Chapter 19
Quantum Aspects of Materials II

We have already seen in Chapter 10 that basic properties of electron states in materials are determined by quantum effects. This impacts all properties of materials, including their mechanical properties, electrical and thermal conductivities, and optical properties. An example of the inherently quantum mechanical nature of electrical properties is provided by the role of virtual intermediate states in the polarizability tensor in Section 15.3.

We will now continue to illustrate quantum effects in materials with a focus on effects that require the use of second quantization or Lagrangian field theory, or at least the knowledge of exchange interactions for a proper treatment. We will start at the molecular level and then discuss the second quantization of basic excitations in condensed materials.

The inception of the Schrödinger equation was accompanied by a large number of immediate successes, including atomic theory, the quantum theory of photon-atom interactions, and quantum tunneling. Another of these important successes was the development of the theory of covalent chemical bonding, which was initiated by Burrau[1], Heitler and London[2], and others. This is an extremely important and well studied subject in chemistry and molecular physics, and yet it never seemed to reach the level of popularity and recognition that other areas of applied quantum mechanics enjoy. One reason for this lack of popularity might be the lack of simple, beautiful model systems which can be solved analytically. Solvable model systems are of great instructive and illustrative value, and often provide a level of insight that is very hard to attain with systems which can only be analyzed by

[1] Ø. Burrau, Naturwissenschaften 15, 16 (1927); K. Danske Vidensk. Selsk., Mat.-fys. Medd. 7(14) (1927).

[2] W. Heitler, F. London, Z. Phys. 44, 455 (1927).

R. Dick, *Advanced Quantum Mechanics*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-25675-7_19

approximation methods. However, the existence and stability of covalent bonds is clearly an important property of molecules and of materials in general, and a basic quantitative understanding of the covalent bond should be part of the toolbox of every chemist, physicist and materials scientist. Indeed, there is a model system which can be analyzed to some extent by analytic methods. If only basic qualitative features are required, the analytic formulation can then be used for numerical evaluations which do not require a huge amount of effort. This model system is the hydrogen molecule ion H_2^+, which is also known as the dihydrogen cation. The analysis of electron states for fixed locations of the two protons in this simplest molecular system have been investigated already in the early years of quantum mechanics[3], and have been a subject of research ever since, both in terms of the semi-analytic analysis in prolate spheroidal coordinates[4] used in Section 19.2, and in terms of high precision variational calculations[5]. Before specializing to H_2^+ we will discuss the interplay of nuclear and electronic coordinates and the role of the Born-Oppenheimer approximation in molecular physics.

19.1 The Born-Oppenheimer approximation

Molecules can be described by first quantized Hamiltonians of the form

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m_e} + \sum_I \frac{\boldsymbol{P}_I^2}{2M_I} + \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\boldsymbol{R}_I - \boldsymbol{R}_J|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,J} \frac{Z_J e^2}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{R}_J|} \tag{19.1}$$

if we use properly anti-symmetrized wave functions for the electrons and symmetrized or anti-symmetrized wave functions for bosonic or fermionic nuclei of the same kind. Here lower case indices enumerate electrons while upper case indices refer to nuclei.

[3] A.H. Wilson, Proc. Roy. Soc. London A 118, 617, 635 (1928); E. Teller, Z. Phys. 61, 458 (1930); E.A. Hylleraas, Z. Phys. 71, 739 (1931); G. Jaffé, Z. Phys. 87, 535 (1934).

[4] See e.g. G. Hunter, H.O. Pritchard, J. Chem. Phys. 46, 2146 (1967); M. Aubert, N. Bessis, G. Bessis, Phys. Rev. A 10, 51 (1974); T.C. Scott, M. Aubert-Frécon, J. Grotendorf, Chem. Phys. 324, 323 (2006).

[5] B. Grémaud, D. Delande, N. Billy, J. Phys. B 31, 383 (1998); M.M. Cassar, G.W.F. Drake, J. Phys. B 37, 2485 (2004); H. Li, J. Wu, B.-L. Zhou, J.-M. Zhu, Z.-C. Yan, Phys. Rev. A 75, 012504 (2007).

Otherwise, we might just as well use the second quantized Schrödinger picture Hamiltonian

$$
\begin{aligned}
H = & \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m_e} \nabla\psi_e^+(\boldsymbol{x}) \cdot \nabla\psi_e(\boldsymbol{x}) + \sum_A \frac{\hbar^2}{2M_A} \nabla\psi_A^+(\boldsymbol{x}) \cdot \nabla\psi_A(\boldsymbol{x}) \right) \\
& + \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{x}-\boldsymbol{x}'|} \left(\sum_{A<B} Z_A Z_B \psi_A^+(\boldsymbol{x}) \psi_B^+(\boldsymbol{x}') \psi_B(\boldsymbol{x}') \psi_A(\boldsymbol{x}) \right. \\
& + \sum_A \frac{Z_A}{2} \psi_A^+(\boldsymbol{x}) \psi_A^+(\boldsymbol{x}') \psi_A(\boldsymbol{x}') \psi_A(\boldsymbol{x}) + \frac{1}{2} \psi_e^+(\boldsymbol{x}) \psi_e^+(\boldsymbol{x}') \psi_e(\boldsymbol{x}') \psi_e(\boldsymbol{x}) \\
& \left. - \sum_A Z_A \psi_e^+(\boldsymbol{x}) \psi_A^+(\boldsymbol{x}') \psi_A(\boldsymbol{x}') \psi_e(\boldsymbol{x}) \right), \qquad (19.2)
\end{aligned}
$$

where the labels A, B enumerate different kinds of nuclei. We assume that there are N_e electrons and $N_n = \sum_A N_A$ nuclei in our molecule. Realistically, we would restrict attention to valence electrons (rather than all electrons), and the numbers A would enumerate different kinds of ion cores. However, in the example of the hydrogen molecule ion below this distinction is void. The choice of kinetic terms also assumes that all the particles are non-relativistic. Indeed, this also informs the choice of interaction terms in the Born-Oppenheimer Hamiltonian. Electromagnetic interactions between non-relativistic charged particles are dominated by the Coulomb interaction, but if there are relativistic charged particles in the system, photon exchange between charged particles through their couplings to the vector potential $\boldsymbol{A}(\boldsymbol{x})$ becomes important. Domination of the Coulomb interaction in the case of non-relativistic electron-nucleus and electron-electron scattering is demonstrated in Sections 22.2 and 22.4, respectively. Equation (22.29) provides an estimate of the relative importance of photon exchange versus Coulomb interactions for non-relativistic electrons and nuclei.

Spin labels are suppressed in (19.2) and also in the corresponding states below, because they enter trivially in the equations of motion[6].

Note that even in the valence electrons plus ion cores approximation, the Hamiltonians (19.1, 19.2) describe an incredibly complicated quantum mechanical system, even in the case of a "simple" diatomic molecule. This is because the complete spectrum of energy levels and eigenstates of (19.1) does not only include bound molecular states (which is complicated enough), but also scattering states of electrons and of molecular fragments. The Hamiltonian for the hydrogen molecule H_2 describes not only bound states of two protons and two electrons, but also electron scattering off an H_2^+ ion, atomic hydrogen-hydrogen scattering, proton scattering off an H^- ion, and a plasma of free protons and electrons. However, our

[6]We would have to be more careful if we would discuss expectation values, because exchange integrals appear in the expectation values of potential terms, see Section 17.7.

primary interest concerns an understanding of the nature of covalent bonds and of ground state properties of molecules. In this case, we don't have to include the scattering states, and we can even neglect the motion of ion cores.

Born and Oppenheimer have pointed out that it makes intuitive sense to separate nuclear and electronic motion by first solving the electronic problem for fixed nuclear coordinates, and then substituting the electronic solution into a remnant nuclear Schrödinger equation[7]. In the framework of quantized Schrödinger theory this amounts to an electronic Hamiltonian

$$H_e = H - \int d^3\boldsymbol{x} \sum_A \frac{\hbar^2}{2M_A} \nabla\psi_A^+(\boldsymbol{x}) \cdot \nabla\psi_A(\boldsymbol{x}) \tag{19.3}$$

with corresponding parameter dependent electronic states

$$|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle = \prod_{i=1}^{N_e} \int d^3\boldsymbol{x}_i \, \psi_e^+(\boldsymbol{x}_i) \prod_{I=1}^{N_n} \psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle \times \langle \boldsymbol{x}_1, \ldots \boldsymbol{x}_{N_e}|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle. \tag{19.4}$$

Here $\psi_e^+(\boldsymbol{x}_i)$ is an electronic creation operator and $\psi_{A(I)}^+(\boldsymbol{X}_I)$ is a creation operator for a nucleus of species A at the location $\boldsymbol{X}_I$. The set of quantum numbers $\boldsymbol{n}$ specifies the state (including the energy level), and the notation $|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle$ indicates that the electronic state also depends on the location of the nuclei.

The equation of motion for the electronic states (19.4) with the Hamiltonian (19.3) then follows as in Section 17.6, except that here we use a time-independent Schrödinger equation. The equation

$$E_{e,\boldsymbol{n}}(\boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n})|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle = H_e|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle$$

yields with the short hand notation $\langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle \equiv \langle \boldsymbol{x}_1, \ldots \boldsymbol{x}_{N_e}|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle$ the equation

$$E_{e,\boldsymbol{n}}(\boldsymbol{X})\langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle = -\frac{\hbar^2}{2m_e} \sum_i \frac{\partial^2}{\partial \boldsymbol{x}_i^2} \langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle + \frac{e^2}{4\pi\epsilon_0} \times \left(\sum_{i<j} \frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_j|} - \sum_{i,I} \frac{Z_{A(I)}}{|\boldsymbol{x}_i - \boldsymbol{X}_I|} + \sum_{I<J} \frac{Z_{A(I)} Z_{A(J)}}{|\boldsymbol{X}_I - \boldsymbol{X}_J|} \right) \langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle. \tag{19.5}$$

The N_e-electron wave functions $\langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle$ are complete in the $3N_e$-dimensional configuration space of the electrons, and therefore the wave functions of the full $(N_e + N_n)$-particle problem can be expanded in the form

$$\langle \boldsymbol{x}, \boldsymbol{X}|E\rangle = \sum_{\boldsymbol{n}} c(\boldsymbol{n}; \boldsymbol{X}) \langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}\rangle. \tag{19.6}$$

[7] M. Born, J.R. Oppenheimer, Annalen Phys. 84, 457 (1927).

The sum over the quantum numbers $\boldsymbol{n}$ also involves at least one integration over a continuous quantum number for the scattering states.

On the level of the second quantized theory, the amplitude (19.6) corresponds to the $(N_e + N_n)$-particle state

$$\begin{aligned}|E\rangle &= \prod_{i=1}^{N_e} \int d^3\boldsymbol{x}_i\, \psi_e^+(\boldsymbol{x}_i) \prod_{I=1}^{N_n} \int d^3\boldsymbol{X}_I\, \psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle \langle \boldsymbol{x}, \boldsymbol{X}|E\rangle \\ &= \prod_{I=1}^{N_n} \int d^3\boldsymbol{X}_I \sum_{\boldsymbol{n}} c(\boldsymbol{n};\boldsymbol{X})|\boldsymbol{n};\boldsymbol{X}\rangle,\end{aligned}$$

where the parameter-dependent electronic state $|\boldsymbol{n};\boldsymbol{X}\rangle$ is given in (19.4).

Substituting (19.6) into the full $(N_e + N_n)$-particle Schrödinger equation

$$H|E\rangle = E|E\rangle$$

yields the equation

$$\sum_{\boldsymbol{n}} \left(\sum_{I=1}^{N_n} \frac{\hbar^2}{2M_{A(I)}} \frac{\partial^2}{\partial \boldsymbol{X}_I^2} - E_{e,\boldsymbol{n}}(\boldsymbol{X}) + E \right) c(\boldsymbol{n};\boldsymbol{X}) \langle \boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle = 0. \tag{19.7}$$

This can be resolved into a set of coupled equations for the nuclear factors $c(\boldsymbol{n};\boldsymbol{X})$ through orthogonality of the electron factors $\langle \boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle$. If this is done, no approximation has been made so far to the problem to solve the molecular Hamiltonian (19.2). However, if we are in the center of mass frame of the nuclei, and if both rotational and vibrational excitations are small, we can neglect the nuclear kinetic terms, and we find for these nuclear configurations $\boldsymbol{X}^{(0)}$ that their energy levels can be approximated by

$$E = E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)}). \tag{19.8}$$

The corresponding full molecular eigenstate in this approximation has a wave function

$$\langle \boldsymbol{x}, \boldsymbol{X}|E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = \delta(\boldsymbol{X} - \boldsymbol{X}^{(0)}) \langle \boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}^{(0)}\rangle, \tag{19.9}$$

and a corresponding second quantized state

$$\begin{aligned}|E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = \prod_{i=1}^{N_e} \int d^3\boldsymbol{x}_i\, \psi_e^+(\boldsymbol{x}_i) \prod_{I=1}^{N_n} \int d^3\boldsymbol{X}_I\, \psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle \\ \times \langle \boldsymbol{x}, \boldsymbol{X}|E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = |\boldsymbol{n};\boldsymbol{X}^{(0)}\rangle.\end{aligned}$$

It might be tempting to conclude from (19.8) that the solution of the electronic equation (19.5) eventually allows us to calculate the nuclear equilibrium configuration $\boldsymbol{X}^{(0)}$ in the aftermath from a requirement $[\partial E_{e,\boldsymbol{n}}(\boldsymbol{X})/\partial \boldsymbol{X}]_{\boldsymbol{X}=\boldsymbol{X}^{(0)}} = 0$. However, *this is not true*: *The energy level $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ for a general nuclear configuration $\boldsymbol{X}$ represents only the electronic energy plus the electrostatic nuclear potential energy for that configuration*. Equation (19.8) only states that within the Born-Oppenheimer approximation, the energy $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ and the full molecular energy coincide in an equilibrium configuration, but that does *not* imply that the two energies coincide in a *neighborhood* of an equilibrium configuration. As a consequence the energy $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ and the full molecular energy can (and generically will) have *different gradients* with respect to the nuclear configuration, even in a molecular equilibrium configuration. The function $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ may have non-vanishing gradient in the molecular equilibrium configuration because it neglects the contributions from nuclear kinetic terms.

Therefore we have to use *a priori* knowledge of the equilibrium configuration $\boldsymbol{X}^{(0)}$, e.g. from scattering experiments, to calculate the molecular energy in the Born-Oppenheimer approximation. *We cannot calculate both the energy and the equilibrium configuration from* (19.5).

19.2 Covalent bonding: The dihydrogen cation

The stability of molecules is an issue in classical physics in the same sense as the stability of atoms is an issue. It is not surprising that sharing of electrons yields a net attractive force between positively charged nuclei or atomic cores. Consider e.g. two protons at separation b with an electron right in the middle between the protons. The net classical electrostatic energy of the system $\propto -3e^2/b$ is attractive, but the problem is again to prevent collapse of the system. The corresponding quantum mechanical system is again stabilized by wave particle duality. Squeezing the particles very tight together implies strongly peaked wave functions, hence too much curvature in the wave functions, and the ensuing increase in kinetic energy eventually cannot be compensated any more by gains in potential energy terms for normalizable wave functions.

