Chapter 16
Separation of Many-Particle Systems

16.1 Introduction

The chapter illustrates a number of steps that are necessary to reduce the many-particle problem to a tractable form. The analysis starts from a system of interacting electrons and nuclei; such a system is not made of identical particles and its Hamiltonian operator is not necessarily separable. Besides that, the number of particles that are present in the typical volume of, e.g., a solid-state device is so huge that the solution of the Schrödinger equation of such a system in the original form is a hopeless task. The first step consists in the application of the adiabatic approximation, by which the system made of the electrons is separated from that of the nuclei. The way in which such a separation is accomplished has the inconvenience that the nuclei are kept fixed in the equilibrium positions; this approximation is too strong, because it prevents the exchange of energy and momentum between the two systems from occurring: in fact, it is used provisionally and is removed at a later stage. The next step deals with the electron system which, despite the separation from the nuclei, is still too complicate to be dealt with directly; using the Ritz method, the Schrödinger equation for the electron system is separated into single-particle equations, in which each electron is subjected to the average field of the others. This step yields the Hartree equations and greatly simplifies the problem; in fact, the equations, besides being separated, are also identical to each other, so that the set of eigenvalues and eigenfunction obtained from one of them is applicable to all electrons. The Hartree equations do not comply with the exclusion principle, which must necessarily be fulfilled because the system under consideration is made of identical particles; a further modification, yielding the Hartree–Fock equations, provides the wave function with the expected antisymmetry property. Finally, the system of nuclei is taken again into consideration to the purpose of eliminating the simplification that the nuclei are fixed in the equilibrium positions: considering the fact that the nuclei are strongly bound together, so that their displacement from the equilibrium position is small, the nuclei are treated as a system of linear harmonic oscillators. In this way, the interaction between an electron and the nuclei is described (in a later chapter) using the quantum-mechanical, first-order perturbation theory applied to the two-particle collision of an electron with a phonon.

M. Rudan, *Physics of Semiconductor Devices*,
DOI 10.1007/978-1-4939-1151-6_16

16.2 System of Interacting Electrons and Nuclei

The analysis of a conservative system of identical particles, started in Sect. 15.7, is based on the single-particle Hamiltonian operator (15.28). It must be noted, however, that the typical systems to be dealt with are not made of identical particles but, rather, of a mixture of subsystems; the particles of each subsystem are identical to each other, but different from those of the other subsystems. Moreover, the Hamiltonian operator of each subsystem is not necessarily separable. It follows that the existence of a single-particle Hamiltonian operator like (15.28) is by no means obvious. It is then necessary to tackle the problem from a more general point of view, starting from the consideration of a mixture of systems, and determining the approximations that may simplify the problem to a level that is practically affordable.

To this purpose, consider a conservative system made of K electrons and N nuclei, interacting with each other. The particles are bound together, so that the system's wave function can be assumed to be normalized to unity. The coordinates associated to the electrons are indicated with small letters and grouped into a single vector $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_K)$; those of the nuclei are indicated with capital letters: $\mathbf{R} = (\mathbf{R}_1, \dots, \mathbf{R}_N)$. The interaction among the particles is assumed to be of the Coulomb type, so that the contributions to the potential energy due to the electron–electron and nucleus–nucleus interactions are, respectively,

$$U_e(\mathbf{r}) = \frac{1}{2} \sum_{i,j=1}^{K} \frac{q^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}, \qquad U_a(\mathbf{R}) = \frac{1}{2} \sum_{i,j=1}^{N} \frac{Z_i Z_j q^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{R}_j|}, \tag{16.1}$$

with $j \neq i$, where $q > 0$ is the electron charge, ε_0 the vacuum permittivity, and $Z_j q$ the charge of the jth nucleus; factor $1/2$ is introduced to avoid a double summation. In addition one must consider the electron–nucleus interaction, whose contribution to the potential energy is

$$U_{ea}(\mathbf{r}, \mathbf{R}) = \sum_{i=1}^{K} \sum_{j=1}^{N} \frac{-Z_j q^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{R}_j|}. \tag{16.2}$$

