The resulting uncoupled or *independent-particle* (IP) Hamiltonian has the form

$$H_{\mathrm{IP}} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + V(\mathbf{r}_i) \right].$$ (4.3)

$V(\mathbf{r})$ is a potential depending on the positions $\mathbf{R}_i$ of the nuclei. As we shall see, its form can be quite complicated; in particular, V depends on the wave function ψ on which the IP Hamiltonian is acting. Moreover, V is often a nonlocal operator which means that the value of $V\psi$, evaluated at position $\mathbf{r}$, is determined by the values of ψ at other positions $\mathbf{r}' \neq \mathbf{r}$, and V depends on the energy in some approaches. These complications are the price we have to pay for an independent electron picture.

In the remaining sections of this chapter we shall study the Hartree–Fock approximation and in the next chapter we shall discuss the density functional theory. We start by considering the the helium atom to illustrate the general techniques which will be developed in later sections.

4.3 The helium atom

4.3.1 Self-consistency

In this section, we find an approximate independent-particle Hamiltonian (4.3) for the helium atom within the Born–Oppenheimer approximation by restricting the electronic wave function to a simple form. The coordinates of the wave function are $\mathbf{x}_1$ and $\mathbf{x}_2$, which are combined position and spin coordinates: $\mathbf{x}_i = (\mathbf{r}_i, s_i)$. As electrons are fermions, the wave function must be antisymmetric in the two coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$ (more details concerning antisymmetry and fermions will be given in Section 4.4). We use the following antisymmetric trial wave function for the ground state:

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)],$$ (4.4)

where $\alpha(s)$ denotes the spin-up and $\beta(s)$ the spin-down wave function and ϕ is an orbital – a function depending on a single spatial coordinate – which is shared by the two electrons.

The Born–Oppenheimer Hamiltonian (4.2) for the helium atom reads

$$H_{\mathrm{BO}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{r_1} - \frac{2}{r_2},$$ (4.5)

where we have used atomic units introduced in Section 3.2.2. We now let this Hamiltonian act on the wave function (4.4). Since the Hamiltonian does not act on the spin, the spin-dependent part drops out on the left and right hand side of the

Schrödinger equation and we are left with:[2]

$$\left[-\frac{1}{2}\nabla_1{}^2 - \frac{1}{2}\nabla_2{}^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) = E\phi(\mathbf{r}_1)\phi(\mathbf{r}_2). \quad (4.6)$$

In order to arrive at a simpler equation we remove the $\mathbf{r}_2$-dependence by multiplying both sides from the left by $\phi^*(\mathbf{r}_2)$ and by integrating over $\mathbf{r}_2$. We then arrive at

$$\left[-\frac{1}{2}\nabla_1{}^2 - \frac{2}{r_1} + \int \mathrm{d}^3 r_2 \, |\phi(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi(\mathbf{r}_1) = E'\phi(\mathbf{r}_1), \quad (4.7)$$

where several integrals yielding a constant (i.e. not dependent on $\mathbf{r}_1$) are absorbed in E'. The third term on the left hand side is recognised as the Coulomb energy of particle 1 in the electric field generated by the charge density of particle 2. To obtain this equation we have used the fact that ϕ is normalised to unity and this normalisation is from now on implicitly assumed for ϕ as occurring in the integral on the left hand side of (4.7). The effective Hamiltonian acting on the orbital of particle 1 has the independent particle form of Eq. (4.3). A remarkable feature is the dependence of the potential on the wave function we are searching for.

Equation (4.7) has the form of a *self-consistency* problem: ϕ is the solution to the Schrödinger equation but the latter is determined by ϕ itself. To solve an equation of this type, one starts with some trial ground state solution $\phi^{(0)}$ which is used in constructing the potential. Solving the Schrödinger equation with this potential, we obtain a new ground state $\phi^{(1)}$ which is used in turn to build a new potential. This procedure is repeated until the ground state $\phi^{(i)}$ and the corresponding energy $E^{(i)}$ of the Schrödinger equation at step i do not deviate appreciably from those in the previous step (if convergence does not occur, we must use some tricks to be discussed in Section 4.7).

The wave function we have used is called *uncorrelated* because of the fact that the probability $P(\mathbf{r}_1, \mathbf{r}_2)$ for finding an electron at $\mathbf{r}_1$ and another one at $\mathbf{r}_2$ is uncorrelated, i.e. it can be written as a product of two one-electron probabilities:

$$P(\mathbf{r}_1, \mathbf{r}_2) = p(\mathbf{r}_1)p(\mathbf{r}_2). \quad (4.8)$$

This does not mean that the electrons do not feel each other: in the determination of the spatial function ϕ, the interaction term $1/|\mathbf{r}_1 - \mathbf{r}_2|$ has been taken into account. But this interaction has been taken into account in an averaged way: it is not the *actual* position of $\mathbf{r}_2$ that determines the wave function for electron 1, but the *average* charge distribution of electron 2. This approach bears much relation to the mean field theory approach in statistical mechanics.