We apply the basic tenet of the Born-Oppenheimer approximation to the hydrogen molecule ion H_2^+ and determine approximate molecular orbitals under the assumption that the two protons are fixed at their equilibrium separation b. The distances of the electron from the two protons are given by

$$r_\pm^2 = x^2 + y^2 + (z \pm (b/2))^2 \tag{19.10}$$

if we assume that the two protons are located on the z axis at $z = \pm b/2$. A suitable set of coordinates for the 2-center Coulomb problem are given by

$$\xi^+ = r_+ + r_-, \quad b \le \xi^+,$$
$$\xi^- = r_+ - r_-, \quad -b \le \xi^- \le b$$

and the azimuthal angle φ around the z axis. These coordinates are known as prolate spheroidal coordinates. They seem to have been used for the analysis of classical 2-center gravitational or electrostatic problems and for acoustic and electromagnetic radiation problems since the 19th century.

The surfaces $\xi^+ = const.$ are ellipsoids with the protons in the focal points, while the surfaces $\xi^- = const.$ are the corresponding hyperboloids. The ξ^- coordinate lines take us from one hyperboloid $\xi^- = const.$ to another hyperboloid $\xi^- = const.$ for constant ξ^+ and φ. For given value of ξ^+, going from $\xi^- = -b$ to $\xi^- = b$ takes us from the south pole of the ellipsoid $\xi^+ = const.$ to its north pole, i.e. ξ^-/b is similar to the ϑ coordinate on a sphere, except that we move from negative z to positive z for increasing ξ^-. The advantage of this is that $z > 0$ corresponds to $\xi^- > 0$, but the right handed prolate spheroidal coordinate system is then $\{\xi^-, \xi^+, \varphi\}$.

The ξ^+ coordinate lines are hyperbolas $\xi^- = const.$, $\varphi = const.$ with the protons in the focal points. $\xi^+ = b$ corresponds to the line $-b/2 \le z \le b/2$ on the z axis and $\xi^+ \to \infty$ takes us to infinite distance from the protons, i.e. ξ^+ plays a role similar to the radius r in spherical coordinates.

We apply the methods of Section 5.4 to determine tangent vectors to the coordinate lines and the relevant differential operators. We have

$$2r^2 + \frac{b^2}{2} = r_+^2 + r_-^2 = \frac{1}{2}(\xi^+)^2 + \frac{1}{2}(\xi^-)^2$$

and

$$z = \frac{\xi^+\xi^-}{2b},$$

and this implies also

$$x^2 + y^2 = \frac{b^2(\xi^+)^2 + b^2(\xi^-)^2 - (\xi^+\xi^-)^2 - b^4}{4b^2} = \frac{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}{4b^2},$$

$$x = \frac{1}{2b}\sqrt{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\cos\varphi,$$

$$y = \frac{1}{2b}\sqrt{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\sin\varphi.$$

The dual basis vectors (5.21) are in the present case

$$\boldsymbol{\nabla}\xi^+ = \frac{1}{2r_+r_-}\left(2\xi^+\boldsymbol{r} - b\xi^-\boldsymbol{e}_z\right), \quad \boldsymbol{\nabla}\xi^- = -\frac{1}{2r_+r_-}\left(2\xi^-\boldsymbol{r} - b\xi^+\boldsymbol{e}_z\right),$$

and

$$\boldsymbol{\nabla}\varphi = \frac{x\boldsymbol{e}_y - y\boldsymbol{e}_x}{x^2 + y^2}.$$

This yields a diagonal inverse metric with components

$$g^{++} = 4\frac{(\xi^+)^2 - b^2}{(\xi^+)^2 - (\xi^-)^2}, \quad g^{--} = 4\frac{b^2 - (\xi^-)^2}{(\xi^+)^2 - (\xi^-)^2},$$
$$g^{\varphi\varphi} = \frac{4b^2}{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]},$$

and the volume measure (5.27) for $d\xi^- d\xi^+ d\varphi$ follows as

$$\sqrt{g} = \left(g^{++} g^{--} g^{\varphi\varphi}\right)^{-1/2} = \frac{1}{8b}[(\xi^+)^2 - (\xi^-)^2]. \tag{19.11}$$

The Laplace operator (5.26) in spheroidal coordinates is therefore

$$\Delta = \frac{4}{(\xi^+)^2 - (\xi^-)^2}\left[\partial_+ \left((\xi^+)^2 - b^2\right)\partial_+ + \partial_- \left(b^2 - (\xi^-)^2\right)\partial_-\right]$$
$$+ \frac{4b^2}{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\partial_\varphi^2. \tag{19.12}$$

On the other hand, the coordinate dependence of the electrostatic potential of the electron is

$$\frac{1}{r_+} + \frac{1}{r_-} = \frac{4\xi^+}{(\xi^+)^2 - (\xi^-)^2},$$

and therefore the Hamiltonian in the $\{\xi^+, \xi^-, \varphi\}$ representation satisfies

$$\frac{m_e}{2\hbar^2}[(\xi^-)^2 - (\xi^+)^2]H = \partial_+ \left((\xi^+)^2 - b^2\right)\partial_+ + \partial_- \left(b^2 - (\xi^-)^2\right)\partial_-$$
$$+ \left(\frac{b^2}{(\xi^+)^2 - b^2} + \frac{b^2}{b^2 - (\xi^-)^2}\right)\partial_\varphi^2 + \frac{m_e e^2}{2\pi\epsilon_0\hbar^2}\xi^+. \tag{19.13}$$

The Hamiltonian H commutes with the azimuthal angular momentum operator L_z, and therefore we can discuss the spectrum and eigenfunctions of H within the subspaces of L_z eigenvalues $m\hbar$,

$$\psi_m(\xi^+, \xi^-, \varphi) = \frac{1}{\sqrt{2\pi}}\psi(\xi^+, \xi^-)\exp(\mathrm{i}m\varphi).$$

Within these subspaces, the normalization condition on the bound electron states becomes with (19.11),

$$\int_b^\infty d\xi^+ \int_{-b}^b d\xi^- \left[(\xi^+)^2 - (\xi^-)^2\right]\left|\psi(\xi^+, \xi^-)\right|^2 = 8b, \tag{19.14}$$

and the Hamiltonian H_m acting within these subspaces satisfies

$$\frac{m_e}{2\hbar^2}[(\xi^-)^2-(\xi^+)^2](H_m-E)=D_{+,m}(\xi^+)-D_{-,m}(\xi^-),$$

$$D_{+,m}(\xi^+)=\partial_+\left((\xi^+)^2-b^2\right)\partial_+-\frac{m^2b^2}{(\xi^+)^2-b^2}+\frac{m_e}{2\hbar^2}E(\xi^+)^2+\frac{m_ee^2}{2\pi\epsilon_0\hbar^2}\xi^+,$$

$$D_{-,m}(\xi^-)=\partial_-\left((\xi^-)^2-b^2\right)\partial_--\frac{m^2b^2}{(\xi^-)^2-b^2}+\frac{m_e}{2\hbar^2}E(\xi^-)^2.$$

Here the energy E differs from the energy E_e (19.8) of the molecule in the Born-Oppenheimer approximation by the electrostatic energy of the nuclei,

$$E_e=E+\frac{e^2}{4\pi\epsilon_0 b}. \tag{19.15}$$

Since H_m is hermitian with respect to the scalar product appearing in (19.14), the differential operators $D_{+,m}$ and $D_{-,m}$ must be hermitian with respect to the scalar products

$$\langle\psi_+|\phi_+\rangle_+=\int_b^\infty d\xi^+\,\psi_+^+(\xi^+)\phi_+(\xi^+)$$

and

$$\langle\psi_-|\phi_-\rangle_-=\int_{-b}^b d\xi^+\,\psi_-^+(\xi^-)\phi_-(\xi^-),$$

respectively. The corresponding Sturm-Liouville type boundary conditions can be read off from the differential operators. We must certainly have

$$\lim_{\xi^+\to\infty}\psi_+(\xi^+)=0. \tag{19.16}$$

For azimuthal quantum numbers $m\neq 0$ we must also require

$$\lim_{\xi^+\to b}\psi_+(\xi^+)=0,\qquad \lim_{\xi^-\to\pm b}\psi_-(\xi^-)=0. \tag{19.17}$$

Note that $\xi^+=b$ corresponds to the interval $-b/2\le z\le b/2$ on the z axis, while $\xi^-=-b$ and $\xi^-=b$ correspond to the half-lines $z\le -b/2$ and $z\ge b/2$ on the z axis, respectively. The boundary conditions (19.17) therefore imply that the wave functions

$$\psi_m(\xi^+,\xi^-,\varphi)=\frac{1}{\sqrt{2\pi}}\psi_+(\xi^+)\psi_-(\xi^-)\exp(\mathrm{i}m\varphi)$$

must vanish on the z axis if $m\neq 0$, which apparently makes sense.

We certainly should not expect that the molecular orbitals with $m = 0$ vanish on the z axis, and the differential operators $D_{\pm,0}$ are actually hermitian on their respective domains without extra boundary conditions at $\xi^- = \pm b$ or $\xi^+ = b$ except that the wave functions should remain finite in those points.

The point of this discourse about hermiticity of the operators $D_{\pm,m}$ is that as a consequence, separation of the electronic Schrödinger equation for the hydrogen molecule ion H_2^+ in terms of prolate spheroidal coordinates will not only give us solutions, but a *complete set* of solutions in the form

$$\psi_{m,\lambda}(\xi^+, \xi^-, \varphi) = \frac{1}{\sqrt{2\pi}} \psi_{+,\lambda}(\xi^+) \psi_{-,\lambda}(\xi^-) \exp(\mathrm{i}m\varphi), \tag{19.18}$$

$$D_{-,m}(\xi^-)\psi_{-,\lambda}(\xi^-) = \lambda \psi_{-,\lambda}(\xi^-), \quad -b \le \xi^- \le b, \tag{19.19}$$

$$D_{+,m}(\xi^+)\psi_{+,\lambda}(\xi^+) = \lambda \psi_{+,\lambda}(\xi^+). \quad \xi^+ \ge b. \tag{19.20}$$

Energy is a third quantum number which is treated as implicit in the notation for the states.

The equation (19.19) and the equation (19.20) for $e^2 = 0$ are relevant for radiation problems and have been studied extensively, see [1] and references there. The solutions are known as angular spheroidal functions and radial spheroidal functions because of the angular and radial interpretation of the coordinates ξ^- and ξ^+, respectively.

The $\xi^+ \to \infty$ limit of equation (19.20) immediately tells us that we can satisfy the boundary condition (19.16) only for negative energy,

$$\frac{m_e}{2\hbar^2} E = -\kappa^2,$$

and the asymptotic form of the solution should be

$$\psi_{+,\lambda}(\xi^+) = f_{+,\lambda}(\xi^+) \exp(-\kappa \xi^+) \quad \kappa > 0. \tag{19.21}$$

with $\lim_{\xi \to \infty} f_{+,\lambda}(\xi) \exp(-\kappa \xi) = 0$.

We wish to analyze in particular the sector $m = 0$, which should contain the ground state of the H_2^+ ion. Equation (19.20) with $m = 0$ has the form

$$\partial_\xi \left(\xi^2 - b^2\right) \partial_\xi \psi_\lambda(\xi) - \kappa^2 \xi^2 \psi_\lambda(\xi) + \frac{2}{a_e} \xi \psi_\lambda(\xi) = \lambda \psi_\lambda(\xi), \tag{19.22}$$

where we substituted $\xi^+ \to \xi$, $\psi_+ \to \psi$ because in the following it will be clear from presence or absence of the Coulomb term $\propto 1/a_e$ whether we are considering the radial or the angular spheroidal coordinates and wave functions.

The length parameter

$$a_e = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = \frac{\mu}{m_e} a$$

is closely related to the Bohr radius (7.62) of the hydrogen atom.

Since our solution should remain finite at $\xi = b$, we make an *ansatz*

$$\psi_{+,\lambda}(\xi) = \sum_{n\geq 0} c_n \left(\frac{\xi - b}{b}\right)^n \exp[\kappa(b-\xi)]. \tag{19.23}$$

Substitution into (19.22) yields a two-step recursion relation

$$\begin{aligned} 2(n+1)^2 c_{n+1} = &\left(\lambda + \kappa^2 b^2 + 2\kappa b - \frac{2b}{a_e} + 4\kappa b n - n(n+1)\right) c_n \\ &+ 2b\left(\kappa n - \frac{1}{a_e}\right) c_{n-1}. \end{aligned} \tag{19.24}$$

On the other hand, $\psi_{-,\lambda}(\xi^-)$ must satisfy the differential equation (19.22) without electrostatic term: $a_e \to \infty$,

$$\partial_\xi \left(\xi^2 - b^2\right) \partial_\xi \psi_\lambda(\xi) - \kappa^2 \xi^2 \psi_\lambda(\xi) = \lambda \psi_\lambda(\xi), \tag{19.25}$$

and on the interval $-b \leq \xi \leq b$. This equation allows for even and odd solutions under $\xi^- \to -\xi^-$, and we expect the ground state solution to be even. Therefore we try an *ansatz*

$$\psi_{-,\lambda}(\xi) = \sum_{n\geq 0} d_n \left(\frac{\xi}{b}\right)^{2n}, \tag{19.26}$$

where we can set e.g.

$$d_0 = 1 \tag{19.27}$$

because the product form $\psi_{+,\lambda}(\xi^+)\psi_{-,\lambda}(\xi^-)/\sqrt{2\pi}$ of the ground state implies a degeneracy between d_0 and the coefficient c_0 in the radial factor (19.23). The constant c_0 is then determined by the normalization condition (19.14).

Substitution of (19.26) into (19.25) yields the recursion relation

$$2(n+1)(2n+1)d_{n+1} = \left(4n^2 + 2n - \lambda\right) d_n - \kappa^2 b^2 d_{n-1}. \tag{19.28}$$

The expansions (19.23) and (19.26) are not the standard expansions. For the angular function (19.26) one rather uses an expansion in terms of Legendre polynomials $P_n(\xi/b)$ (or associated Legendre polynomials $P_n^m(\xi/b)$ for $m \neq 0$), which are orthogonal polynomials in $-b \leq \xi \leq b$ and satisfy (19.25) or (19.19) for $\kappa = 0$ and $\lambda = n(n+1)$. For the polynomial factors in the radial function (19.23) one rather uses Laguerre polynomials $L_n(2\kappa(\xi - b))$ or $L_n^m(2\kappa(\xi - b))$, because $L_n^m(2\kappa(\xi - b))\exp[-\kappa(\xi - b)]$ are complete orthogonal functions in $b \leq \xi \leq \infty$. The corresponding two-step recursion relations for the coefficients in these expansions then follow from the differential equations and recursion relations of the orthogonal

polynomials. However, for our purposes the simpler expansions (19.23) and (19.26) are sufficient for the illustration of basic solution techniques for the dihydrogen cation.