Remembering (15.3), letting $\mathbf{r}_i = (x_{i1}, x_{i2}, x_{i3})$, $\mathbf{R}_i = (X_{j1}, X_{j2}, X_{j3})$, and defining

$$\nabla_i^2 = \frac{\partial^2}{\partial x_{i1}^2} + \frac{\partial^2}{\partial x_{i2}^2} + \frac{\partial^2}{\partial x_{i3}^2}, \qquad \nabla_j^2 = \frac{\partial^2}{\partial X_{j1}^2} + \frac{\partial^2}{\partial X_{j2}^2} + \frac{\partial^2}{\partial X_{j3}^2}, \tag{16.3}$$

the kinetic parts of the system's Hamiltonian operator are

$$\mathcal{T}_e = -\sum_{i=1}^{K} \frac{\hbar^2}{2m} \nabla_i^2, \qquad \mathcal{T}_a = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \nabla_j^2. \tag{16.4}$$

The time-independent Schrödinger equation of the system then reads

$$\mathcal{H} w = E w, \qquad \mathcal{H} = \mathcal{T}_e + \mathcal{T}_a + U_e + U_a + U_{ea} + U_{\text{ext}}, \tag{16.5}$$

where the eigenfunctions depend on all variables, $w = w(\mathbf{r}, \mathbf{R})$. In (16.5), $U_{\text{ext}} = U_{\text{ext}}(\mathbf{r}, \mathbf{R})$ is the potential energy due to an external, conservative field acting on the system. If it were $U_{ea} + U_{\text{ext}} = 0$, the Hamiltonian would be separable with respect to the two subsystems, $\mathcal{H} = \left(\mathcal{T}_e + U_e\right) + \left(\mathcal{T}_a + U_a\right)$. The time-independent equations resulting from the separation would be

$$\left(\mathcal{T}_e + U_e\right) u = E_e\, u, \qquad \left(\mathcal{T}_a + U_a\right) v = E_a v, \tag{16.6}$$

with $u = u(\mathbf{r})$, $v = v(\mathbf{R})$; due to the general properties of separable operators (compare with Sect. 10.3), the eigenvalues and eigenfunctions of (16.5) would have the form $w = u\, v$, $E = E_e + E_a$. As in general it is $U_{ea} + U_{\text{ext}} \neq 0$, the Schrödinger Eq. (16.5) is not actually separable, and its solution may often present a formidable challenge: considering by way of example that the concentration of atoms in solid matter is of the order of 5×10^{22} cm^{-3}, and that to a nucleus there correspond Z electrons, with Z the atomic number, the number of scalar coordinates necessary to describe a cubic centimeter of solid matter is of the order of $15\,(Z + 1) \times 10^{22}$. It is then necessary to make a number of approximations; they are introduced step by step and, as illustrated in Sects. 16.3, 16.4, and 16.5, they are capable to bring the problem back to the solution of single-particle equations.

16.3 Adiabatic Approximation

The problem of solving the Schrödinger Eq. (16.5) for a system of interacting electrons and nuclei is simplified by observing that the mass of a nucleus is much larger than that of the electron. As a first consequence, one expects that the interaction with an individual electron influences little the motion of a nucleus; rather, the latter is expected to be influenced by the average interaction with many electrons. A second consequence is that, if the particles' dynamics is provisionally considered in classical terms, the motion of the nuclei is much slower than that of the electrons; as a consequence, the classical positions $\mathbf{R}$ of the nuclei can be considered as slowly-varying parameters when the electron dynamics is investigated. For this reason, the procedure shown below, based on the latter observation, is called *adiabatic approximation* or also *Born-Oppenheimer approximation* [62, Sect. 8]. In quantum terms, the approximation leads to the splitting of the original Eq. (16.5) into a set of two coupled equations. To this purpose, let

$$\mathcal{H}_e = \mathcal{T}_e + U_e + U_{ea} + U_{\text{ext}}, \tag{16.7}$$

where the dependence on $\mathbf{R}$ is algebraic only. Considering such a dependence, the Hamiltonian operator $\mathcal{H}_e$ provides an eigenvalue equation whose eigenvalues and eigenfunctions depend on $\mathbf{R}$; they read

$$\mathcal{H}_e\, u = E_e u, \qquad E_e = E_e(\mathbf{R}), \qquad u = u(\mathbf{r}, \mathbf{R}). \tag{16.8}$$

