\Psi}^0. \quad (1.5)$$

The energy E^0 is simply the sum of the energies ε_i of the individual electrons,

$$E^0 = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_Z. \quad (1.6)$$

The wavefunction $\tilde{\Psi}^0$ then follows as an antisymmetrized product built from the single-particle functions $\varphi_i(\mathbf{r}, m_s)$ for the Z electrons (Slater determinantal wavefunction, see below and Section 7.2), where \mathbf{r} is the spatial vector and m_s the spin magnetic quantum number.

This approach yields the *shell model* of the atom in which, under the restrictions of the Pauli principle[†] and according to the aufbau principle,[‡] the electrons i are placed in the spin-orbitals $\varphi_i(\mathbf{r}, m_s)$. For example, the shell structure of the magnesium atom is sketched schematically in Fig. 1.1.

Due to the properties of determinants, a Slater determinantal wavefunction $\tilde{\Psi}^0$ automatically fulfils the Pauli principle and takes care of the antisymmetric character of fermions. If written explicitly in terms of the single-particle orbitals,

[†] The *Pauli exclusion principle* [Pau25] states that occupied electron orbitals must differ in at least one of the quantum numbers n, ℓ, m_ℓ, m_s .

[‡] In the *aufbau* (German: building-up) principle the electrons of the atoms are placed in the lowest unoccupied orbitals, starting with the $1s$ orbital and filling the other orbitals one after the other (see, for example [Som19] Vol. I, p. 168). The irregularities which exist for the filling of nd and nf shells are not considered here (see Section 5.3.1).

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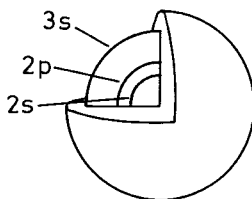


Figure 1.1 Schematic sketch of the shell structure of the magnesium atom. The atom has spherical symmetry, and one quadrant of the sphere has been cut out in order to show the shells which are indicated as part of a circular orbit for 3s, 2p and 2s electrons (the inner 1s shell is not visible).

$\tilde{\Psi}^0$ is defined as

$$\begin{aligned} \tilde{\Psi}^0(1, \dots, Z) &= \{\varphi_1, \dots, \varphi_Z\} \\ &= \frac{1}{\sqrt{Z!}} \begin{vmatrix} \varphi_1(1) & \cdots & \varphi_1(Z) \\ \vdots & & \vdots \\ \varphi_Z(1) & \cdots & \varphi_Z(Z) \end{vmatrix}, \end{aligned} \quad (1.7a)$$

where the subscripts 1– Z stand for the four single-electron quantum numbers:

n = principal quantum number

ℓ = orbital angular momentum quantum number

m_ℓ = magnetic quantum number of the orbital angular momentum (component of ℓ along a preferred direction which is usually called the quantization axis or z -axis)

m_s = spin magnetic quantum number (component of spin along the preferred direction).

(Usually, the values $\ell = 0, 1, 2, 3$ are termed s, p, d, f, respectively, the names coming from observations in the alkali spectra where *sharp*, *principal*, *diffuse*, and *fundamental* series have been distinguished [Ryd89]; higher ℓ -values are then named in alphabetical order.) The numbers within the brackets label the electrons from 1 to Z . Hence, the most compact form which will be used in discussions can be written as

$$\tilde{\Psi}^0(1, \dots, Z) = \{n_1 \ell_1 m_{\ell_1}^{s_1}, \dots, n_Z \ell_Z m_{\ell_Z}^{s_Z}\}. \quad (1.7b)$$

For example, the ground state $\tilde{\Psi}^0$ of the magnesium atom for which 12 electrons must be placed in the spin-orbitals $1s0^{m_s}, 2s0^{m_s}, 2p m_\ell^{m_s}, 3s0^{m_s}$ is represented by the Slater determinantal wavefunction

$\{1s0^+, 1s0^-, 2s0^+, 2s0^-, 2p1^+, 2p1^-, 2p0^+, 2p0^-, 2p-1^+, 2p-1^-, 3s0^+, 3s0^-\}$.