We cannot go ahead and simply solve the recursion relations (19.24) and (19.28) to some finite order to get approximate wave functions for the electron, because for generic values of λ and $\kappa^2 b^2$ the resulting wave functions will not be regular and square integrable in the domains $-b \leq \xi^- \leq b$ and $1 \leq \xi^+ \leq \infty$. Therefore, one first has to determine which pairs of parameters λ and $\kappa^2 b^2$ allow for regular and square integrable solutions.

A classical method for the approximate calculation of the allowed parameter pairs λ and $\kappa^2 b^2$ in a two-step recursion relation like (19.28) uses the ratios $f_n = d_{n+1}/d_n$ with the initial condition from (19.28), $f_0 = -\lambda/2$. The recursion relation (19.28) can then be written as an upwards recursion $f_{n-1} \to f_n$,

$$f_n = \frac{n}{n+1} - \frac{\lambda}{2(n+1)(2n+1)} - \frac{\kappa^2 b^2}{2(n+1)(2n+1) f_{n-1}}, \tag{19.29}$$

or as a downwards recursion $f_{n+1} \to f_n$,

$$f_n = \frac{\kappa^2 b^2}{2(n+1)(2n+3) - \lambda - 2(n+2)(2n+3) f_{n+1}}. \tag{19.30}$$

The requirement of finite limits $\psi_{-,\lambda}(\pm b)$ of the angular wave function implies that the solution of (19.29, 19.30) should satisfy

$$\lim_{n \to \infty} f_n = 0.$$

One way to derive the resulting condition on λ and $\kappa^2 b^2$ in approximate form is to use both relations (19.30) and (19.29) for f_n with the approximation $f_N = 0$ for some $N \gg n$. Iteration of equation (19.30) in $N - n - 1$ steps yields a relation of the form $f_n = f_n^{(-)}(\lambda, \kappa^2 b^2, f_N) \simeq f_n^{(-)}(\lambda, \kappa^2 b^2, 0)$, while on the other hand f_n is also determined in n steps from equation (19.29) and $f_0 = -\lambda/2$ to yield functions $f_n = f_n^{(+)}(\lambda, \kappa^2 b^2)$. The condition

$$f_n^{(-)}(\lambda, \kappa^2 b^2, 0) = f_n^{(+)}(\lambda, \kappa^2 b^2)$$

then implicitly determines the relation between λ and $\kappa^2 b^2$.

Another way to derive the relation between λ and $\kappa^2 b^2$ writes the recursion relation (19.28) as a matrix relation

$$\underline{F} \cdot \boldsymbol{d} = \lambda \boldsymbol{d}$$

with matrix elements

$$F_{n \geq 0, n' \geq 0} = (4n^2 + 2n)\delta_{n,n'} - \kappa^2 b^2 \delta_{n,n'+1} - 2(n+1)(2n+1)\delta_{n,n'-1}.$$

The condition

$$\det(\underline{F} - \lambda \underline{1}) = 0 \tag{19.31}$$

is then cut off for an $(N+1) \times (N+1)$ submatrix $F_{0 \le n \le N, 0 \le n' \le N}$ to yield a relation between λ and $\kappa^2 b^2$.

Once the relation between λ and $\kappa^2 b^2$ is established, application of the same techniques to (19.24) implies a relation between the remaining parameter $\kappa^2 b^2$ and the parameter b/a_e. Since $\kappa^2 b^2 \propto -E$, this relation determines the quantized energies of the even states (due to the even *ansatz* (19.26)), with $m = 0$.

Application of the same techniques with an odd *ansatz* for $\psi_{-,\lambda}(\xi^-)$ or to the equations with general m yields the approximate energy levels and wave functions of the electron in the dihydrogen cation with fixed centers. The matrix and determinant condition for equation (19.24) are

$$\begin{aligned} C_{n \ge 0, n' \ge 0} = &\left(n(n+1) + 2\frac{b}{a_e} - 4n\kappa b - 2\kappa b - \kappa^2 b^2 \right) \delta_{n,n'} \\ &+ 2b \left(\frac{1}{a_e} - n\kappa \right) \delta_{n,n'+1} + 2(n+1)^2 \delta_{n,n'-1}, \\ \det(\underline{C} - \lambda \underline{1}) = 0 \end{aligned} \tag{19.32}$$

Using only 3×3 matrices $\underline{F}$ and $\underline{C}$ in the conditions (19.31) and (19.32) yields a ground state energy

$$E_e = \frac{e^2}{4\pi\epsilon_0 b} - \frac{2\hbar^2}{m_e}\kappa^2 = -14.2\,\text{eV}$$

with eigenvalues $\lambda = -0.490$ and $\kappa b = 1.42$ for a bond length $b = 105$ pm. Using the equivalent of a 4×4 matrix $\underline{F}$ and a 6×6 matrix $\underline{C}$ in the expansions with Legendre and Laguerre polynomials, Aubert *et al.*[8] found $E_e = -16.4\,\text{eV}$ with $\kappa b = 1.485$ for $b = 2a$. Either way, we find that the ground state energy E_e is smaller than the energy $E_1 = -13.6\,\text{eV}$ of a hydrogen atom and a proton at large distance, i.e. sharing the electron stabilizes the dihydrogen cation in spite of the electrostatic repulsion of the protons. The actual dissociation energy $D = E_1 - E_e$ for the dihydrogen cation is about 2.6 eV, i.e. the value of Aubert *et al.* from higher order approximation of the recursion relations is much better, as expected.

The coefficients which follow from the relations (19.24), (19.28), (19.27) and (19.14) for $\lambda = -0.490$ and $\kappa b = 1.42$ are

$$\begin{aligned} &d_0 = 1, \quad d_1 = 0.2451, \quad d_2 = -0.0357, \\ &c_0 = 1.869, \quad c_1 = 0.3760, \quad c_2 = -0.0712. \end{aligned} \tag{19.33}$$

[8] M. Aubert, N. Bessis, G. Bessis, Phys. Rev. A 10, 51 (1974).

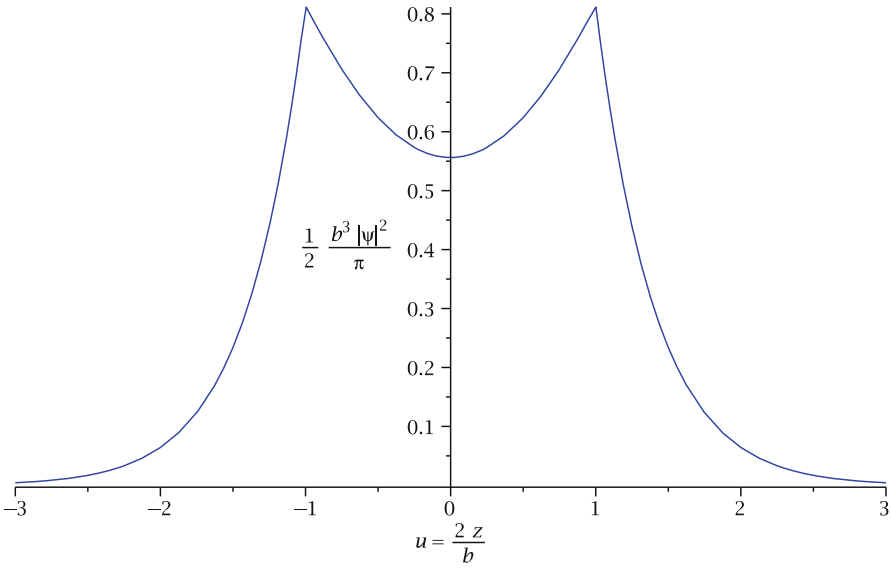

Fig. 19.1 The function $b^3|\psi(\xi^+,\xi^-)|^2/2\pi$ for the approximate ground state (19.33) is displayed along the symmetry axis of the dihydrogen cation. The protons are located at $u = \pm 1$. The abscissa $u = 2z/b$ is $u = \xi^-/b$ in the range $-1 < u < 1$, where $\xi^+ = b$. Outside of this range we have $u = -\xi^+/b$ for $u < -1$ ($\xi^- = -b$) and $u = \xi^+/b$ for $u > 1$ ($\xi^- = b$)

The resulting function $b^3|\psi(\xi^+,\xi^-)|^2/2\pi$ along the symmetry axis of the cation is displayed in Figure 19.1. The abscissa u is related to the z coordinate from equation (19.10) through $u = 2z/b$.

This low order approximation has already all the characteristic features of the real ground state as confirmed by higher order approximations. The electronic wave functions fall off with a linear exponential for large values of the radial coordinate ξ^+, and a double peak appears at the locations of the two protons. However, higher order approximations yield lower energies with a corresponding stronger exponential drop $\exp(-\kappa\xi^+)$, $\kappa b > 1.42$. This implies that the values of $b^3|\psi(\xi^+,\xi^-)|^2$ along the symmetry axis are actually underestimated in the approximation in Figure 19.1, and the cusps become more pronounced in higher order approximations.

Cusps are inevitable in many-particle wave functions for charged particles. Kato had demonstrated that these wave functions have cusps for coalescence of any two charged particles[9]. Specifically, if r_{12} is the separation between two particles with charges $Z_1 e$ and $Z_2 e$, and if the wave function does not vanish for $r_{12} \to 0$, the directional average of $\partial\psi/\partial r_{12}$ in the limit $r_{12} \to 0$ satisfies

$$\lim_{r_{12}\to 0} \frac{1}{4\pi} \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi\ \sin\vartheta\, \frac{\partial\psi}{\partial r_{12}} = \gamma_{12}\psi\Big|_{r_{12}=0}.$$

[9]T. Kato, Commun. Pure Appl. Math. 10, 151 (1957). See also R.T. Pack, W.B. Brown, J. Chem. Phys. 45, 556 (1966) and Á. Nagy, C. Amovilli, Phys. Rev. A 82, 042510 (2010).

The constant γ_{12} is

$$\gamma_{12} = Z_1 Z_2 \alpha \frac{\mu_{12} c}{\hbar} = Z_1 Z_2 \frac{\mu_{12}}{m_e} \frac{1}{a_e},$$

where $\mu_{12} = m_1 m_2/(m_1 + m_2)$ is the reduced mass of the charged particles. In particular, coalescence of two electrons or of electrons and protons corresponds to

$$\gamma_{e^-e^-} = \frac{1}{2a_e} \quad \text{and} \quad \gamma_{e^-p^+} = -\frac{1}{a}.$$

19.3 Bloch and Wannier operators

The use of second quantized Hamiltonians is ubiquitous in condensed matter physics, and in the following sections we will introduce very common and useful examples for this, *viz.* the Hubbard Hamiltonian for electron-electron interactions, phonons, and a basic Hamiltonian for electron-phonon coupling. We will motivate the model Hamiltonians from basic Schrödinger field theory or the classical Hamiltonian for lattice vibrations, respectively, and refer the reader to more specialized monographs for alternative derivations of these Hamiltonians.

However, before we embark on this journey, we should generalize the results from Sections 10.1, 10.2 and 10.3 to three dimensions and combine them with what we had learned in Chapter 17 about quantization and Schrödinger field operators.

The basic Schrödinger picture Hamiltonian for an electron gas has the form

$$\begin{aligned} H &= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\boldsymbol{x}) \psi_{\sigma'}^+(\boldsymbol{x}') \frac{e^2}{8\pi\epsilon_0 |\boldsymbol{x} - \boldsymbol{x}'|} \psi_{\sigma'}(\boldsymbol{x}') \psi_\sigma(\boldsymbol{x}) \\ &\quad + \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \nabla \psi_\sigma^+(\boldsymbol{x}) \cdot \nabla \psi_\sigma(\boldsymbol{x}) \\ &= \int d^3\boldsymbol{k} \int d^3\boldsymbol{k}' \int d^3\boldsymbol{q} \sum_{\sigma,\sigma'} a_\sigma^+(\boldsymbol{k} + \boldsymbol{q}) a_{\sigma'}^+(\boldsymbol{k}' - \boldsymbol{q}) \frac{e^2}{16\pi^3 \epsilon_0 \boldsymbol{q}^2} a_{\sigma'}(\boldsymbol{k}') a_\sigma(\boldsymbol{k}) \\ &\quad + \int d^3\boldsymbol{k} \sum_\sigma \frac{\hbar^2 \boldsymbol{k}^2}{2m} a_\sigma^+(\boldsymbol{k}) a_\sigma(\boldsymbol{k}). \end{aligned} \tag{19.34}$$

Suppose that this electron gas exists in a lattice with basis vectors $\boldsymbol{a}_i$ and dual basis vectors $\boldsymbol{a}^i$ (4.18). The lattice points are $\boldsymbol{\ell} = n^i \boldsymbol{a}_i$ with a triplet of integers n^i. However, we can also use the basis $\boldsymbol{a}_i$ as a basis in $\mathbb{R}^3$,

$$\boldsymbol{x} = x^i \boldsymbol{e}_i = \nu^i \boldsymbol{a}_i, \quad \nabla = \boldsymbol{e}^i \frac{\partial}{\partial x^i} = \boldsymbol{a}^i \frac{\partial}{\partial \nu^i}.$$

Note that the coordinates x^i and the lattice basis vectors $\boldsymbol{a}_i$ have the dimensions of length, while the dual basis vectors have dimension length^{-1}. The coordinates ν^i are dimensionless.

A Brillouin zone $\mathcal{B}$ is a unit cell in the dual lattice stretched by a factor 2π and then shifted such that the center of the Brillouin zone is a dual lattice point,

$$\boldsymbol{k} = \kappa_i \boldsymbol{a}^i, \quad -\pi < \kappa_i \leq \pi, \tag{19.35}$$

see also (10.10), where this notion was introduced for one-dimensional lattices.

The $\boldsymbol{k}$ vectors in a Brillouin zone have the following useful properties, which are easily derived from Fourier transformation on a one-dimensional lattice[10] $\kappa_i \equiv \kappa_i + 2\pi$,

$$\int_{\mathcal{B}} d^3\boldsymbol{k}\, \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{\ell}-\boldsymbol{\ell}')] = (2\pi)^3 \tilde{V}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'}, \quad d^3\boldsymbol{k} = \tilde{V} d\kappa_1 d\kappa_2 d\kappa_3, \tag{19.36}$$

$$\sum_{\boldsymbol{\ell}} \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{\ell}] = (2\pi)^3 \tilde{V}\delta(\boldsymbol{k}-\boldsymbol{k}'). \tag{19.37}$$

Recall that the volume of a unit cell $\tilde{V}$ in the dual lattice is related to the volume of a unit cell in the direct lattice through $\tilde{V} = 1/V$, (4.19).