Also, from the Schrödinger Eq. (16.8) one finds that, for any function v that depends only on $\mathbf{R}$, the following holds: $\mathcal{H}_e u\, v = E_e\, u\, v$. As v is undetermined, one may seek a form of v such that $w = u\,v$ is also an eigenfunction of the full Hamiltonian operator $\mathcal{H}$ of (16.5). From the definition of $\mathcal{H}_e$ it follows $\mathcal{H} = \mathcal{T}_a + U_a + \mathcal{H}_e$, whence the original Schrödinger Eq. (16.5) is recast as

$$\left(\mathcal{T}_a + U_a + \mathcal{H}_e\right) uv = E uv. \tag{16.9}$$

The second relation in (16.4) shows that each Laplacian operator in $\mathcal{T}_a$ acts on both u and v, specifically, $\nabla_j^2\, u\, v = u\, \nabla_j^2\, v + v\, \nabla_j^2\, u + 2\, \nabla_j\, u \cdot \nabla_j\, v$. Multiplying the latter by $-\hbar^2/\left(2m_j\right)$ and adding over j transforms (16.9) into

$$u\left(\mathcal{T}_a + U_a + E_e\right) v + v\mathcal{T}_a u + \mathcal{G}_a u\, v = E uv, \tag{16.10}$$

where the short-hand notation $\mathcal{G}_a uv = -\sum_{j=1}^{N} \left(\hbar^2/m_j\right) \nabla_j u \cdot \nabla_j v$ has been used. To proceed one notes that the coefficients in the Schrödinger Eq. (16.8) are real, so that u can be taken real as well. Remembering that the particles described by u are bound, one finds that u is normalizable so that, for any $\mathbf{R}$,

$$\int u^2(\mathbf{r}, \mathbf{R}) \mathrm{d}r = 1, \qquad \mathrm{d}r = \mathrm{d}^3 r_1 \ldots \mathrm{d}^3 r_K, \tag{16.11}$$

with the integral extended to the whole K-dimensional space $\mathbf{r}$. Remembering that ∇_j acts on $\mathbf{R}_j$, from (16.11) one derives

$$\int u\, \nabla_j u \mathrm{d}r = \frac{1}{2} \int \nabla_j\, u^2 \mathrm{d}r = \frac{1}{2} \nabla_j \int u^2 \mathrm{d}r = 0, \tag{16.12}$$

whence

$$\int u\, \mathcal{G}_a uv \mathrm{d}r = -\sum_{j=1}^{N} \frac{\hbar^2}{m_j} \nabla_j v \cdot \int u \nabla_j u \mathrm{d}r = 0. \tag{16.13}$$

Left multiplying (16.10) by u, integrating over $\mathbf{r}$, and using (16.11, 16.13), yields

$$\left(\mathcal{T}_a + U_a + E_e + U_u\right) v = E v, \qquad U_u(\mathbf{R}) = \int u \mathcal{T}_a u \mathrm{d}r. \tag{16.14}$$

In this way, the original Schrödinger Eq. (16.5) is eventually split into two coupled equations, (16.8) and (16.14); the former is written in extended form as

$$\left(\mathcal{T}_e + U_e + U_{ea} + U_{\mathrm{ext}}\right) u = E_e u. \tag{16.15}$$

The first equation, (16.14), is the equation for the nuclei, in fact its kinetic operator $\mathcal{T}_a$ acts on $\mathbf{R}$ only, and its potential-energy term $U_a + E_e + U_u$ depends on $\mathbf{R}$ only; this equation is coupled with the second one, (16.15), because E_e is an eigenvalue of (16.15) and U_u is given by the integral in (16.14) that involves the eigenfunctions of (16.15). In turn, (16.15) is the equation for the electrons, in fact its kinetic operator $\mathcal{T}_e$ acts on $\mathbf{r}$ only; in turn, the part $U_{ea} + U_{\mathrm{ext}}$ of its potential-energy term couples (16.15) with (16.14) due to the dependence on $\mathbf{R}$.

In principle, one may solve (16.15) after fixing $\mathbf{R}$ and, from the solution, calculate E_e and U_u to be used in (16.14). From v one then determines the expectation value of $\mathbf{R}$, that updates the starting point for the solution of (16.15). Considering the case of solid matter, and still reasoning in classical terms, a zero-order solution for the iterative procedure depicted above is found by observing that the nuclei, being massive and tightly bound together, are expected to depart little from their equilibrium positions $\mathbf{R}_0$. One then fixes $\mathbf{R} = \mathbf{R}_0$ in (16.15) to find, for the electrons' Schrödinger equation, the approximate form

$$\left(\mathcal{T}_e + V_e\right) u = E_e u, \qquad V_e(\mathbf{r}) = U_e(\mathbf{r}) + U_{ea}\left(\mathbf{r}, \mathbf{R}_0\right) + U_{\text{ext}}\left(\mathbf{r}, \mathbf{R}_0\right). \tag{16.16}$$