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[2] This equation cannot be satisfied exactly with the form of trial function chosen, as the left hand side depends on $\mathbf{r}_1 - \mathbf{r}_2$ whereas the right hand side does not. We are, however, after the optimal wave function within the set of functions of the form (4.4) in a variational sense, along the lines of the previous chapter, but we want to avoid the complications of carrying out the variational procedure formally. This will be done in Section 4.5.2 for arbitrary numbers of electrons.

The neglect of correlations sometimes leads to unphysical results. An example is found in the dissociation of the hydrogen molecule. Suppose the nuclei are placed at positions $\mathbf{R}_A$ and $\mathbf{R}_B$ and we approximate the one-electron orbitals by spherically symmetric (1s) basis orbitals centred on the two nuclei: $u(\mathbf{r} - \mathbf{R}_A)$ and $u(\mathbf{r} - \mathbf{R}_B)$. Because of the symmetry of the hydrogen molecule, the ground state orbital solution of the independent particle Hamiltonian is given by the symmetric combination of these two basis orbitals:

$$\phi(\mathbf{r}) = u(\mathbf{r} - \mathbf{R}_A) + u(\mathbf{r} - \mathbf{R}_B). \tag{4.9}$$

The total wave function, which contains the product $\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$ therefore contains ionic terms in which both electrons sit on the same nucleus. This is not so disastrous if the two nuclei are close, but if we separate them, these terms should not be present: they contain the wrong physics and they result in a serious over-estimation of the energy. Physically, this is caused by the fact that electron 1 in our present approximation feels the potential resulting from the *average* charge distribution of electron 2, which is symmetrically distributed over the two nuclei, and thus it ends up on A or B with equal probability. If electron 1 was to feel the *actual* potential caused by electron 2, it would end up on a different nucleus from electron 2. A better description of the state would therefore be

$$\psi(\mathbf{r}_1; \mathbf{r}_2) = \tfrac{1}{2}[u(\mathbf{r}_1 - \mathbf{R}_A)u(\mathbf{r}_2 - \mathbf{R}_B) + u(\mathbf{r}_2 - \mathbf{R}_A)u(\mathbf{r}_1 - \mathbf{R}_B)], \tag{4.10}$$

which must then be multiplied by an antisymmetric spin wave function. This wave function is however not of the form (4.4).

The fact that the spatial part of the wave function is equal for the two electrons is specific for the case of two electrons: the antisymmetry is taken care of by the spin part of the wave function. If there are more than two electrons, the situation becomes more complicated and requires much more bookkeeping; this case will be treated in Section 4.5. Neglecting the antisymmetry requirement, one can, however, generalise the results obtained for two electrons to systems with more electrons. Writing the wave function as a product of spin-orbitals $\psi_k(\mathbf{x})$ (spin-orbitals are functions depending on the spatial and spin coordinates of one electron), the following equation for these spin-orbitals is obtained:

$$\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + \sum_{l=1}^{N} \int dx' |\psi_l(\mathbf{x}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_k(\mathbf{x}) = E'\psi_k(\mathbf{x}).$$
$$\tag{4.11}$$

Here k and l label the spin-orbitals; $\int dx'$ denotes a sum over the spin s' and an integral over the spatial coordinate $\mathbf{r}'$: $\int dx' = \sum_{s'} \int d^3 r'$. As the Hamiltonian does not act on the spin-dependent part of the spin-orbitals, ψ_k can be written as a product of a spatial orbital with a one-electron spin wave function. In the last term

on the left hand side we recognise the potential resulting from a charge distribution caused by all the electrons; it is called the *Hartree potential*. There is something unphysical about this term: it contains a coupling between orbital k and itself, since this orbital is included in the electron density, even though an electron clearly does not interact with itself. This can be remedied by excluding k from the sum over l in the Hartree term, but then every orbital feels a different potential. In the next subsection, we shall see that this problem is automatically solved in the Hartree–Fock theory which takes the antisymmetry of the many-electron wave function fully into account. Note that in our discussion of the helium case, we have already taken the self-interaction into account because the electron–electron interaction is half the size of that in (4.11) (after summation over the spin in this equation). Equation (4.11) was derived in 1927 by Hartree [2]; it neglects exchange as well as other correlations.

Before studying the problem of more electrons with an antisymmetric wave function, we shall now describe the construction of a program for actually calculating the solution of Eq. (4.7).

4.3.2 A program for calculating the helium ground state

In this section we construct a program for calculating the ground state energy and wave function for the helium atom. In the previous section we have restricted the form of the wave function to be uncorrelated; here we restrict it even further by writing it as a linear combination of four fixed, real basis functions in the same way as in Section 3.2.2. Let us first consider the form assumed by the Schrödinger equation for the independent particle formulation, Eq. (4.7). The parametrisation

$$\phi(\mathbf{r}) = \sum_{p=1}^{4} C_p \chi_p(\mathbf{r}) \tag{4.12}$$

leads directly to

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \sum_{r,s=1}^{4} C_r C_s \int \mathrm{d}^3 r_2 \; \chi_r(\mathbf{r}_2)\chi_s(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \sum_{q=1}^{4} C_q \chi_q(\mathbf{r}_1)$$