If a unit cell in the lattice contains N ions, electrons in the lattice will also experience a lattice potential

$$H_V(\boldsymbol{x}) = -\sum_{\boldsymbol{\ell},A} \frac{n_A e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|}, \tag{19.38}$$

where

$$\boldsymbol{r}_{\boldsymbol{\ell},A} = \boldsymbol{\ell} + \boldsymbol{r}_A \quad 1 \leq A \leq N,$$

enumerates the locations of the ions in the unit cell $\boldsymbol{\ell} = n^i\boldsymbol{a}_i$, and $n_A e$ is the effective charge of the A-th ion. On the level of the quantized Schrödinger field theory, the potential (19.38) adds the operator

$$H_V = -\sum_{\boldsymbol{\ell},A} \int d^3\boldsymbol{x} \sum_{\sigma} \psi_\sigma^+(\boldsymbol{x}) \frac{n_A e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|} \psi_\sigma(\boldsymbol{x}), \tag{19.39}$$

to the Hamiltonian (19.34). We will focus on this potential term in the remainder of this section and neglect the electron-electron interaction term in (19.34). The corresponding first quantized Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + H_V(\mathbf{x}),$$

[10] We have seen the corresponding one-dimensional equations in (10.1–10.4). However, when comparing equations (19.36) and (19.37) with (10.1–10.4) please keep in mind that the continuous variables κ_i play the role of x there, while the discrete lattice sites $\boldsymbol{\ell} = n^i\boldsymbol{a}_i$ compare to the discrete momenta $2\pi n/a$ in equations (10.1–10.4), see also (10.12).

is invariant under lattice translations,

$$\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{p}\right) H \exp\left(-\frac{\mathrm{i}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{p}\right) = \frac{\mathbf{p}^2}{2m} + H_V(\mathbf{x}+\boldsymbol{\ell}) = H,$$

and therefore admits a complete set of Bloch type eigenstates, see (10.14) for the one-dimensional case. We can decompose the Schrödinger picture field operators $\psi_\sigma(\boldsymbol{x})$ in terms of a complete set of Bloch type eigenstates

$$\psi_\sigma(\boldsymbol{x}) = \sum_n \sqrt{\frac{V}{(2\pi)^3}} \int_{\mathcal{B}} d^3\boldsymbol{k}\, a_{n,\sigma}(\boldsymbol{k}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}), \tag{19.40}$$

$$a_{n,\sigma}(\boldsymbol{k}) = \sqrt{\frac{V}{(2\pi)^3}} \int d^3\boldsymbol{x}\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) u_n^+(\boldsymbol{k},\boldsymbol{x}) \psi_\sigma(\boldsymbol{x}), \tag{19.41}$$

with periodic Bloch factors

$$u_n(\boldsymbol{k},\boldsymbol{x}+\boldsymbol{\ell}) = u_n(\boldsymbol{k},\boldsymbol{x}).$$

We denote integration over the unit cell of the lattice with $\int_V d^3\boldsymbol{x}$. Normalization of the Bloch energy eigenfunctions then yields

$$\begin{aligned}\delta_{mn}\delta(\boldsymbol{k}-\boldsymbol{k}') &= \frac{V}{(2\pi)^3}\int d^3\boldsymbol{x}\, \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}] u_m^+(\boldsymbol{k}',\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}) \\ &= \frac{V}{(2\pi)^3}\sum_{\boldsymbol{\ell}} \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{\ell}] \\ &\quad \times \int_V d^3\boldsymbol{x}\, \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}] u_m^+(\boldsymbol{k}',\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}),\end{aligned} \tag{19.42}$$

and with (19.37) we find

$$\int_V d^3\boldsymbol{x}\, u_m^+(\boldsymbol{k},\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}) = \delta_{mn}.$$

Equation (19.42) also implies with the canonical anticommutation relations for the Schrödinger field operators $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ that the the operators $a_{n,\sigma}(\boldsymbol{k})$ satisfy the relations

$$\{a_{n,\sigma}(\boldsymbol{k}), a_{n',\sigma'}(\boldsymbol{k}')\} = 0 \quad \{a_{n,\sigma}(\boldsymbol{k}), a^+_{n',\sigma'}(\boldsymbol{k}')\} = \delta_{n,n'}\delta_{\sigma\sigma'}\delta(\boldsymbol{k}-\boldsymbol{k}').$$

The second quantized state

$$|n,\sigma,\boldsymbol{k}\rangle = a^+_{n,\sigma}(\boldsymbol{k})|0\rangle$$

is therefore a state with an electron in the first quantized orbital Bloch state

$$\phi_n(\boldsymbol{k},\boldsymbol{x}) = \sqrt{\frac{V}{(2\pi)^3}}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})u_n(\boldsymbol{k},\boldsymbol{x}) \tag{19.43}$$

and spin projection σ. Equation (19.41) and the conjugate equation for $a^+_{n,\sigma}(\boldsymbol{k})$ are a special case of our general observations (17.59) and (17.58) how annihilation and creation operators for particles in specific states relate to the generic operators $\psi_\sigma(\boldsymbol{x})$ and $\psi^+_\sigma(\boldsymbol{x})$.

Since the operators $a_{n,\sigma}(\boldsymbol{k})$ are restricted to the Brillouin zone, or equivalently are periodic in the rescaled dual lattice with the Brillouin zone as unit cell,

$$a_{n,\sigma}(\boldsymbol{k}) = a_{n,\sigma}(\boldsymbol{k}+2\pi\tilde{\boldsymbol{\ell}}), \quad \tilde{\boldsymbol{\ell}} = n_i\boldsymbol{a}^i,$$

we can expand them using equations (19.36, 19.37),

$$a^+_{n,\sigma}(\boldsymbol{k}) = \sqrt{\frac{V}{(2\pi)^3}}\sum_{\boldsymbol{\ell}}\psi^+_{n,\sigma}(\boldsymbol{\ell})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}), \tag{19.44}$$

$$\psi^+_{n,\sigma}(\boldsymbol{\ell}) = \sqrt{\frac{V}{(2\pi)^3}}\int_{\mathcal{B}} d^3\boldsymbol{k}\, a^+_{n,\sigma}(\boldsymbol{k})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}). \tag{19.45}$$

The operators $\psi_{n,\sigma}(\boldsymbol{\ell})$ in the direct lattice satisfy

$$\{\psi_{n,\sigma}(\boldsymbol{\ell}),\psi_{n',\sigma'}(\boldsymbol{\ell}')\} = 0 \quad \{\psi_{n,\sigma}(\boldsymbol{\ell}),\psi^+_{n',\sigma'}(\boldsymbol{\ell}')\} = \delta_{n,n'}\delta_{\sigma\sigma'}\delta(\boldsymbol{\ell}-\boldsymbol{\ell}').$$

Substitution of (19.41) into (19.45) yields

$$\psi^+_{n,\sigma}(\boldsymbol{\ell}) = \int d^3\boldsymbol{x}\, w_n(\boldsymbol{\ell},\boldsymbol{x})\psi^+_\sigma(\boldsymbol{x})$$

with the Wannier states

$$w_n(\boldsymbol{\ell},\boldsymbol{x}) = \frac{V}{(2\pi)^3}\int_{\mathcal{B}} d^3\boldsymbol{k}\, u_n(\boldsymbol{k},\boldsymbol{x})\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{\ell})] = w_n(\boldsymbol{x}-\boldsymbol{\ell}). \tag{19.46}$$

These states satisfy the usual completeness relations as a consequence of the completeness relations of the Bloch states $\phi_n(\boldsymbol{k},\boldsymbol{x})$,

$$\int d^3\boldsymbol{x}\, w^+_n(\boldsymbol{\ell},\boldsymbol{x})w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}) = \delta_{n,n'}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'},$$

$$\sum_{n,\boldsymbol{\ell}} w_n(\boldsymbol{\ell},\boldsymbol{x})w^+_n(\boldsymbol{\ell},\boldsymbol{x}') = \delta(\boldsymbol{x}-\boldsymbol{x}').$$

The operator $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ therefore generates an electron with spin projection σ in the Wannier state $w_n(\boldsymbol{\ell},\boldsymbol{x})$.

We denote the operators $a_{n,\sigma}(\boldsymbol{k})$ and $a^+_{n,\sigma}(\boldsymbol{k})$ as Bloch operators, and the operators $\psi_{n,\sigma}(\boldsymbol{\ell})$ and $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ as Wannier operators.

19.4 The Hubbard model

The Hubbard model treats electron-electron interactions in a tight binding approximation. Therefore we wish to use the creation operators $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ for electrons in Wannier states.

The kinetic electron operator transforms into Wannier type operators according to

$$\begin{aligned} H_0 &= \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \nabla\psi^+_\sigma(\boldsymbol{x}) \cdot \nabla\psi_\sigma(\boldsymbol{x}) \\ &= \int d^3\boldsymbol{x} \sum_{\sigma,n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} \psi^+_{n,\sigma}(\boldsymbol{\ell}) \frac{\hbar^2}{2m} \nabla w^+_n(\boldsymbol{\ell},\boldsymbol{x}) \cdot \nabla w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}) \psi_{n',\sigma}(\boldsymbol{\ell}'). \end{aligned} \tag{19.47}$$

This has the form of a hopping Hamiltonian for jumps $n', \boldsymbol{\ell}' \to n, \boldsymbol{\ell}$,

$$H_0 = \sum_{\sigma,n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} t_{n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} \psi^+_{n,\sigma}(\boldsymbol{\ell}) \psi_{n',\sigma}(\boldsymbol{\ell}') \tag{19.48}$$

with a hopping parameter

$$t_{n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} = \int d^3\boldsymbol{x} \frac{\hbar^2}{2m} \nabla w^+_n(\boldsymbol{\ell},\boldsymbol{x}) \cdot \nabla w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}).$$

On the other hand, the electron-electron interaction Hamiltonian becomes

$$H_{ee} = \frac{1}{2} \sum_{\sigma,\sigma',m,\boldsymbol{l},m',\boldsymbol{l}',n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} U_{m,\boldsymbol{l},m',\boldsymbol{l}',n',\boldsymbol{\ell}',n,\boldsymbol{\ell}} \psi^+_{m,\sigma}(\boldsymbol{l}) \psi^+_{m',\sigma'}(\boldsymbol{l}') \psi_{n',\sigma'}(\boldsymbol{\ell}') \psi_{n,\sigma}(\boldsymbol{\ell})$$

with the Coulomb matrix element

$$\begin{aligned} U_{m,\boldsymbol{l},m',\boldsymbol{l}',n',\boldsymbol{\ell}',n,\boldsymbol{\ell}} = \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}'\, w^+_m(\boldsymbol{l},\boldsymbol{x}) w^+_{m'}(\boldsymbol{l}',\boldsymbol{x}') \\ \times \frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{x}'|} w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}') w_n(\boldsymbol{\ell},\boldsymbol{x}). \end{aligned}$$

H_{ee} would certainly be dominated by terms on the same lattice site, and if we restrict the discussion to a single band index, the electron-electron interaction Hamiltonian $H = H_0 + H_{ee}$ assumes the simple form

$$H = \sum_{\boldsymbol{\ell},\boldsymbol{\ell}',\sigma} t_{\boldsymbol{\ell},\boldsymbol{\ell}'} \psi_\sigma^+(\boldsymbol{\ell})\psi_\sigma(\boldsymbol{\ell}') + U \sum_{\boldsymbol{\ell}} n_{\uparrow,\boldsymbol{\ell}} n_{\downarrow,\boldsymbol{\ell}}, \tag{19.49}$$

with the spin polarized occupation number operators for lattice site $\boldsymbol{\ell}$,

$$n_{\sigma,\boldsymbol{\ell}} = \psi_\sigma^+(\boldsymbol{\ell})\psi_\sigma(\boldsymbol{\ell}).$$

The Hamiltonian (19.49) is known as the *Hubbard Hamiltonian*[11]. This Hamiltonian was invented for the analysis of ferromagnetic behavior in transition metals, and soon became a very widely used model Hamiltonian in condensed matter theory not only for magnetic ordering, but also for the general investigation of electron correlations, conductivity properties and disorder effects in many different classes of materials[12]. However, the Hubbard model also provides basic insight into the relevance of delocalized Bloch states versus localized Wannier states, as we will now discuss.

We assume that the hopping term is invariant under translation and symmetric between sites, i.e.

$$t_{\boldsymbol{\ell},\boldsymbol{\ell}'} = t_{\boldsymbol{\ell}-\boldsymbol{\ell}'} = t_{\Delta\boldsymbol{\ell}} = t_{-\Delta\boldsymbol{\ell}}.$$

If hopping is suppressed,

$$t_{\boldsymbol{\ell},\boldsymbol{\ell}'} = t\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'},$$

the Hamiltonian involves only the number operators $n_{\sigma,\boldsymbol{\ell}}$,

$$H = t \sum_{\sigma,\boldsymbol{\ell}} n_{\sigma,\boldsymbol{\ell}} + U \sum_{\boldsymbol{\ell}} n_{\uparrow,\boldsymbol{\ell}} n_{\downarrow,\boldsymbol{\ell}}, \tag{19.50}$$

and the eigenstates and energy levels are given by $N = N_1 + 2N_2$ particle states

$$|\sigma_1, \boldsymbol{\ell}_1; \ldots \sigma_N, \boldsymbol{\ell}_N\rangle = \psi_{\sigma_1}^+(\boldsymbol{\ell}_1) \ldots \psi_{\sigma_N}^+(\boldsymbol{\ell}_N)|0\rangle$$

with energy

$$E(N_1, N_2) = t(N_1 + 2N_2) + UN_2.$$

[11] J. Hubbard, Proc. Roy. Soc. London A 276, 238 (1963), see also M.C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963).

[12] See e.g. J.E. Hirsch, Phys. Rev. B 31, 4403 (1985); I. Affleck, J.B. Marston, Phys. Rev. B 37, 3774 (1988); Y.M. Vilk, A.-M.S. Tremblay, J. Physique I 7, 1309 (1997). More comprehensive textbook discussions can be found in references [5, 11].

Here N_1 and N_2 are the numbers of single and double occupied lattice sites, respectively. This is also denoted as the atomic limit, since the electrons are fixed at the atoms and the total energy is a sum of atomic terms.