This separates completely the equation for the electrons, that may be thought of as forming a separate system of total energy E_e. Admittedly, keeping the positions of the nuclei fixed is rather crude an approximation; in this way, in fact, the nuclei can not exchange momentum and energy with the electrons any more. On the other hand it can be shown that the solution of (16.16) provides an acceptable approximation for the energy of the electrons. Another advantage of keeping the nuclei in the equilibrium positions occurs in the investigation of materials where the nuclei are arranged in periodic structures; in fact, one exploits in this case the properties of differential equations having periodic coefficients (compare with Sects. 13.4 and 17.5.1). In conclusion, the present analysis will continue by provisionally considering only the system of electrons as described by (16.16); obviously the problem of the exchange of momentum and energy with the system of nuclei can not be dispensed with, and will be resumed at a later stage (Sect. 16.6).

16.4 Hartree Equations

Equation (16.16), describing the separate system of K electrons after fixing the nuclei to the equilibrium positions $\mathbf{R}_0$, lends itself to the application of the Ritz method outlined in Sect. 16.7.1. For the sake of generality, one starts by assuming that the K particles are distinguishable; for this reason, the symbols $\mathcal{T}_e$, V_e, u, and E_e of (16.16) are not used. Also, the application of the Ritz method will be carried out in the case where the external forces are absent, $U_{\text{ext}} = 0$; such forces will be introduced again into the problem in Sect. 19.2.1, where the single-particle dynamics is described. Given these premises, the operator $\mathcal{A}$, its minimum eigenvalue A_1, and the corresponding eigenfunction v_1 used in Sect. 16.7.1 for describing the Ritz method are indicated here with $\mathcal{A} = \mathcal{H}$, $A_1 = E_1$, $v_1 = w_1$, where

$$\mathcal{H} = \sum_{i=1}^{K} \mathcal{T}_i + \sum_{i=1}^{K} \sum_{j<i} V_{ij}, \qquad \mathcal{T}_i = -\frac{\hbar^2 \nabla_i^2}{2\, m_i}, \qquad V_{ij} = \frac{\sigma_{ij}\, q^2\, Z_i\, Z_j}{4\, \pi\, \varepsilon_0\, |\mathbf{r}_i - \mathbf{r}_j|}, \tag{16.17}$$

with $\sigma_{ij} = \pm 1$. The above describe a system of different particles interacting through Coulomb potentials. Introducing the auxiliary function f as in (16.37), one minimizes the functional $\langle f_1 \dots f_K|\mathcal{H}|f_1 \dots f_K\rangle$ subjected to the K constraints $\langle f_i|f_i\rangle = 1$. Using the method of Lagrange multipliers, this is equivalent to finding the absolute minimum of

$$F_{\mathcal{H}}\big[f_1, \dots, f_K\big] = \langle f_1 \dots f_K|\mathcal{H}|f_1 \dots f_K\rangle - \sum_{i=1}^{K} \varepsilon_i \langle f_i|f_i\rangle, \tag{16.18}$$

with ε_i the multipliers. The terms related to $\mathcal{T}_i$ are separable, while those related to V_{ij} are separable in pairs. From the orthonormalization condition it follows

$$F_{\mathcal{H}} = \sum_{i=1}^{K} \left(\langle f_i|\mathcal{T}_i|f_i\rangle - \varepsilon_i \langle f_i|f_i\rangle + \sum_{j=1}^{i-1} \langle f_i\, f_j|V_{ij}|f_i\, f_j\rangle \right). \tag{16.19}$$

The minimum of $F_{\mathcal{H}}$ is found by letting $\delta F_{\mathcal{H}} = F_{\mathcal{H}}\big[f_1 + \delta f_1, \dots, f_K + \delta f_K\big] - F_{\mathcal{H}}\big[f_1, \dots, f_K\big] = 0$. Neglecting the second-order terms and observing that $\mathcal{T}_i$ is Hermitean yields

$$\delta\langle f_i|\mathcal{T}_i|f_i\rangle = \langle \delta f_i|\mathcal{T}_i|f_i\rangle + \langle f_i|\mathcal{T}_i|\delta f_i\rangle = 2\,\Re\langle \delta f_i|\mathcal{T}_i|f_i\rangle. \tag{16.20}$$