The electronic structure of the atom then follows from the properties of $\tilde{\Psi}^0$. For a short characterization one quotes the *electron configuration* and the observables of the state considered:

$$\tilde{\Psi}^0: \text{electron configuration, state numbers.} \quad (1.8)$$

The electron configuration is described by the contributing spin-orbitals omitting the projection quantum numbers m_ℓ and m_s . The state numbers characterize the resulting state and follow from the solution of the stationary Schrödinger equation, i.e., they represent the eigenvalues of all operators which commute with the Hamiltonian, because these quantities can be measured simultaneously. In general these quantities are the energy E , the total angular momentum J and its projection M along a preferred direction (e.g., z-axis), and the parity π .

Since in many cases the Coulomb interaction between the electrons dominates their spin-orbit interaction (see the Hamiltonian in equ. (1.1)),

$$\sum_{i < j} \frac{1}{r_{ij}} \gg \sum_i \zeta(r_i) \ell_i \cdot \mathbf{s}_i, \quad (1.9)$$

and the Coulomb interaction preserves the spin and orbital angular momentum, one can also include in the state numbers the angular momenta L and S which are defined by the vector sum of individual angular momenta

$$\mathbf{L} = \sum \ell_i \quad \text{and} \quad \mathbf{S} = \sum \mathbf{s}_i. \quad (1.10)$$

From these, one gets the total angular momentum J from the coupling

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (1.11)$$

Summarizing, the short characterization for the electronic structure of a given state follows from

$$\tilde{\Psi}^0: (\text{electron configuration})^{2S+1} L_J^\pi. \quad (1.12)$$

In this expression $2S + 1$ is called the *multiplicity* because if the spin-orbit interaction of the electrons is taken into account in a perturbative approach, the pure LS state splits in energy for the different couplings of L with S leading to J (the LSJ -coupling case), and the number of term splittings is given for $L \geq S$ by $2S + 1$. It is therefore common to say ‘singlet’, ‘doublet’, ‘triplet’ and so on for $2S + 1$ equal to 1, 2, 3, . . . For $L < S$ the number of possible terms is smaller than the multiplicity, e.g., 3S_1 has only one term even though it is called a triplet, ${}^5P_{3,2,1}$ has only three terms even though it is called a quintet.

The parity π of the resulting state reflects the behaviour of the wavefunction with respect to inversion through the origin, i.e.,

$$\Pi \tilde{\Psi}^0(\mathbf{r}_1, \dots, \mathbf{r}_Z) = \tilde{\Psi}^0(-\mathbf{r}_1, \dots, -\mathbf{r}_Z) = \pi \tilde{\Psi}^0(\mathbf{r}_1, \dots, \mathbf{r}_Z). \quad (1.13a)$$

Since two operations of Π restore the arguments, the parity operator can have only two eigenvalues, $+1$ (called *even parity*) and -1 (called *odd parity*):

$$\pi = \pm 1. \quad (1.13b)$$

For the spherical symmetric systems considered here, the eigenvalue π follows from the property of the spherical harmonics

$$\Pi Y_{\ell m}(\vartheta, \varphi) = Y_{\ell m}(\pi - \vartheta, \pi + \varphi) = (-1)^\ell Y_{\ell m}(\vartheta, \varphi) \quad (1.14a)$$

attached to the orbital angular momentum quantum numbers ℓ and m of the electron. Hence, one gets for the parity π of many electrons with angular

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momenta ℓ_i

$$\pi = (-1)^{\sum \ell_i}. \quad (1.14b)$$

The eigenvalue $\pi = +1$ is indicated by the upper symbol 'e' (even), the eigenvalue $\pi = -1$ by the symbol 'o' (odd).