On the other hand, if we can neglect the electron-electron interaction term, $U = 0$, we end up with a quadratic Hamiltonian

$$H = \sum_{\boldsymbol{\ell},\Delta\boldsymbol{\ell},\sigma} t_{\Delta\boldsymbol{\ell}} \psi_\sigma^+(\boldsymbol{\ell} + \Delta\boldsymbol{\ell})\psi_\sigma(\boldsymbol{\ell}). \tag{19.51}$$

We can map the electron operators on lattice sites to electron operators (19.44) in the Brillouin zone,

$$a_\sigma(\boldsymbol{k}) = \frac{\sqrt{V}}{\sqrt{2\pi}^3} \sum_{\boldsymbol{\ell}} \psi_\sigma(\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}), \tag{19.52}$$

This diagonalizes the Hamiltonian (19.51),

$$H = \int_{\mathcal{B}} d^3\boldsymbol{k}\, E(\boldsymbol{k}) \sum_\sigma a_\sigma^+(\boldsymbol{k}) a_\sigma(\boldsymbol{k}), \tag{19.53}$$

$$E(\boldsymbol{k}) = \sum_{\Delta\boldsymbol{\ell}} t_{\Delta\boldsymbol{\ell}} \exp(-\mathrm{i}\boldsymbol{k}\cdot\Delta\boldsymbol{\ell}) = \sum_{\Delta\boldsymbol{\ell}} t_{\Delta\boldsymbol{\ell}} \cos(\boldsymbol{k}\cdot\Delta\boldsymbol{\ell}). \tag{19.54}$$

The single particle eigenstate of the Hamiltonian (19.53) with energy $E(\boldsymbol{k})$,

$$a_\sigma^+(\boldsymbol{k})|0\rangle = \frac{\sqrt{V}}{\sqrt{2\pi}^3} \sum_{\boldsymbol{\ell}} \psi_\sigma^+(\boldsymbol{\ell}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell})|0\rangle,$$

is a Bloch state, while the single particle eigenstate $\psi_\sigma^+(\boldsymbol{\ell})|0\rangle$ of the Hamiltonian (19.50) is a Wannier state. The magnitude of the hopping terms $t_{\Delta\boldsymbol{\ell}\neq\boldsymbol{0}}$ relative to U will therefore determine the importance of itinerant (or delocalized) Bloch electron states versus localized Wannier electron states in the lattice.

19.5 Vibrations in molecules and lattices

Another basic excitation of lattices concerns oscillations of lattice ions or atoms around their equilibrium configurations. This kind of excitation is particularly amenable to description in classical mechanical terms, but at the quantum level lattice vibrations are very similar to quantum excitations of the vacuum like electrons or photons. In particular, elementary lattice vibrations can be spontaneously created and absorbed like photons, and therefore require a quantum field theory which is similar to the field theory for photons.

We will discuss the classical theory of small oscillations of N-particle systems in the present section as a preparation for the discussion of quantized lattice vibrations in Section 19.6. We suspend summation convention in this section, because we often encounter expressions with three identical indices in a multiplicative term, and also terms like $m_i \ddot{x}_i{}^j$ without summation over the repeated index.

Normal coordinates and normal oscillations

We consider an N particle system with potential $V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N)$. The equilibrium condition

$$\nabla_i V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N)\Big|_{\boldsymbol{r}_j = \boldsymbol{r}_j^{(0)}} = \boldsymbol{0} \tag{19.55}$$

implies for the second order expansion around an equilibrium configuration $\boldsymbol{r}_1^{(0)}, \ldots \boldsymbol{r}_N^{(0)}$,

$$V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N) = V(\boldsymbol{r}_1^{(0)}, \ldots \boldsymbol{r}_N^{(0)}) + \frac{1}{2} \sum_{ijkl} V_{ik,jl} x_i{}^k x_j{}^l,$$

where $\boldsymbol{x}_i = \boldsymbol{r}_i - \boldsymbol{r}_i^{(0)}$ parametrize the deviations from equilibrium and the coefficients $V_{ik,jl}$ are

$$V_{ik,jl} = \frac{\partial^2}{\partial y_i{}^k \partial y_j{}^l} V(\boldsymbol{r}_1^{(0)} + \boldsymbol{y}_1, \ldots \boldsymbol{r}_N^{(0)} + \boldsymbol{y}_N)\Big|_{\boldsymbol{y}_m = \boldsymbol{0}}.$$

The second order Lagrange function for small oscillations of the system,

$$L = \frac{1}{2} \sum_{ik} m_i \dot{x}_i{}^k \dot{x}_i{}^k - \frac{1}{2} \sum_{ijkl} V_{ik,jl} x_i{}^k x_j{}^l, \tag{19.56}$$

yields $3N$ coupled equations of motion

$$m_i \ddot{x}_i{}^k = -\sum_{jl} V_{ik,jl} x_j{}^l. \tag{19.57}$$

Fourier transformation

$$x_i{}^k(t) = \int d\omega \, a_i{}^k(\omega) \exp(-\mathrm{i}\omega t), \quad [a_i{}^k(\omega)]^+ = a_i{}^k(-\omega), \tag{19.58}$$

yields the conditions

$$\sum_{jl} (V_{ik,jl} - m_i \omega^2 \delta_{ij} \delta_{kl}) a_j{}^l(\omega) = 0. \tag{19.59}$$

Writing this in the form

$$\sum_{jl}\left(\frac{V_{ik,jl}}{\sqrt{m_i m_j}}-\omega^2\delta_{ij}\delta_{kl}\right)\sqrt{m_j}a_j{}^l(\omega)=0$$

tells us that the $3N$-dimensional vector

$$\boldsymbol{Q}(\omega)=\{\sqrt{m_1}a_1{}^1(\omega),\ldots\sqrt{m_N}a_N{}^3(\omega)\}=\boldsymbol{Q}^+(-\omega) \tag{19.60}$$

must have the form

$$\boldsymbol{Q}(\omega)=\sum_{I=1}^{3N}\left[\boldsymbol{Q}_I\delta(\omega-\omega_I)+\boldsymbol{Q}_{-I}\delta(\omega+\omega_I)\right], \tag{19.61}$$

where $\boldsymbol{Q}_I=\{\sqrt{m_1}a_{I,1}{}^1,\ldots\sqrt{m_N}a_{I,N}{}^3\}=\boldsymbol{Q}_{-I}^+$ is an eigenvector of the symmetric $3N\times 3N$ matrix

$$\Omega^2_{ik,jl}=\frac{V_{ik,jl}}{\sqrt{m_i m_j}} \tag{19.62}$$

with eigenvalue ω_I^2. We assume that $\boldsymbol{r}_1^{(0)},\ldots\boldsymbol{r}_N^{(0)}$ is a stable equilibrium configuration such that all eigenvalues of $\Omega^2_{ik,jl}$ satisfy $\omega_I^2\geq 0$, and we define $\omega_I=\sqrt{\omega_I^2}\geq 0$ as the positive semi-definite roots.

Since $\underline{\Omega^2}$ is a symmetric real $3N\times 3N$ matrix, we can find $3N$ orthogonal normalized real vectors

$$\hat{\boldsymbol{Q}}_I=\{\sqrt{m_1}\hat{a}_{I,1}{}^1,\ldots\sqrt{m_N}\hat{a}_{I,N}{}^3\}$$

which solve the eigenvalue problem

$$\underline{\Omega^2}\cdot\hat{\boldsymbol{Q}}_I=\omega_I^2\hat{\boldsymbol{Q}}_I. \tag{19.63}$$

The general solution $\boldsymbol{Q}_I$ (19.60) of the eigenvalue problem with eigenvalue ω_I^2 will then have the form

$$\boldsymbol{Q}_I=q_I\hat{\boldsymbol{Q}}_I$$

with arbitrary complex factors $q_I=|q_I|\exp(\mathrm{i}\varphi_I)$. The mode expansion (19.58) will therefore take the form

$$\begin{aligned}x_i{}^k(t)&=\sum_{I=1}^{3N}\hat{a}_{I,i}{}^k\left[q_I\exp(-\mathrm{i}\omega_I t)+q_I^+\exp(\mathrm{i}\omega_I t)\right]\\&=2\sum_{I=1}^{3N}\hat{a}_{I,i}{}^k\,|q_I|\left[\cos(\varphi_I)\cos(\omega_I t)+\sin(\varphi_I)\sin(\omega_I t)\right].\end{aligned} \tag{19.64}$$

Equation (19.63) and $V_{ik,jl} = V_{jl,ik} = V^{+}_{ik,jl}$ imply the orthogonality relations

$$0 = \sum_{ijkl} (\hat{a}_{I,i}{}^{k} V_{ik,jl} \hat{a}_{J,j}{}^{l} - \hat{a}_{I,i}{}^{k} V_{ik,jl} \hat{a}_{J,j}{}^{l}) = \sum_{ik} m_i \hat{a}_{\pm I,1}{}^{k} \hat{a}_{J,j}{}^{k} (\omega_I^2 - \omega_J^2).$$

This yields

$$\sum_{ik} m_i \hat{a}_{I,i}{}^{k} \hat{a}_{J,i}{}^{k} = \delta_{IJ}, \tag{19.65}$$

where we assume that eigenvectors $\hat{\boldsymbol{Q}}_I$ within degeneracy subspaces have been orthonormalized.

Note that the normalization changes the dimensions and the physical meaning of the coefficients. The amplitudes $a_{I,i}{}^{k}$ in equation (19.64) have the dimensions of a length, and the related eigenvectors $\boldsymbol{Q}_I$ and factors q_I have the dimension of mass$^{1/2}$ × length. The normalized eigenvectors $\hat{\boldsymbol{Q}}_I$ are dimensionless, and therefore the related coefficients $\hat{a}_{I,i}{}^{k}$ have dimension mass$^{-1/2}$. We will denote the related $3N$ dimensional vector $\hat{\boldsymbol{a}}_I = \{\hat{a}_{I,1}{}^{1}, \ldots, \hat{a}_{I,N}{}^{3}\}$ as an *amplitude vector*.

The small oscillations of the system are then determined by the eigenmodes $\hat{\boldsymbol{a}}_I$ (or equivalently $\hat{\boldsymbol{Q}}_I$), and how strongly these eigenmodes of oscillation are excited,

$$x_i{}^{k}(t) = \sum_{I=1}^{3N} \hat{a}_{I,i}{}^{k} \left[q_I \exp(-\mathrm{i}\omega_I t) + q_I^{+} \exp(\mathrm{i}\omega_I t) \right], \tag{19.66}$$

$$\dot{x}_i{}^{k}(t) = -\mathrm{i} \sum_{I=1}^{3N} \omega_I \hat{a}_{I,i}{}^{k} \left[q_I \exp(-\mathrm{i}\omega_I t) - q_I^{+} \exp(\mathrm{i}\omega_I t) \right], \tag{19.67}$$

$$q_I = \frac{1}{2} \exp(\mathrm{i}\omega_I t) \sum_{ik} m_i \hat{a}_{I,i}{}^{k} \left(x_i{}^{k}(t) + \frac{\mathrm{i}}{\omega_I} \dot{x}_i{}^{k}(t) \right). \tag{19.68}$$

The $3N$ complex amplitudes q_I are denoted as *normal coordinates* of the oscillating N particle system, and the related eigenmodes of oscillation are also denoted as *normal modes*. Note from equations (19.66) or (19.68) that we can think of the coefficients $\hat{a}_{I,i}{}^{k}$ also as the components of a $3N \times 3N$ transformation matrix between the $3N$ Cartesian coordinates $x_i{}^{k}(t)$ and the $3N$ normal coordinates q_I of the oscillating system. These $3N \times 3N$ matrices satisfy the mass weighted orthogonality properties (19.65) and

$$\sum_{I} \hat{a}_{I,i}{}^{k} \hat{a}_{I,j}{}^{l} = \frac{1}{m_i} \delta_{ij} \delta^{kl}, \tag{19.69}$$

which follows from re-substitution of q_I (19.68) into $x_i{}^{k}(t)$ (19.66).

Appearance of the particular eigenvalue $\omega_I^2 = 0$ implies that the system is symmetric under rotations or translations. The corresponding amplitude vectors $\hat{\boldsymbol{a}}_I = \{\hat{a}_{I,i}{}^k\}$ denote the tangential directions to rotations or translations of the system.

We have learned that small oscillations of a system are always superpositions of the normal oscillation modes or eigenoscillations of the system. *A priori* this does not seem to be particularly helpful to determine the actual small oscillations of a system, because finding the eigenmodes is equivalent to the diagonalization of the $3N \times 3N$ matrix $\Omega^2_{ik,jl}$, which is anyhow the main task in the solution of the equations of motion (19.57) using the Fourier *ansatz* (19.64).

However, if the equilibrium configuration of the system has symmetries, then we can often guess the form of some of the eigenmodes which leaves us with a smaller diagonalization problem for the determination of the remaining eigenmodes.

Eigenmodes of three masses

A simple example for the identification of normal modes of a coupled particle system is given by three identical masses in a regular triangle, see Figure 19.2.

We will determine the eigenmodes in the plane of the triangle. The potential of the coupled system in the harmonic approximation is

$$\begin{aligned} V &= \frac{K}{2}\Big((|\boldsymbol{r}_1 - \boldsymbol{r}_2| - d)^2 + (|\boldsymbol{r}_1 - \boldsymbol{r}_3| - d)^2 + (|\boldsymbol{r}_2 - \boldsymbol{r}_3| - d)^2\Big) \\ &\simeq \frac{K}{2}\Big((x_1{}^1 - x_2{}^1)^2 + \frac{1}{4}(x_1{}^1 - x_3{}^1)^2 + \frac{1}{4}(x_2{}^1 - x_3{}^1)^2 + \frac{3}{4}(x_1{}^2 - x_3{}^2)^2 \\ &\quad + \frac{3}{4}(x_2{}^2 - x_3{}^2)^2 + \frac{\sqrt{3}}{2}(x_1{}^1 x_1{}^2 - x_1{}^1 x_3{}^2 - x_2{}^1 x_2{}^2 + x_2{}^1 x_3{}^2 \\ &\quad - x_3{}^1 x_1{}^2 + x_3{}^1 x_2{}^2)\Big). \end{aligned}$$

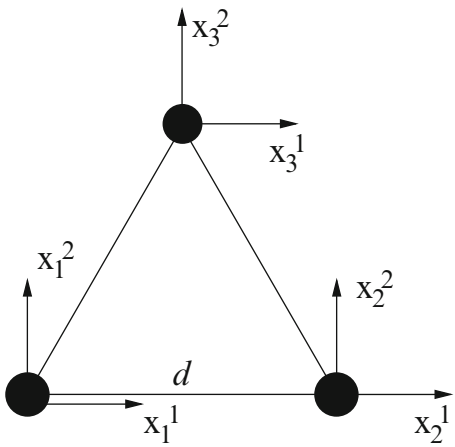

Fig. 19.2 Three elastically bound masses with equilibrium distance d

The matrix $V_{ik,jl}$ is

$$\underline{V} = m\underline{\Omega^2} = K \begin{pmatrix} \frac{5}{4} & \frac{\sqrt{3}}{4} & -1 & 0 & -\frac{1}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{3}{4} & 0 & 0 & -\frac{\sqrt{3}}{4} & -\frac{3}{4} \\ -1 & 0 & \frac{5}{4} & -\frac{\sqrt{3}}{4} & -\frac{1}{4} & \frac{\sqrt{3}}{4} \\ 0 & 0 & -\frac{\sqrt{3}}{4} & \frac{3}{4} & \frac{\sqrt{3}}{4} & -\frac{3}{4} \\ -\frac{1}{4} & -\frac{\sqrt{3}}{4} & -\frac{1}{4} & \frac{\sqrt{3}}{4} & \frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & -\frac{3}{4} & \frac{\sqrt{3}}{4} & -\frac{3}{4} & 0 & \frac{3}{2} \end{pmatrix},$$

and we must have

$$\mathrm{Det}(\underline{V} - m\omega^2 \underline{\mathbf{1}}) = 0.$$

Absence of external forces on the coupled system implies that there must be two translational and one rotational eigenmode, see Figures 19.2 and 19.3,

$$\hat{\boldsymbol{Q}}_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_2 = \frac{1}{\sqrt{3}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_3 = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ -\sqrt{3} \\ 1 \\ \sqrt{3} \\ -2 \\ 0 \end{pmatrix}.$$