By the same token one finds $\delta\varepsilon_i\langle f_i|f_i\rangle = \varepsilon_i\, 2\,\Re\langle \delta f_i|f_i\rangle$ and $\delta\langle f_i\, f_j|V_{ij}|f_i\, f_j\rangle = 2\,\Re\langle f_i\, \delta f_j|V_{ij}|f_i\, f_j\rangle + 2\,\Re\langle f_j\, \delta f_i|V_{ij}|f_i\, f_j\rangle$. The symmetry of the Coulomb terms yields $V_{ji} = V_{ij}$, whence

$$\sum_{j=1}^{i-1} \big(\langle f_i\, \delta f_j|V_{ij}|f_i\, f_j\rangle + \langle f_j\, \delta f_i|V_{ij}|f_i\, f_j\rangle \big) = \sum_{j=1}^{K} \langle f_j\, \delta f_i|V_{ij}|f_i\, f_j\rangle, \tag{16.21}$$

with $j \neq i$ at the right hand side. The minimization condition of (16.19) then reads

$$2\,\Re \sum_{i=1}^{K} \left(\langle \delta f_i|\mathcal{T}_i|f_i\rangle - \varepsilon_i\, \langle \delta f_i|f_i\rangle + \sum_{j=1}^{K} \langle f_j\, \delta f_i|V_{ij}|f_i\, f_j\rangle \right) = 0, \tag{16.22}$$

with $j \neq i$ in the inner sum. As the variations δf_i are independent of each other, the term within parentheses in (16.22) must vanish for each i, this yielding a system of K coupled equations. The inner sum has a double integral in it, and is recast as

$$\sum_{j=1}^{K} \langle f_j\, \delta f_i|V_{ij}|f_i\, f_j\rangle = \langle \delta f_i|U_i|f_i\rangle, \qquad U_i(\mathbf{r}_i) = \sum_{j=1}^{K} \langle f_j|V_{ij}|f_j\rangle, \tag{16.23}$$

still with $j \neq i$. The ith equation of the system then reads

$$\langle \delta f_i|\mathcal{T}_i|f_i\rangle - \varepsilon_i\, \langle \delta f_i|f_i\rangle + \langle \delta f_i|U_i|f_i\rangle = \langle \delta f_i|\, (\mathcal{T}_i + U_i - \varepsilon_i)\, f_i\rangle = 0. \tag{16.24}$$

As the above holds for any δf_i, the terms on the right hand side of the scalar products of (16.24) must cancel each other. In conclusion, the minimization condition provides a set of K single-particle equations coupled through the terms U_i:

$$(\mathcal{T}_i + U_i)\, f_i = \varepsilon_i\, f_i, \qquad i = 1, \dots, K. \tag{16.25}$$

The above are called *Hartree equations*, and constitute a set of Schrödinger equations whose potential energy is given by the second relation in (16.23):

$$U_i(\mathbf{r}_i) = \sum_{j=1}^{K} \int \frac{\sigma_{ij}\, q^2\, Z_i\, Z_j}{4\,\pi\,\varepsilon_0\,|\mathbf{r}_i - \mathbf{r}_j|}\, |f_j|^2\, \mathrm{d}r_j, \qquad j \neq i. \tag{16.26}$$

The potential energy of the ith particle is the sum of two-particle potential energies averaged with the localization probabilities of the particles different from the ith. The eigenvalue ε_i is then the energy of the ith particle in the field of the other $K-1$ particles (for this reason, the sum $\varepsilon_1 + \ldots + \varepsilon_N$ is not the total energy of the system).

The solution of (16.25) is found by iteration; one starts with $i = 1$ and provides an initial guess for $f_2, \ldots, f_K$, so that the initial guess for U_1 is calculated from (16.26) and used in (16.25). The solution of the latter yields the first iteration for f_1 and, remembering the Ritz method outlined in Sect. 16.7.1, the parameters embedded in f_1 are exploited at this stage to lower the eigenvalue; then, one proceeds with $i = 2$, using the first iteration for f_1 and the initial guess for $f_3, \ldots, f_K$, and so on. It must be noted that the initial guess is used within an integral, whose effect is that of averaging the difference between the initial guess and the actual solution; therefore, it may happen that the accuracy of the first iteration is sufficient, to the extent that the iterative process may be brought to an end. In this case, the K Eqs. (16.25) become independent of each other and the solution effort is greatly reduced.