With these definitions, the ground state of the magnesium atom is then represented by the electron configuration for the orbitals 1s, 2s, 2p, and 3s (see Fig. 1.1) and the symbols for the angular momenta and parity as

$$\tilde{\Psi}^0: 1s^2 2s^2 2p^6 3s^2 \ ^1S_0^e.$$

The *LSJ*-coupling scheme introduced above is called the Russell–Saunders coupling scheme [RSa25]. It is based on the validity of equ. (1.9). The other extreme coupling case follows if the spin–orbit interaction dominates the Coulomb interaction between the electrons. This is called the *jjJ*-coupling scheme and requires that

$$\mathbf{j}_i = \ell_i + \mathbf{s}_i \quad \text{and} \quad \mathbf{J} = \sum \mathbf{j}_i. \quad (1.15)$$

In reality, intermediate coupling is more common, and lies somewhere between these two limits. An example is discussed in Section 7.4.3 and applied to K–LL Auger transitions in Section 3.1.3. As a rough rule, one can use *LSJ*-coupling for the outer shells in low-*Z* elements, and *jjJ*-coupling for inner shells in large-*Z* elements.

1.1.2 Ground state wavefunctions (helium)

Apart from the demands of the Pauli principle, the motion of electrons described by the wavefunction $\tilde{\Psi}^0$ attached to the Hamiltonian H^0 is independent. This situation is called the *independent particle* or *single-particle* picture. Examples of single-particle wavefunctions are the hydrogenic functions $\varphi_i(\mathbf{r}, m_s)$ introduced above, and also wavefunctions from a Hartree–Fock (HF) approach (see Section 7.3). HF wavefunctions follow from a *self-consistent* procedure, i.e., they are derived from an *ab initio* calculation without any adjustable parameters. Therefore, they represent the *best* wavefunctions within the independent particle model. As mentioned above, the description of the *Z*-electron system by independent particle functions then leads to the shell model. However, if the Coulomb interaction between the electrons is taken more accurately into account (not by a mean-field approach), this simplified picture changes and the electrons are subject to a correlated motion which is not described by the shell model. This correlated motion will be explained for the simplest correlated system, the ground state of helium.

In the independent particle picture, the ground state of helium is given by $1s^2 \ ^1S_0^e$. For this two-electron system it is always possible to write the Slater determinantal wavefunction as a product of space- and spin-functions with certain symmetries. In the present case of a singlet state, the spin function has to be

antisymmetric, χ_a , and one gets

$$\tilde{\Psi}^0(1s^2 \ ^1S_0^e) = \Phi^0(\mathbf{r}_1, \mathbf{r}_2)\chi_a, \quad (1.16a)$$

where

$$\Phi^0(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s0}(\mathbf{r}_1)\varphi_{1s0}(\mathbf{r}_2) \quad (1.16b)$$

and

$$\chi_a = \frac{1}{\sqrt{2}}[\chi_{1/2}^+(1)\chi_{1/2}^-(2) - \chi_{1/2}^+(2)\chi_{1/2}^-(1)], \quad (1.16c)$$

where the superscripts on the spinor-functions $\chi_{1/2}^{ms}$ characterize the $\pm 1/2$ spin projections parallel or antiparallel to the selected quantization axis.

There are many ways to improve this independent-particle model by incorporating electron correlation in the spatial part $\Phi^0(\mathbf{r}_1, \mathbf{r}_2)$ of the wavefunction. Here the Hylleraas function [Hyl29] and the method of configuration interaction (CI) will be used as illustrations.

The fundamental idea of Hylleraas was that the attractive force between the nuclear charge and each of the electrons is well accounted for in the single-particle orbitals $\varphi_{1s0}(\mathbf{r}_1)$ and $\varphi_{1s0}(\mathbf{r}_2)$ by their exponential functions with negative exponents in the coordinates \mathbf{r}_i (see Section 7.1.1):

$$\varphi_{1s0}(\mathbf{r}) = \frac{2}{\sqrt{4\pi}} Z^{3/2} e^{-Zr}. \quad (1.17)$$