The equations $\underline{V} \cdot \hat{\boldsymbol{Q}}_I = \mathbf{0}$ for $I = 1, 2, 3$ are readily verified.
The symmetry reveals that another eigenmode can be read off from Figure 19.4.
This yields the corresponding normalized eigenvector

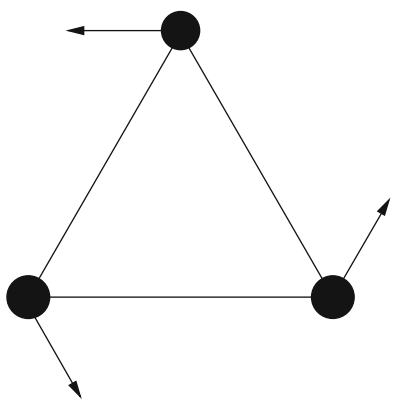

Fig. 19.3 The rotation mode $\hat{\boldsymbol{Q}}_3$

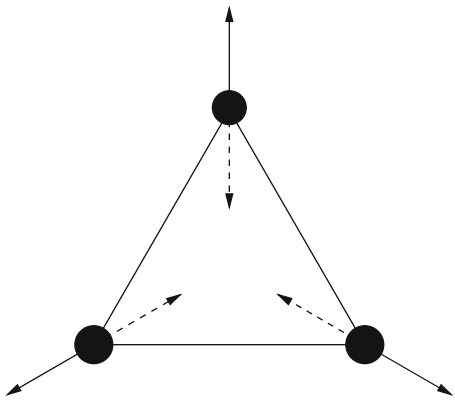

Fig. 19.4 The eigenmode $\hat{\boldsymbol{Q}}_4 = \sqrt{m}\hat{\boldsymbol{a}}_4$

$$\hat{\boldsymbol{Q}}_4 = \sqrt{m}\begin{pmatrix} {a_{4,1}}^1 \\ {a_{4,1}}^2 \\ {a_{4,2}}^1 \\ {a_{4,2}}^2 \\ {a_{4,3}}^1 \\ {a_{4,3}}^2 \end{pmatrix} = \frac{1}{2\sqrt{3}}\begin{pmatrix} \sqrt{3} \\ 1 \\ -\sqrt{3} \\ 1 \\ 0 \\ -2 \end{pmatrix},$$

and application of

$$\omega_4^2\hat{\boldsymbol{Q}}_4 = \frac{1}{m}\underline{V}\cdot\hat{\boldsymbol{Q}}_4,$$

yields for the corresponding frequency

$$\omega_4^2 = \frac{3K}{m}.$$

So far we have found four eigenmodes of the planar system, and there must still be two remaining eigenmodes, which must be orthogonal on the eigenmodes $\hat{\boldsymbol{Q}}_1, \ldots \hat{\boldsymbol{Q}}_4$. This yields for

$$\hat{\boldsymbol{Q}}_I = \sqrt{m}\begin{pmatrix} {a_{I,1}}^1 \\ {a_{I,1}}^2 \\ {a_{I,2}}^1 \\ {a_{I,2}}^2 \\ {a_{I,3}}^1 \\ {a_{I,3}}^2 \end{pmatrix}, \quad I = 5, 6$$

the conditions

$$\sqrt{3}({a_{I,1}}^1 - {a_{I,2}}^1) + {a_{I,1}}^2 + {a_{I,2}}^2 - 2{a_{I,3}}^2 = 0,$$

$$
\begin{aligned}
&a_{I,1}{}^1 + a_{I,2}{}^1 + a_{I,3}{}^1 = 0,\\
&a_{I,1}{}^2 + a_{I,2}{}^2 + a_{I,3}{}^2 = 0,\\
&a_{I,1}{}^1 + a_{I,2}{}^1 - 2a_{I,3}{}^1 + \sqrt{3}(a_{I,2}{}^2 - a_{I,1}{}^2) = 0,
\end{aligned}
$$

with general solutions

$$
\hat{\boldsymbol{Q}}_{I=5,6} \sim \frac{A}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ -1 \\ -\sqrt{3} \\ -1 \\ 0 \\ 2 \end{pmatrix} + \frac{B}{2\sqrt{3}} \begin{pmatrix} 1 \\ \sqrt{3} \\ 1 \\ -\sqrt{3} \\ -2 \\ 0 \end{pmatrix}.
$$

Application of $\underline{\Omega^2}$ reveals that these are degenerate eigenvectors with eigenvalue

$$
\omega_5^2 = \omega_6^2 = \frac{3K}{2m},
$$

and an orthonormal basis in the degeneracy subspace is provided by

$$
\hat{\boldsymbol{Q}}_5 = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ -1 \\ -\sqrt{3} \\ -1 \\ 0 \\ 2 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_6 = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ \sqrt{3} \\ 1 \\ -\sqrt{3} \\ -2 \\ 0 \end{pmatrix}.
$$

The corresponding eigenmodes are shown in Figure 19.5.

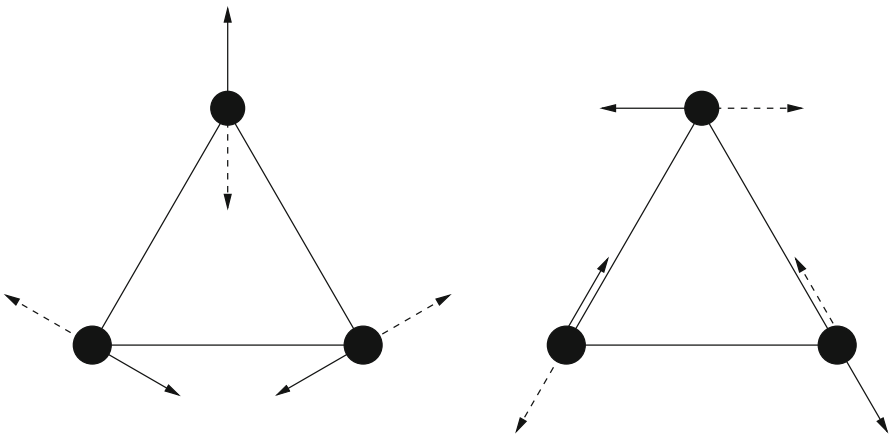

Fig. 19.5 The eigenmodes $\hat{\boldsymbol{Q}}_5$ and $\hat{\boldsymbol{Q}}_6$

The general small oscillation with $\omega > 0$ is then given by

$$\begin{pmatrix} x_1{}^1(t) \\ x_1{}^2(t) \\ x_2{}^1(t) \\ x_2{}^2(t) \\ x_3{}^1(t) \\ x_3{}^2(t) \end{pmatrix} = \sum_{I=4}^{6} \hat{\boldsymbol{Q}}_I x_I(t)$$

with

$$x_I(t) = x_I(0)\cos(\omega_I t) + \frac{\dot{x}_I(0)}{\omega_I}\sin(\omega_I t).$$

The diatomic linear chain

Lines of harmonically bound atoms provide important model systems for oscillations in solid state physics. We consider in particular a diatomic chain of $2N$ atoms with masses m and M, respectively. This model is shown in Figure 19.6. The force constant between the atoms is K and their equilibrium distance is $a/2$. The number N of atom pairs is assumed to be even for simplicity.

We label the pairs of atoms with an index n, $1 - (N/2) \leq n \leq N/2$, and we use periodic boundary conditions for the displacements x_n and X_n,

$$x_{n+N} = x_n, \quad X_{n+N} = X_n.$$

The Lagrange function

$$L = \sum_{n=1-(N/2)}^{N/2} \left(\frac{m}{2}\dot{x}_n^2 + \frac{M}{2}\dot{X}_n^2 - \frac{K}{2}(X_n - x_n)^2 - \frac{K}{2}(x_n - X_{n-1})^2 \right)$$

yields equations of motion

$$m\ddot{x}_n = -K(2x_n - X_n - X_{n-1}), \quad M\ddot{X}_n = -K(2X_n - x_n - x_{n+1}), \tag{19.70}$$

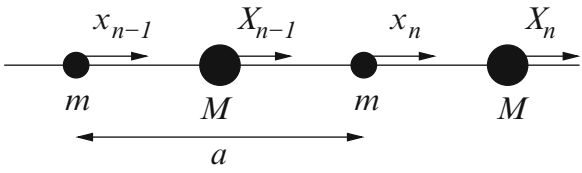

Fig. 19.6 A diatomic linear chain with masses m and M and lattice constant a

which can be solved using Fourier decomposition on a finite periodic chain,

$$x_n(t) = \frac{1}{\sqrt{N}} \sum_k \tilde{q}_k(t) \exp(\mathrm{i}nka), \tag{19.71}$$

$$X_n(t) = \frac{1}{\sqrt{N}} \sum_k \tilde{Q}_k(t) \exp(\mathrm{i}nka),$$

with

$$k = \frac{2\pi\tilde{n}}{Na}, \quad 1 - \frac{N}{2} \leq \tilde{n} \leq \frac{N}{2}.$$

The geometric series

$$\sum_{n=1-(N/2)}^{N/2} \exp\left(2\pi \mathrm{i}n\frac{\tilde{n}-\tilde{m}}{N}\right) = \exp\left[\mathrm{i}\pi\left(\frac{2}{N}-1\right)(\tilde{n}-\tilde{m})\right]$$
$$\times \sum_{n=0}^{N-1} \exp\left(2\pi \mathrm{i}n\frac{\tilde{n}-\tilde{m}}{N}\right) = \exp\left[\mathrm{i}\pi\left(\frac{2}{N}-1\right)(\tilde{n}-\tilde{m})\right]$$
$$\times \frac{1-\exp[2\pi\mathrm{i}(\tilde{n}-\tilde{m})]}{1-\exp\left[\frac{2\pi\mathrm{i}}{N}(\tilde{n}-\tilde{m})\right]} = N\delta_{\tilde{n},\tilde{m}} \tag{19.72}$$

implies that the inversion of (19.71) is

$$\tilde{q}_k(t) = \frac{1}{\sqrt{N}} \sum_{n=1-(N/2)}^{N/2} x_n(t) \exp(-\mathrm{i}nka) = \tilde{q}^+_{-k}(t).$$

Since the resulting system of ordinary differential equations for $\tilde{q}_k(t)$ and $\tilde{Q}_k(t)$ is linear with constant coefficients, we also use Fourier transformation to the frequency domain,

$$\tilde{q}_k(t) = \int d\omega\, \tilde{q}_k(\omega) \exp(-\mathrm{i}\omega t),$$

and the coupled set of equations (19.70) separate into coupled pairs of equations for different wave numbers k,

$$(m\omega^2 - 2K)\tilde{q}_k(\omega) + K(1 + \exp(-\mathrm{i}ka))\tilde{Q}_k(\omega) = 0, \tag{19.73}$$

$$(M\omega^2 - 2K)\tilde{Q}_k(\omega) + K(1 + \exp(\mathrm{i}ka))\tilde{q}_k(\omega) = 0. \tag{19.74}$$

This implies that there is a unique set of frequencies $\omega = \omega_k$ for each wave number k which has to satisfy

$$mM\omega_k^4 - 2K(m+M)\omega_k^2 + 2K^2(1-\cos(ka)) = 0.$$

This condition has two solutions (up to irrelevant overall signs of $\omega_{k\pm}$),

$$\begin{aligned}\omega_{k\pm}^2 &= K\left(\frac{1}{M}+\frac{1}{m}\right) \pm K\sqrt{\frac{1}{M^2}+\frac{1}{m^2}+\frac{2}{mM}\cos(ka)} \\ &= K\left(\frac{1}{M}+\frac{1}{m}\right) \pm K\sqrt{\left(\frac{1}{M}+\frac{1}{m}\right)^2 - \frac{4}{mM}\sin^2\left(\frac{ka}{2}\right)},\end{aligned} \tag{19.75}$$

and we have

$$\tilde{q}_k(\omega) = \tilde{q}_{k+}\delta(\omega-\omega_{k+}) + \tilde{q}_{k-}\delta(\omega-\omega_{k-}).$$

Equation (19.75) reads in terms of the reduced mass $\mu = mM/(m+M)$ of the atom pair in the unit cell

$$\omega_{k\pm}^2 = \frac{K}{\mu}\left(1 \pm \sqrt{1-\frac{4\mu}{m+M}\sin^2\left(\frac{ka}{2}\right)}\right). \tag{19.76}$$

An example of these dispersion relations with $M = 1.5m$ is displayed in Figure 19.7.

Note that the Lagrange function for a single atom pair in the unit cell is

$$L = \frac{1}{2}(m+M)\dot{R}^2 + \frac{\mu}{2}\dot{r}^2 - \frac{K}{2}r^2, \quad r = x-X, \quad R = \frac{mx+MX}{m+M},$$

and therefore the oscillation frequency of the single pair is $\sqrt{K/\mu}$.

The frequencies at $k=0$ are $\omega_{0-} = 0$ and $\omega_{0+} = \sqrt{2K/\mu}$.