16.5 Hartree–Fock Equations

It is now necessary to investigate the problem originally introduced in Sect. 16.3, namely, that of Eq. (16.16), which describes the separate system of electrons after fixing the nuclei to the equilibrium positions $\mathbf{R}_0$. The Hartree Eqs. (16.25) can not be applied as they stand, because they have been deduced for a system made of distinguishable particles. To treat a system of electrons, instead, it is necessary to account for the particles' spin, that was not considered in Sects. 16.3 and 16.4, and ensure the antisymmetry of the wave function (Sect. 15.7). The procedure is similar to that depicted in Sect. 16.4, the difference being that the auxiliary function f is not expressed as a product like in (16.37), but is given by a Slater determinant (15.37), whose entries depend on the position and spin coordinates of the corresponding particle [62, Sect. 8], [99, Sect. 16.3].

The calculations are rather involved and are not reported here. It is important to mention that, like in Sect. 16.4, the derivation is carried out by assuming that the external forces are absent ($U_{\text{ext}} = 0$). The procedure yields a set of K equations, coupled with each other, that generalize the Hartree Eqs. (16.25) and are called *Hartree–Fock equations*. If the accuracy of the first iteration is sufficient, the original Hamiltonian operator of (16.16), describing the system of electrons as a whole, is separated into K single-particle, identical operators:

$$\mathcal{T}_e + V_e = \sum_{i=1}^{K} \left[-\frac{\hbar^2}{2\,m} \nabla_i^2 + V_{ei}(\mathbf{r}_i) \right]. \tag{16.27}$$

In this way the form (15.28) of the Schrödinger equation for the electrons, sought at the beginning of Sect. 16.2, is recovered.

16.6 Schrödinger Equation for the Nuclei

In the process of separating the Schrödinger equation for the electrons, (16.15), from that of the nuclei, (16.14), that is carried out in Sect. 16.3, the positions of the nuclei are fixed to the equilibrium values $\mathbf{R} = \mathbf{R}_0$. This is done to the purpose of calculating the coefficients E_e and U_u (compare with (16.6) and (16.14), respectively); such coefficients depend on $\mathbf{R}$ and can be obtained only by solving the equation for the electrons. After this step is accomplished, one turns to the equation for the nuclei, in which E_e and U_u are fixed to constants from the previous iteration; the potential energy of (16.14) then becomes

$$V_a(\vec{R}) = U_a(\vec{R}) + E_e(\vec{R}_0) + U_u(\vec{R}_0). \tag{16.28}$$

If the positions of the nuclei are kept fixed, that is, the iterative procedure outlined in Sect. 16.3 is brought to an end without solving (16.14), the exchange of momentum and energy between the system of electrons and that of nuclei can not take place. It is then necessary to proceed to the solution of (16.14); such a solution is obtained by means of an approximation shown below, and the iterative procedure for the solution of (16.14) and (16.15) is stopped right after. In this way, one keeps for the energy of the electrons the eigenvalues obtained with the nuclei fixed at $\mathbf{R}_0$, which is a convenient choice due to the advantages illustrated in Sect. 16.3.

As for the nuclei, it has already been observed in Sect. 16.3 with respect to the case of solid matter, that the nuclei, being massive and tightly bound together, are expected to depart little from their equilibrium positions $\mathbf{R}_0$. To improve with respect to the zero-order approximation $\mathbf{R} = \mathbf{R}_0$, and provisionally reasoning in classical terms, one assumes that the instantaneous displacement $\mathbf{R} - \mathbf{R}_0$ with respect to the equilibrium point is small, so that V_a in (16.28) can be approximated with a second-order Taylor expansion around $\mathbf{R}_0$. The classical form of the problem is thus brought to the case already solved in Sects. 3.9 and 3.10: indicating with $T_a + V_a$ the classical equivalent of the operator $\mathcal{T}_a + V_a$, the vibrational state of the nuclei is described in terms of the normal coordinates b_σ, whose conjugate moments are $\dot{b}_\sigma$, and the total energy of the nuclei reads (compare with (3.50)):

$$T_a + V_a = \sum_{\sigma=1}^{3N} H_\sigma + V_{a0}, \qquad H_\sigma = \frac{1}{2}\,\dot{b}_\sigma^2 + \frac{1}{2}\,\omega_\sigma^2\, b_\sigma^2, \tag{16.29}$$

with $\omega_\sigma > 0$ the angular frequency of the mode. As a consequence, the quantum operator takes the form

$$\mathcal{T}_a + V_a = \sum_{\sigma=1}^{3N} \mathcal{H}_\sigma + V_{a0}, \qquad \mathcal{H}_\sigma = -\frac{\hbar^2}{2}\,\frac{\partial^2}{\partial b_\sigma^2} + \frac{1}{2}\,\omega_\sigma^2\, b_\sigma^2 \tag{16.30}$$

which, introduced into (16.14), yields

$$\sum_{\sigma=1}^{3N} \mathcal{H}_\sigma \, v = E' v, \qquad E' = E - V_{a0}. \tag{16.31}$$