Hence, one expects that the mutual repulsion of the electrons at the positions \mathbf{r}_1 and \mathbf{r}_2 can be described by an exponential function with a positive exponent in the relative coordinate r_{12} :

$$e^{r_{12}} \quad \text{with} \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{(r_1^2 + r_2^2 - 2r_1r_2 \cos \vartheta_{12})}. \quad (1.18)$$

As a consequence, elliptical coordinates

$$s = r_1 + r_2, \quad t = r_2 - r_1 \quad \text{and} \quad u = r_{12} \quad (1.19)$$

are introduced, and the correlated wavefunction is expanded in terms of these coordinates. The condition that E_g , the energy of the ground state, has to be a minimum then allows the determination of the unknown expansion coefficients by a variational procedure. In the lowest approximation one gets the three-parameter Hylleraas function,

$$\Phi_{\text{Hyll}}(\mathbf{r}_1, \mathbf{r}_2) = N e^{-1.815s}(1 + 0.30u + 0.13t^2), \quad (1.20)$$

with the normalization factor $N = 1.32135$ and the energy eigenvalue

$$E_g(\text{Hyll.}) = -2.90244 \text{ au.} \quad (1.21)$$

Before the individual parts of this function are discussed, the energy eigenvalue will be considered. The ground state energy E_g of the helium atom is just the energy value for double-ionization which can be determined accurately by several different kinds of experiments. Before the experimental value can be compared with the calculated one, some small corrections (for the reduced mass effect, mass polarization, relativistic effects, Lamb shift) are necessary which, for simplicity, are

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not considered here. Having established the corrected $E_g(\text{exp.}) = -2.90372$ au, this can be compared to the theoretical results: in the present context to $E_g(3\text{-param. Hyll.}) = -2.90244$ au and, for comparison, also to the Hartree–Fock value $E_g(\text{HF}) = -2.862$ au (see Section 7.3.1). There is rather close agreement between $E_g(3\text{-param. Hyll.})$ and $E_g(\text{exp.})$, but $E_g(\text{HF})$ is larger. This indicates a considerable improvement of the Hylleraas wavefunction in equ. (1.20) as compared to the HF function.[†]

The Hylleraas function, with its improved properties as compared to a Hartree–Fock function, is called a *correlated* wavefunction, $\Phi_{\text{corr.}}(\mathbf{r}_1, \mathbf{r}_2)$, because it takes into account the mutual electron–electron interaction much better, and the motion of electrons beyond a mean-field average is termed *correlated motion* or the effect of *electron correlations*. (The definition of electron correlation is used here in the strict terminology. The mean-field average of electron–electron interactions is frequently also called electron correlation.) Comparing equ. (1.20) with equ. (1.16b) one has

$$\Phi_{\text{corr.}}(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{\text{Hyll.}}(\mathbf{r}_1, \mathbf{r}_2) = \Phi^0(\mathbf{r}_1, \mathbf{r}_2) f_{\text{corr.}}(\mathbf{r}_1, \mathbf{r}_2), \quad (1.22a)$$

where the uncorrelated function is now described by screened hydrogenic wavefunctions (effective nuclear charge $Z = 1.815$ instead of the value $Z = 2$ for the bare nucleus),

$$\Phi^0(\mathbf{r}_1, \mathbf{r}_2) = N e^{-1.815(r_1 + r_2)} \quad (1.22b)$$

and a correction or, equivalently, a correlation factor is introduced:

$$f_{\text{corr.}}(\mathbf{r}_1, \mathbf{r}_2) = 1 + 0.30r_{12} + 0.13(r_2 - r_1)^2. \quad (1.22c)$$

The correlation factor can be analysed with respect to two different correlated motions of the electrons (see [Sla60] and Fig. 1.2):

- (i) *Angular* correlation: Here one assumes both electrons to be on the same radius, and one obtains

$$f_{\text{corr.}}(r_1 = r_2 = r; \vartheta_{12}) = 1 + 0.30r_{12} = 1 + 0.30\sqrt{[2r^2(1 - \cos \vartheta_{12})]}. \quad (1.23a)$$

This factor is responsible for an increase in the correlated wavefunction amplitude and hence in the charge distribution of both electrons when these electrons are on opposite sides of the nucleus ($\vartheta_{12} = 180^\circ$; see Fig. 1.2(b)).