The solution of (19.73, 19.74) for $\omega_{0-} = 0$: $\tilde{q}_{0-} = \tilde{Q}_{0-}$, is a uniform translation of the whole chain,

$$x_n(t) = X_n(t) = \tilde{q}_{0-}/\sqrt{N}.$$

The solution for ω_{0+}: $m\tilde{q}_{0+} = -M\tilde{Q}_{0+}$, is an oscillation

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = A\begin{pmatrix} M \\ -m \end{pmatrix}\cos\left(\sqrt{\frac{2K}{\mu}}t + \varphi\right).$$

The acoustic solution for $ka = \pi$ is

$$\omega_{(\pi/a)-} = \sqrt{\frac{2K}{M}}, \quad \tilde{q}_{(\pi/a)-} = 0,$$

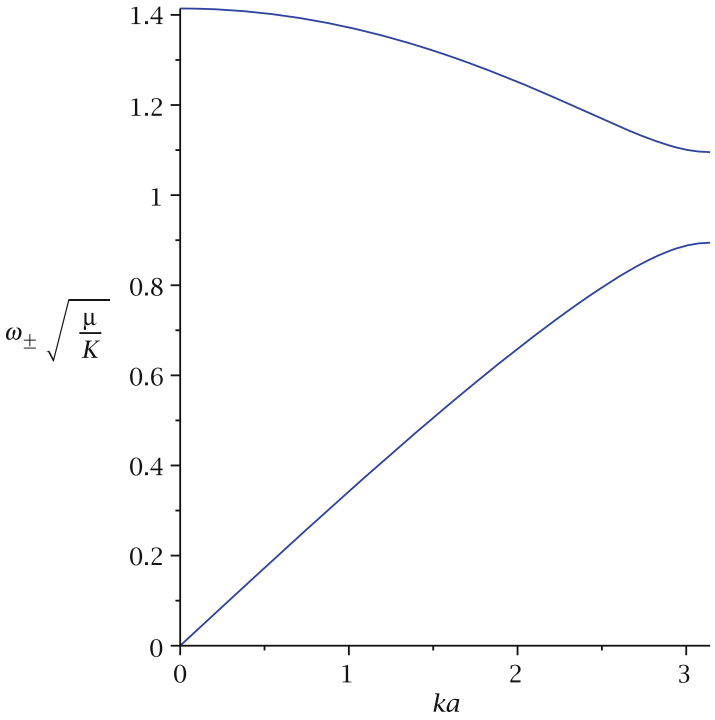

Fig. 19.7 The frequencies $\omega_{k\pm}$ from the dispersion relation (19.76) for $M = 1.5m$ and $0 \leq ka \leq \pi$. The frequencies $\omega_{k\pm}$ are displayed in units of $\sqrt{K/\mu}$, where μ is the reduced mass of the atom pair in a unit cell

i.e. only the heavy atoms oscillate,

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = (-)^n A \begin{pmatrix} 0 \\ 1 \end{pmatrix} \cos\left(\sqrt{\frac{2K}{M}}t + \varphi\right).$$

On the other hand, the optical eigenmode with $ka = \pi$,

$$\omega_{(\pi/a)+} = \sqrt{\frac{2K}{m}}, \quad \tilde{Q}_{(\pi/a)+} = 0,$$

corresponds to an oscillation of the light atoms,

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = (-)^n A \begin{pmatrix} 1 \\ 0 \end{pmatrix} \cos\left(\sqrt{\frac{2K}{m}}t + \varphi\right).$$

The general longitudinal oscillation will be a superposition of all longitudinal eigenvibrations.

Quantization of N-particle oscillations

The Lagrange function (19.56) implies canonical commutation relations

$$[x_i{}^k(t), \dot{x}_j{}^l(t)] = \frac{\mathrm{i}\hbar}{m_i}\delta_{ij}\delta^{kl}, \quad [x_i{}^k(t), x_j{}^l(t)] = 0, \quad [\dot{x}_i{}^k(t), \dot{x}_j{}^l(t)] = 0.$$

This yields commutation relations for the normal coordinates

$$[q_I, q_J] = 0, \quad [q_I, q_J^+] = \frac{\hbar}{2\omega_I}\delta_{IJ}.$$

Therefore we find canonical annihilation and creation operators for the eigenvibrations in the form

$$a_I = \sqrt{\frac{2\omega_I}{\hbar}}q_I, \quad a_I^+ = \sqrt{\frac{2\omega_I}{\hbar}}q_I^+.$$

The discussion of the diatomic chain taught us that for lattice oscillations the eigenmodes also depend on wave vectors in a Brillouin zone, and the following section will show that there can be up to $3N$ branches if we have N atoms per unit cell. Therefore we will have annihilation and creation operators for lattice vibrations which are related to the corresponding normal modes through

$$a_I(\boldsymbol{k}) = \sqrt{\frac{2\omega_{I,\boldsymbol{k}}}{\hbar}}q_I(\boldsymbol{k}), \quad a_I^+(\boldsymbol{k}) = \sqrt{\frac{2\omega_{I,\boldsymbol{k}}}{\hbar}}q_I^+(\boldsymbol{k}).$$

The elementary excitations $a_I^+(\boldsymbol{k})|0\rangle$ of the lattice vibrations are denoted as *phonons*.

19.6 Quantized lattice vibrations: Phonons

We will first generalize the previous discussion of vibrations in N-particle systems to the case of three-dimensional lattices, and then quantize the lattice vibrations

We denote the three basis vectors of a three-dimensional lattice with $\boldsymbol{a}_i$, $1 \leq i \leq 3$. Each location $\boldsymbol{\ell} = n^i\boldsymbol{a}_i$ in the lattice denotes a particular location of a corresponding unit cell, and we can use $\boldsymbol{\ell}$ or equivalently the three integers n^i also to address the particular unit cell to which the point $\boldsymbol{\ell}$ belongs. Suppose we have N atoms (or ions) per unit cell in the lattice. We denote the displacement of the A-th atom from its equilibrium value in cell $\boldsymbol{\ell}$ by $\boldsymbol{x}_{\boldsymbol{\ell},A}(t)$, and in the harmonic approximation the displacements satisfy equations of motion

$$m_A\ddot{\boldsymbol{x}}_{\boldsymbol{\ell},A} + \sum_{\boldsymbol{\ell}',A'} \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{x}_{\boldsymbol{\ell}',A'} = \boldsymbol{0}, \tag{19.77}$$

corresponding to a Lagrange function

$$L = \frac{1}{2}\sum_{\boldsymbol{\ell},A} m_A \dot{\boldsymbol{x}}^2_{\boldsymbol{\ell},A} - \frac{1}{2}\sum_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \boldsymbol{x}_{\boldsymbol{\ell},A} \cdot \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{x}_{\boldsymbol{\ell}',A'}. \tag{19.78}$$

Substitution of Fourier transforms

$$\boldsymbol{x}_{\boldsymbol{\ell},A}(t) = \frac{1}{\sqrt{m_A}} \int d\omega\, \boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) \exp(-\mathrm{i}\omega t)$$

into the equations of motion (19.77) yields the eigenvalue conditions

$$\sum_{\boldsymbol{\ell}',A'} \underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{Q}_{\boldsymbol{\ell}',A'}(\omega) = \omega^2 \boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) \tag{19.79}$$

with the symmetric matrices

$$\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \frac{1}{\sqrt{m_A m_B}} \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \underline{\Omega^2}^T_{\boldsymbol{\ell}',B;\boldsymbol{\ell},A}. \tag{19.80}$$

Translation invariance in the lattice implies that $\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B}$ cannot depend on $\boldsymbol{\ell} + \boldsymbol{\ell}'$. Therefore we can write

$$\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \underline{\Omega^2}_{A,B}(\boldsymbol{\ell} - \boldsymbol{\ell}') = \frac{V}{(2\pi)^3} \int_{\mathcal{B}} d^3\boldsymbol{k}\, \underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k}) \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{\ell} - \boldsymbol{\ell}')], \tag{19.81}$$

with inversion

$$\underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k}) = \sum_{\boldsymbol{\ell}} \underline{\Omega^2}_{A,B}(\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\ell}).$$

Symmetry of the real matrix $\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B}$ under $i, \boldsymbol{\ell}, A \leftrightarrow j, \boldsymbol{\ell}', B$ implies

$$\begin{aligned}
\tilde{\Omega}^2_{iA,jB}(\boldsymbol{k}) &= \sum_{\boldsymbol{\ell}} \Omega^2_{iA,jB}(\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\ell}) = \sum_{\boldsymbol{\ell}} \Omega^2_{jB,iA}(-\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\ell}) \\
&= \sum_{\boldsymbol{\ell}} \Omega^2_{jB,iA}(\boldsymbol{\ell}) \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\ell}) = \tilde{\Omega}^{2,*}_{jB,iA}(\boldsymbol{k}) = \tilde{\Omega}^{2,+}_{iA,jB}(\boldsymbol{k}) \\
&= \tilde{\Omega}^2_{jB,iA}(-\boldsymbol{k}),
\end{aligned}$$

i.e.

$$\underline{\tilde{\Omega}^2}(\boldsymbol{k}) = \underline{\tilde{\Omega}^2}^{+}(\boldsymbol{k}) = \underline{\tilde{\Omega}^2}^{T}(-\boldsymbol{k}). \tag{19.82}$$

Substitution of (19.81) and

$$\boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) = \frac{V}{(2\pi)^3}\int_{\mathcal{B}} d^3\boldsymbol{k}\,\tilde{\boldsymbol{Q}}_{\boldsymbol{k},A}(\omega)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}).$$

in (19.79) yields ,

$$\sum_B \underline{\tilde{\Omega}}^2_{A,B}(\boldsymbol{k})\cdot\tilde{\boldsymbol{Q}}_{\boldsymbol{k},B}(\omega) = \omega^2\tilde{\boldsymbol{Q}}_{\boldsymbol{k},A}(\omega). \tag{19.83}$$

For fixed value of $\boldsymbol{k}$, this is a hermitian eigenvalue problem for the $3N$-dimensional complex vector

$$\tilde{\boldsymbol{Q}}_{\boldsymbol{k}}(\omega) = \{\tilde{Q}^i_{\boldsymbol{k},A}(\omega)\},\quad 1\le i\le 3,\quad 1\le A\le N.$$

Reality of the displacement vectors $\boldsymbol{x}_{\boldsymbol{\ell},A}(t)$ implies $\boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) = \boldsymbol{Q}^+_{\boldsymbol{\ell},A}(-\omega)$ and

$$\tilde{\boldsymbol{Q}}^+_{\boldsymbol{k}}(\omega) = \tilde{\boldsymbol{Q}}_{-\boldsymbol{k}}(-\omega).$$

For each point $\boldsymbol{k}$ in the Brillouin zone, there will be $3N$ solutions $\omega^2_I(\boldsymbol{k})$ and $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ of (19.83) which satisfy the orthogonality property

$$\begin{aligned}\hat{\boldsymbol{Q}}^+_I(\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_J(\boldsymbol{k}) &\equiv \sum_A \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_{J,A}(\boldsymbol{k}) \equiv \sum_{i,A}\hat{Q}^{i+}_{I,A}(\boldsymbol{k})\hat{Q}^i_{J,A}(\boldsymbol{k})\\ &= \delta_{IJ}.\end{aligned} \tag{19.84}$$

The hermiticity and transposition properties imply that we have as a consequence of (19.83) for the normalized solutions,

$$\sum_B \underline{\tilde{\Omega}}^2_{A,B}(\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_{I,B}(\boldsymbol{k}) = \omega^2_I(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}), \tag{19.85}$$

also the equations

$$\sum_B \underline{\tilde{\Omega}}^2_{A,B}(-\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}^+_{I,B}(\boldsymbol{k}) = \omega^2_I(\boldsymbol{k})\hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k}) \tag{19.86}$$

and

$$\sum_A \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\cdot\underline{\tilde{\Omega}}^2_{A,B}(-\boldsymbol{k}) = \omega^2_I(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,B}(\boldsymbol{k}). \tag{19.87}$$

Up to linear combinations within degeneracy subspaces, the general set of solutions of the conditions (19.83) will then have the form

$$\tilde{\boldsymbol{Q}}_{\boldsymbol{k}}(\omega) = \sum_I\Big(q_I(\boldsymbol{k})\hat{\boldsymbol{Q}}_I(\boldsymbol{k})\delta(\omega-\omega_I(\boldsymbol{k})) + q^+_I(-\boldsymbol{k})\hat{\boldsymbol{Q}}^+_I(-\boldsymbol{k})\delta(\omega+\omega_I(-\boldsymbol{k}))\Big)$$

with complex factors $q_I(\boldsymbol{k})$. This yields the general lattice vibration in terms of the orthonormalized solutions of (19.83),

$$\boldsymbol{x}_{\boldsymbol{\ell},A}(t) = \frac{V}{(2\pi)^3\sqrt{m_A}} \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \Big[q_I(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \exp\Big(\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell} - \omega_I(\boldsymbol{k})t]\Big) + q_I^+(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{k}) \exp\Big(-\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell} - \omega_I(\boldsymbol{k})t]\Big)\Big], \tag{19.88}$$

$$\dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}(t) = \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \frac{-\mathrm{i}\omega_I(\boldsymbol{k})V}{(2\pi)^3\sqrt{m_A}} \Big[q_I(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \exp\Big(\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell} - \omega_I(\boldsymbol{k})t]\Big) - q_I^+(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{k}) \exp\Big(-\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell} - \omega_I(\boldsymbol{k})t]\Big)\Big], \tag{19.89}$$

$$q_I(\boldsymbol{k}) = \frac{1}{2} \sum_{\boldsymbol{\ell},A} \exp\Big(-\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell} - \omega_I(\boldsymbol{k})t]\Big)\sqrt{m_A} \times \hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{k}) \cdot \left(\boldsymbol{x}_{\boldsymbol{\ell},A}(t) + \frac{\mathrm{i}}{\omega_I(\boldsymbol{k})}\dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}(t)\right). \tag{19.90}$$

The dual orthogonality relation to (19.84) follows from re-substitution of $q_I(\boldsymbol{k})$ into (19.88),

$$\frac{V}{(2\pi)^3} \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}_{I,B}^+(\boldsymbol{k}) \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{\ell} - \boldsymbol{\ell}')] = \delta_{AB}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'}\underline{1}. \tag{19.91}$$

This is actually fulfilled due to two more fundamental completeness relations. The first relation is completeness of $3N$ orthonormal unit vectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k}) \equiv \{\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\}_{1\le A\le N}$ in a $3N$-dimensional vector space,

$$\sum_I \hat{\boldsymbol{Q}}_I(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}_I^+(\boldsymbol{k}) = \underline{1},$$

where $\underline{1}$ is the $3N \times 3N$ unit matrix, or if the atomic indices are spelled out,

$$\sum_I \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}_{I,B}^+(\boldsymbol{k}) = \delta_{AB}\underline{1}, \tag{19.92}$$

where now $\underline{1}$ is the 3×3 unit matrix referring to the spatial indices. The second relation is the completeness relation (19.36).