$$= E' \sum_{q=1}^{4} C_q \chi_q(\mathbf{r}_1). \tag{4.13}$$

Note that the C_p are real as the functions $\chi_p(\mathbf{r})$ are real. From now on we implicitly assume sums over indices $p, q, \ldots$ to run from 1 to the number of basis functions N, which is 4 in our case. Multiplying Eq. (4.13) from the left by $\chi_p(\mathbf{r}_1)$ and integrating

over $\mathbf{r}_1$ leads to

$$\sum_{pq}\left(h_{pq} + \sum_{rs}C_rC_sQ_{prqs}\right)C_q = E'\sum_{pq}S_{pq}C_q \tag{4.14}$$

with

$$h_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 - \frac{2}{r}\right| \chi_q \right\rangle; \tag{4.15a}$$

$$Q_{prqs} = \int d^3r_1 d^3r_2 \chi_p(\mathbf{r}_1)\chi_r(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\chi_q(\mathbf{r}_1)\chi_s(\mathbf{r}_2) \quad \text{and} \tag{4.15b}$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle. \tag{4.15c}$$

Unfortunately, (4.14) is not a generalised eigenvalue equation because of the presence of the variables C_r and C_s between the brackets on the left hand side. However, if we carry out the self-consistency iteration process as indicated in the previous section, the C_r and C_s are kept *fixed*, and finding the C_q in (4.14) reduces to solving a generalised eigenvalue equation. We then replace C_r, C_s by the solution found and start the same procedure again.

The matrix elements from (4.15) remain to be found. We shall use Gaussian $l = 0$ basis functions (s-functions), just as in the case of the hydrogen atom (see Section 3.2.2). Of course, the optimal exponents α_p occurring in the Gaussian s-basis functions χ_p,

$$\chi_p(\mathbf{r}) = e^{-\alpha_p r^2}, \tag{4.16}$$

are different from those of the hydrogen atom. Again, rather than solve the non-linear variational problem, which involves not only the prefactors C_p but also the exponents α_p as parameters of the wave function, we shall take the optimal values calculated from a different program which we do not go into here. They are

$$\alpha_1 = 0.298\,073$$
$$\alpha_2 = 1.242\,567$$
$$\alpha_2 = 5.782\,948,$$
$$\alpha_4 = 38.474\,970.$$

The matrix elements of the kinetic and the Coulomb energy are similar to those calculated for the hydrogen atom (see Eq. (3.29)), except for an extra factor of 2 in the nuclear attraction (due to the nuclear charge). In Section 4.8, the matrix element Q_{prqs} will be calculated; the result is given by

$$Q_{prqs} = \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s)\sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}}. \tag{4.17}$$

The program is constructed as follows.

- First, the 4×4 matrices h_{pq}, S_{pq} and the $4 \times 4 \times 4 \times 4$ array Q_{prqs} are calculated.
- Then initial values for C_p are chosen; they can, for example, all be taken to be equal (of course, you are free to choose other initial values – for this simple system most initial values will converge to the correct answer).
- These C-values are used for constructing the matrix F_{pq} given by

$$F_{pq} = h_{pq} + \sum_{rs} Q_{prqs} C_r C_s. \tag{4.18}$$

It should be kept in mind that the vector $\mathbf{C}$ should always be normalised to unity via the overlap matrix *before* inserting it into Eq. (4.18):

$$\sum_{p,q=1}^{4} C_p S_{pq} C_q = 1 \tag{4.19}$$

(see Problem 3.2).
- Now the generalised eigenvalue problem

$$\mathbf{FC} = E'\mathbf{SC} \tag{4.20}$$

is solved. For the ground state, the vector $\mathbf{C}$ is the one corresponding to the *lowest* eigenvalue.
- The energy for the state found is not simply given by E' as follows from the derivation of the self-consistent Schrödinger equation, Eq. (4.7). The ground state energy can be found by evaluating the expectation value of the Hamiltonian for the ground state just obtained:

$$E_{\mathrm{G}} = 2\sum_{pq} C_p C_q h_{pq} + \sum_{pqrs} Q_{prqs} C_p C_q C_r C_s, \tag{4.21}$$

where the (normalised) eigenvector $\mathbf{C}$ results from the last diagonalisation of $\mathbf{F}$.
- The solution $\mathbf{C}$ of the generalised eigenvalue problem (4.20) is then used to build the matrix $\mathbf{F}$ again and so on.

<div align="center">PROGRAMMING EXERCISE</div>

Write a program for calculating the ground state wave function of the helium atom.

Check 1 If your program is correct, the resulting ground state energy should be equal to $-2.855\,160\,38$ a.u. (remember that the atomic energy unit is the Hartree, see Section 3.2.2). The effect of using a small basis set can be judged by comparing with the value -2.8616 a.u. resulting from calculations using continuum integration techniques within the framework of the present calculation as described in Chapter 5. The effect of neglecting correlations in our approach results in the deviation from the exact value -2.903 a.u. (very accurate calculations can be performed for systems containing small numbers of electrons [3]).