- (ii) *Radial* correlation: Here one assumes both electrons to be on the same radius vector ($\vartheta_{12} = 0^\circ$) and analyses equ. (1.22c) for $r_1 + r_2 = \text{const} = 1$ au. This corresponds to the case in which the wavefunction has a large amplitude, i.e., in which there is a high probability of finding electrons. The correction factor then gives

$$f_{\text{corr.}}(r_1, r_2; \vartheta_{12} = 0^\circ) = 1 + 0.30r_{12} + 0.13r_{12}^2. \quad (1.23b)$$

[†] An extension of the Hylleraas function, slightly generalized, and with 39 parameters leads to $E_g(\text{theor.}) = -2.9037225$ au [Kin57]. If the necessary corrections are applied to this numerical value, one gets perfect agreement with the experimental result (for a correlated wavefunction of the ground state of helium which leads to E_g with an accuracy of 13 digits, $E_g(\text{theor.}) = -2.903724377033$ au, see [FPe66]).

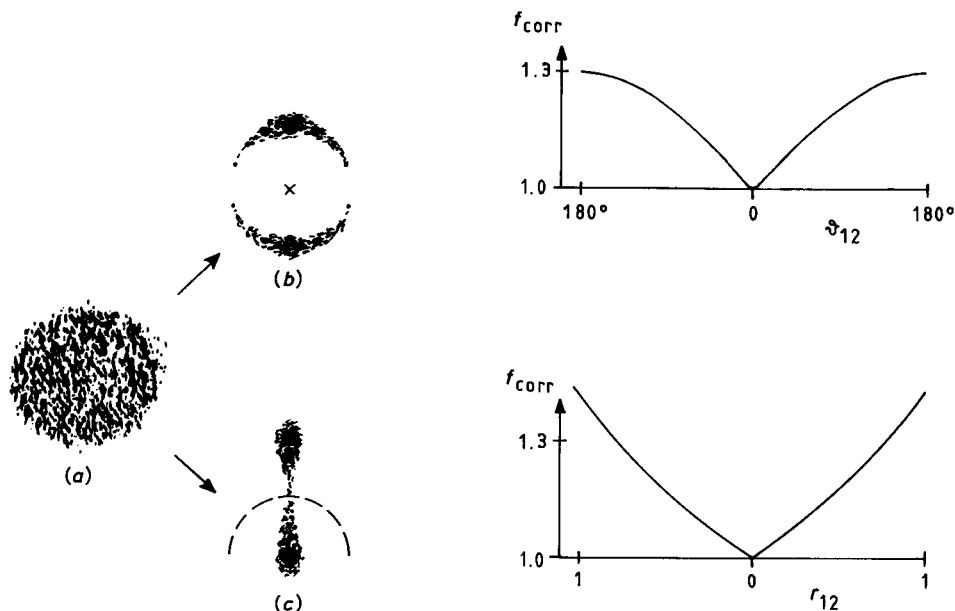


Figure 1.2 Sketch of the charge density distribution for (a) uncorrelated and (b) and (c) correlated motion of the two 1s-electrons in helium. Angular correlation is shown in (b) for $r_1 = r_2 = 0.5$ au; radial correlation in (c) for $\vartheta_{12} = 0^\circ$ and $r_1 + r_2 = 1$ au. Even though all visual pictures of the electron motion in an atom fail in detail, one can get an impression of what is meant by the correlated motions as follows: by looking at the uncorrelated motion of the electrons with half-closed eyes one obtains the picture in (a) with a fluctuating granular structure, but overall homogeneity. Focusing then on one specific region (following the arrows in (a)), the homogeneity is destroyed and a certain spatial structure becomes apparent which reflects the correlated motion of the electrons, namely, angular correlation ((b): the cross indicates the position of the nucleus) and radial correlation ((c): the centre of the circle indicates the position of the nucleus). The quantitative description of both types of correlation is given by the correlation factors f_{corr} , which follow from equ. (1.23a) and (1.23b), respectively, and this factor is shown at the right-hand side ((b) angular correlation; (c) radial correlation).