This procedure provides the separation of the degrees of freedom of the nuclei, and completes the separation process whose usefulness was anticipated in Sect. 16.2. The solution of (16.31) is illustrated in Sect. 12.5, and shows that the mode's energy is ascribed to the set of phonons belonging to the mode itself. As the phonons are bosons, the equilibrium distribution of their occupation numbers is given by the Bose–Einstein statistics. The description of the interaction between an electron and the nuclei is obtained from the quantum-mechanical, first-order perturbation theory applied to the two-particle collision of an electron with a phonon.

16.7 Complements

16.7.1 Ritz Method

Let $\mathcal{A}$ be a Hermitean operator with a discrete spectrum and a complete, orthonormal set of eigenfunctions. For the sake of simplicity, the eigenvalues are assumed non degenerate:

$$\mathcal{A} v_n = A_n v_n, \qquad \langle v_m | v_n \rangle = \delta_{mn}. \tag{16.32}$$

Consider the expansion of a function f in terms of the eigenfunctions of $\mathcal{A}$, $f = \sum_{n=1}^{\infty} c_n \, v_n$, with $c_n = \langle v_n | f \rangle$. From Parseval theorem (8.41) one finds

$$\langle f | \mathcal{A} | f \rangle = \sum_{n=1}^{\infty} A_n \, |c_n|^2. \tag{16.33}$$

As the eigenvalues are real, one orders them in a non-decreasing sequence: $A_1 \le A_2 \le A_3 \le \ldots$, whence

$$\langle f | \mathcal{A} | f \rangle \ge A_1 \sum_{n=1}^{\infty} |c_n|^2 = A_1 \, \langle f | f \rangle. \tag{16.34}$$

More generally, if f is orthogonal to the first $s-1$ eigenfunctions, then $c_1 = c_2 = \ldots = c_{s-1} = 0$, and

$$f = \sum_{n=s}^{\infty} c_n \, v_n, \qquad \langle f | \mathcal{A} | f \rangle \ge A_s \, \langle f | f \rangle, \tag{16.35}$$

where the equality holds if and only if $f = \text{const} \times v_s$. In conclusion, the functional

$$G_{\mathcal{A}}[f] = \frac{\langle f | \mathcal{A} | f \rangle}{\langle f | f \rangle} \tag{16.36}$$

has a minimum for $f = v_s$, whose value is A_s. The findings above are the basis of the *Ritz method*, that provides approximations for the eigenvalues and eigenfunctions of $\mathcal{A}$. For instance, the minimum eigenvalue A_1 and the corresponding eigenfunction $v_1(\mathbf{r})$ are approximated by letting $v_1 \simeq f\big(\mathbf{r}, \alpha_1, \alpha_2, \dots\big)$, where the form of f is prescribed and $\alpha_1, \alpha_2, \dots$ are parameters. The latter are then used to minimize $G_{\mathcal{A}}[f]$. The constraint $\langle f|f\rangle = 1$ is imposed along the calculation, yielding $A_1 \simeq \min_\alpha G_{\mathcal{A}}[f] = \langle f|\mathcal{A}|f\rangle$. When A_1, v_1 have been found, the next pair A_2, v_2 is determined by using an approximating function orthonormal to v_1, and so on. For a system made of N particles, the eigenfunctions depend on $3\,N$ coordinates: $v_n = v_n\big(\mathbf{r}_1, \dots, \mathbf{r}_N\big)$. It is convenient to approximate them by separating the variables:

$$f = f_1(\mathbf{r}_1) \dots f_N(\mathbf{r}_N), \tag{16.37}$$

where each f_i may also depend on parameters. The normalization constraint then yields

$$\langle f_i|f_i\rangle = 1, \qquad i = 1, \dots, N. \tag{16.38}$$