It can be seen that the correlated wavefunction has a minimum for $r_{12} = 0$ which corresponds to $r_1 = r_2 = 0.5$ au, i.e., higher values of the wavefunction are obtained when the electrons are further apart (see Fig. 1.2(c)).

The other approach most frequently used to describe a correlated wavefunction beyond the independent-particle model is based on *configuration interaction* (CI). (If the expansion is made on grounds of other basis sets, the approach is often called *superposition of configurations*, SOC, in order to distinguish it from the CI method.) According to the general principles of quantum mechanics, the exact wavefunction which is a solution of the full Hamiltonian H can be obtained as an expansion in any complete set of basis functions which have the same symmetry properties:

$$\tilde{\Psi}_{\text{corr.}} = \sum a_\nu \tilde{\Psi}_\nu^0, \quad (1.24)$$

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where \int indicates summation over discrete and integration over continuous basis functions. In atoms, it is the Coulomb interaction between the nuclear charge and the electrons which is responsible for a strong central potential. Hence, it is natural and convenient to use as a complete set of basis functions the solutions of H^0 following from equ. (1.5). The set of basis functions $\tilde{\Psi}_v^0$ then has to be constructed to implement different electron configurations. This is the reason why the approach is called configuration interaction.

Following these ideas, the ground state of helium which includes electron correlations can then be represented as

$$\begin{aligned} \tilde{\Psi}_{\text{corr.}}('1s^2\ ^1S_0^e') = & A_1 \tilde{\Psi}^0(1s^2\ ^1S_0^e) + a_2 \tilde{\Psi}^0(1s2s\ ^1S_0^e) \\ & + a_3 \tilde{\Psi}^0(2s^2\ ^1S_0^e) + a_4 \tilde{\Psi}^0(2p^2\ ^1S_0^e) + \dots, \end{aligned} \quad (1.25a)$$

where the admixed wavefunctions $\tilde{\Psi}_v^0$ belong to different electron configurations whose weight is described by the absolute value squared of the respective mixing coefficients $A_1, a_2, a_3, a_4, \dots$. Several comments have to be made concerning this expansion:

- (i) The expansion theorem given above requires an expansion into a *complete* set of basis functions. This requirement cannot be fulfilled in reality, because for practical reasons all expansions have to be truncated to a finite number. Therefore, the correlated wavefunction $\tilde{\Psi}_{\text{corr.}}$ can only approach the exact wavefunction $\tilde{\Psi}_{\text{exact}}$, and its quality will depend on the kind and number of selected basis functions. Ultimately this approximate treatment can be traced back to the many-body problem of classical quantum mechanics which also can be solved only approximately. In this general context of the many-body problem, atoms can provide a convenient test case for different theoretical models, because all interaction forces are known and the system can be varied from a three-body case (helium) to a full many-body system (heavier atoms).
- (ii) The admixed electron configurations should not be confused with a state, even though they are characterized by $^{2S+1}L_J^{\pi}$. This, however, is a consequence of the requirement that the admixed electron configurations must have the same symmetry properties. (How the state function for such a correlated function can be derived from the admixed functions is demonstrated in Section 7.4.) The admixed functions are *basis* functions which are needed to modify the uncorrelated wavefunction in such a way that the correlated motion of the electrons is taken into account. In cases where $|A_1|$ is larger than $|a_i|$, the whole state might be still named after this dominant electron configuration, and this is indicated in the present example by writing ' $1s^2\ ^1S_0^e$ '.
- (iii) To each admixed electron configuration is attached a different state which might also be related to an observable state. (This depends strongly on the selected kind and number of basis functions (see Section 7.4.) In the present