The canonical quantization relations

$$[x_{\boldsymbol{\ell},A}^i(t), \dot{x}_{\boldsymbol{\ell}',B}^j(t)] = \frac{\mathrm{i}\hbar}{m_A}\delta_{AB}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'}\delta^{ij},$$

$$[x_{\boldsymbol{\ell},A}^i(t), x_{\boldsymbol{\ell}',B}^j(t)] = 0, \quad [\dot{x}_{\boldsymbol{\ell},A}^i(t), \dot{x}_{\boldsymbol{\ell}',B}^j(t)] = 0,$$

imply

$$[q_I(\boldsymbol{k}), q_J(\boldsymbol{k}')] = 0, \quad [q_I(\boldsymbol{k}), q_J^+(\boldsymbol{k}')] = \frac{\hbar}{2\omega_I(\boldsymbol{k})}\frac{(2\pi)^3}{V}\delta_{IJ}\delta(\boldsymbol{k}-\boldsymbol{k}'),$$

i.e. the phonon annihilation operator for the Ith mode with wave vector $\boldsymbol{k}$ in the lattice is

$$a_I(\boldsymbol{k}) = \frac{1}{2}\sqrt{\frac{\omega_I(\boldsymbol{k})V}{\pi^3\hbar}}q_I(\boldsymbol{k}), \tag{19.93}$$

and the displacement operators in terms of the phonon operators are given by

$$\boldsymbol{x}_{\ell,A}(t) = \sum_I \boldsymbol{x}_{I,\ell,A}(t), \tag{19.94}$$

with

$$\begin{aligned}\boldsymbol{x}_{I,\ell,A}(t) = \sqrt{\frac{\hbar V}{(2\pi)^3 m_A}}\int_{\mathcal{B}}\frac{d^3\boldsymbol{k}}{\sqrt{2\omega_I(\boldsymbol{k})}}\Big[a_I(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\exp\Big(\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell}-\omega_I(\boldsymbol{k})t]\Big)\\ + a_I^+(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{k})\exp\Big(-\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell}-\omega_I(\boldsymbol{k})t]\Big)\Big].\end{aligned} \tag{19.95}$$

The Lagrange function (19.78) implies a Hamiltonian for the lattice vibrations,

$$H = \frac{1}{2}\sum_{\ell,A} m_A\dot{\boldsymbol{x}}_{\ell,A}^2 + \frac{1}{2}\sum_{\ell,A;\ell',A'}\sqrt{m_A m_{A'}}\boldsymbol{x}_{\ell,A}\cdot\underline{\Omega}^2_{\ell,A;\ell',A'}\cdot\boldsymbol{x}_{\ell',A'}.$$

This yields after substitution of equations (19.94, 19.95) and use of the eigenvalue, hermiticity and orthogonality conditions for the eigenvalue problem (19.85–19.87) the result[13]

$$H = \int_{\mathcal{B}} d^3\boldsymbol{k}\sum_I \hbar\omega_I(\boldsymbol{k})a_I^+(\boldsymbol{k})a_I(\boldsymbol{k}). \tag{19.96}$$

It is uncommon but helpful for a better understanding of Bloch and Wannier states of electrons to point out an analogy with lattice vibrations at this point.

[13] You also have to use that the matrix $\underline{\tilde{\Omega}}^2(\boldsymbol{k})$ has a positive semi-definite square root $\underline{\tilde{\Omega}}(\boldsymbol{k})$, see Problem 19.2. Therefore we also have e.g.

$$\sum_{A,B}\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\cdot\underline{\tilde{\Omega}}^2_{A,B}(-\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_{J,B}(-\boldsymbol{k}) = \omega_I(\boldsymbol{k})\omega_J(-\boldsymbol{k})\sum_A\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\hat{\boldsymbol{Q}}_{J,A}(-\boldsymbol{k}).$$

We have seen in Sections 10.1, 10.2 and 10.3 that electrons in lattices can be described in terms of delocalized Bloch states $\psi_n(k,x,t) = \psi_n(k,x)\exp[-\mathrm{i}\omega_n(k)t]$ or corresponding Wannier states $w_{n,\nu}(x)$, $w_{n,\nu}(x,t)$. Here ν labelled the different cells in the lattice and n labelled the different electron energy bands in the periodic potential of the crystal. We have encountered the corresponding states in three-dimensional lattices in equations (19.43, 19.46). To make the connection to lattice vibrations, we re-express the result (19.88) for the particular phonon energy band I in the form

$$\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t) = \frac{V}{(2\pi)^3}\int d^3\boldsymbol{k}\,\tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}),$$

$$\begin{aligned}\tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t) &= \sum_{\boldsymbol{\ell}}\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}) = \tilde{\boldsymbol{x}}^{+}_{I,-\boldsymbol{k},A}(t)\\ &= \frac{q_I(\boldsymbol{k})}{\sqrt{m_A}}\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\exp[-\mathrm{i}\omega_I(\boldsymbol{k})t]\\ &\quad + \frac{q_I^{+}(-\boldsymbol{k})}{\sqrt{m_A}}\hat{\boldsymbol{Q}}^{+}_{I,A}(-\boldsymbol{k})\exp[\mathrm{i}\omega_I(-\boldsymbol{k})t].\end{aligned}$$

Instead of the continuous dependence of the Bloch or Wannier type wave functions $\phi_n(\boldsymbol{k},\boldsymbol{x},t) \sim \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})u_n(\boldsymbol{k},\boldsymbol{x},t)$ and $w_n(\boldsymbol{\ell},\boldsymbol{x},t)$ on location $\boldsymbol{x}$, we have displacement variables at the discrete locations $\{\boldsymbol{\ell},A\}$ in the lattice. However with the correspondence of band indices $n \leftrightarrow I$, the Brillouin zone representation $\tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t)$ of the displacements corresponds to the Bloch waves (19.43) for electron states, while the set of displacements $\{\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t)\}_{1\le A\le N}$ in the unit cell at $\boldsymbol{\ell}$ corresponds to the Wannier states (19.46).

19.7 Electron-phonon interactions

Phonons in the lattice of a solid material naturally couple to electrons through the electrostatic interaction between the electrons and the ion cores. If we neglect electron-electron interactions, the basic Schrödinger picture Hamiltonian for quantized electrons in a lattice of ion cores with N atoms in the unit cell has the form

$$H = -\int d^3\boldsymbol{x}\sum_{\sigma}\psi^{+}_{\sigma}(\boldsymbol{x})\left(\frac{\hbar^2}{2m}\Delta + \sum_{\boldsymbol{\ell},A}\frac{n_A e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|}\right)\psi_{\sigma}(\boldsymbol{x}).$$

We assume that the A-th atom or ion in the unit cell couples to the electron with an effective charge $n_A e$, and we treat the atoms or ions as classical sources of electrostatic fields. However, we treat the lattice vibrations on the quantum level, which according to Sections 19.5 and 19.6 amounts to canonical quantization of the lattice displacements

$$\boldsymbol{x}_{\boldsymbol{\ell},A} = \boldsymbol{r}_{\boldsymbol{\ell},A} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}.$$

The leading order expansion of the Coulomb term

$$\frac{n_A e}{|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|} \simeq \frac{n_A e}{|\boldsymbol{x}-\boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|} + n_A e \frac{(\boldsymbol{x}-\boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A})\cdot \boldsymbol{x}_{\boldsymbol{\ell},A}}{|\boldsymbol{x}-\boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|^3} \tag{19.97}$$

corresponds to a dipole approximation in the language of Chapter 15, except that here the dipole operator $\boldsymbol{d}_{\boldsymbol{\ell},A} = n_A e \boldsymbol{x}_{\boldsymbol{\ell},A}$ is quantized according to (19.94, 19.95). This yields an electron-phonon interaction Hamiltonian of the form

$$H_{e-q} = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \int d^3\boldsymbol{x} \sum_{\sigma,I,\boldsymbol{\ell},A} \psi^+_\sigma(\boldsymbol{x})\psi_\sigma(\boldsymbol{x}) \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \frac{e}{\sqrt{m_A}}$$
$$\times \boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x})\cdot\Big[a_I(\boldsymbol{q})\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q})\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\ell}) + a^+_I(\boldsymbol{q})\hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{q})\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\ell})\Big],$$

where we substituted the time-independent phonon operators $\boldsymbol{x}_{\boldsymbol{\ell},A}(0)$ for the Hamiltonian in the Schrödinger picture. For the electron operators, we could substitute Bloch or Wannier type operators. However, Bloch operators make much more sense, because the dipole approximation (19.97) is a small oscillation approximation in the sense $|\boldsymbol{x}_{\boldsymbol{\ell},A}| \ll |\boldsymbol{x}-\boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|$, or otherwise we should include quadrupole and higher order terms. This implies that matrix elements of electron states with the lattice electric fields $\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x})$ must not be dominated by large terms from the ion cores. The linear phonon coupling Hamiltonian H_{e-q} should therefore not be a good approximation for the localized electrons in Wannier states. Evaluation of the substitution of the free electron operators through Bloch operators (19.41) in H_{e-q} uses the fact that integration over $\boldsymbol{x}$ can be split into summation over the lattice $\boldsymbol{l}$ and integration over the unit lattice cell V,

$$\int d^3\boldsymbol{x} f(\boldsymbol{x}) = \sum_{\boldsymbol{l}} \int_V d^3\boldsymbol{x} f(\boldsymbol{l}+\boldsymbol{x}),$$

and that the lattice electric fields satisfy

$$\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) = \boldsymbol{E}_{\boldsymbol{0},A}(\boldsymbol{x}-\boldsymbol{\ell}).$$

We denote the Bloch operators for the electrons by $c_{n,\sigma}(\boldsymbol{k})$ to avoid confusion with the phonon operators. This yields the following form for the electron-phonon interaction operator,

$$H_{e-q} = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \sum_{\sigma,I,\boldsymbol{\ell},A,n,n'} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_V d^3\boldsymbol{x} \frac{e}{\sqrt{m_A}}$$
$$\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x})\cdot\Big[u^+_n(\boldsymbol{k}+\boldsymbol{q},\boldsymbol{x})c^+_{n,\sigma}(\boldsymbol{k}+\boldsymbol{q})a_I(\boldsymbol{q})\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q})\exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{x})]$$
$$+ u^+_n(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{x})c^+_{n,\sigma}(\boldsymbol{k}-\boldsymbol{q})a^+_I(\boldsymbol{q})\hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{q})\exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{\ell})]\Big]$$
$$\times c_{n',\sigma}(\boldsymbol{k})u_{n'}(\boldsymbol{k},\boldsymbol{x}). \tag{19.98}$$

We can also write this as

$$H_{e-q} = \sum_{\sigma,I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k} \left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) \cdot \underline{U}_I(\boldsymbol{k},\boldsymbol{q}) \cdot c_\sigma(\boldsymbol{k}) a_I(\boldsymbol{q}) \right.$$
$$\left. + a_I^+(\boldsymbol{q}) c_\sigma^+(\boldsymbol{k}) \cdot \underline{U}_I^+(\boldsymbol{k},\boldsymbol{q}) \cdot c_\sigma(\boldsymbol{k}+\boldsymbol{q}) \right], \tag{19.99}$$

with coupling matrices between the phonons and the Bloch electrons,

$$U_{I,n,n'}(\boldsymbol{k},\boldsymbol{q}) = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \int_V d^3\boldsymbol{x} \sum_{\boldsymbol{\ell},A} \frac{e}{\sqrt{m_A}} \exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{x})]$$
$$\times u_n^+(\boldsymbol{k}+\boldsymbol{q},\boldsymbol{x}) \boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) \cdot \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q}) u_{n'}(\boldsymbol{k},\boldsymbol{x}). \tag{19.100}$$

The products in (19.99) contain summations over the electron energy band indices n, n'.

Below we will need the following property of the electron-phonon coupling functions,

$$U_{I,n,n'}(\boldsymbol{k}+\boldsymbol{q},-\boldsymbol{q}) = U_{I,n',n}^+(\boldsymbol{k},\boldsymbol{q}). \tag{19.101}$$

The full Hamiltonian also contains the free Hamiltonian for the phonons and the Bloch electrons

$$H_0 = \int_{\mathcal{B}} d^3\boldsymbol{k} \left(\sum_I \hbar\omega_I(\boldsymbol{k}) a_I^+(\boldsymbol{k}) a_I(\boldsymbol{k}) + \sum_\sigma c_\sigma^+(\boldsymbol{k}) \cdot \underline{E}(\boldsymbol{k}) \cdot c_\sigma(\boldsymbol{k}) \right)$$

with

$$E_{n,n'}(\boldsymbol{k}) = \frac{\hbar^2}{2m} \left(\int_V d^3\boldsymbol{x}\, \nabla u_n^+(\boldsymbol{k},\boldsymbol{x}) \cdot \nabla u_{n'}(\boldsymbol{k},\boldsymbol{x}) \right.$$
$$\left. - \mathrm{i}\boldsymbol{k} \cdot \int_V d^3\boldsymbol{x}\, u_n^+(\boldsymbol{k},\boldsymbol{x}) \overleftrightarrow{\nabla} u_{n'}(\boldsymbol{k},\boldsymbol{x}) + \boldsymbol{k}^2 \delta_{n,n'} \right). \tag{19.102}$$

The two interaction terms in (19.99) describe absorption and emission of a phonon of wave number $\boldsymbol{q}$ by a Bloch electron. The resulting exchange of virtual phonons between electron pairs will generate an effective interaction between the electrons. If interband couplings can be neglected, $U_{I,n,n'}(\boldsymbol{k},\boldsymbol{q}) \propto \delta_{n,n'}$ and $E_{n,n'}(\boldsymbol{k}) \propto \delta_{n,n'}$, a simple method to estimate this phonon mediated electron-electron interaction eliminates the first order phonon coupling through the Lemma 1 (6.22) for exponentials of operators. A unitary transformation $|\Phi\rangle \to |\Phi'\rangle = \exp(A)|\Phi\rangle$ with

$$A = \sum_{\sigma,I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k}\, \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})}$$
$$\times \left[a_I^+(\boldsymbol{q}) c_\sigma^+(\boldsymbol{k}) U_I^+(\boldsymbol{k},\boldsymbol{q}) c_\sigma(\boldsymbol{k}+\boldsymbol{q}) - c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_\sigma(\boldsymbol{k}) a_I(\boldsymbol{q}) \right]$$

eliminates the leading order electron-phonon coupling term due to

$$[A, H_0] + H_{e-q} = 0,$$

and generates a direct electron-electron coupling term

$$H_{e-e}^{(q)} = \left[\frac{1}{2} \overset{2}{[A, H_0]} + [A, H_{e-q}] \right]_{c^+c^+cc} = \frac{1}{2} [A, H_{e-q}] \Big|_{c^+c^+cc}$$
$$= \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{4\omega_I(\boldsymbol{q})} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})}$$
$$\times \left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k}) \right.$$
$$\left. + c_\sigma^+(\boldsymbol{k}) c_{\sigma'}^+(\boldsymbol{k}'+\boldsymbol{q}) U_I^+(\boldsymbol{k},\boldsymbol{q}) U_I(\boldsymbol{k}',\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}') c_\sigma(\boldsymbol{k}+\boldsymbol{q}) \right].$$

In the next step we substitute

$$\boldsymbol{k} \to \boldsymbol{k} + \boldsymbol{q}, \quad \boldsymbol{k}' \to \boldsymbol{k}' + \boldsymbol{q}, \quad \boldsymbol{q} \to -\boldsymbol{q},$$

in the second term in $H_{e-e}^{(q)}$ and use the properties (19.101) and $\omega_I(\boldsymbol{q}) = \omega_I(-\boldsymbol{q})$. This yields

$$H_{e-e}^{(q)} = \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{4\omega_I(\boldsymbol{q})} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q})$$
$$\times U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k})$$
$$\times \left[\frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})} - \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) + \hbar\omega_I(\boldsymbol{q})} \right]$$
$$= \frac{\hbar}{2} \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} d^3\boldsymbol{q} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, \frac{1}{[E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k})]^2 - \hbar^2\omega_I^2(\boldsymbol{q})}.$$
$$\times c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k}). \tag{19.103}$$

Phonons with frequencies which are large compared to the electron energy difference,

$$\hbar\omega_I(\boldsymbol{q}) > |E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k})|,$$

lower the energy of a two-electron state, thus implying an energetically favorable correlation between electrons. Effectively, a negative coefficient of $c_\sigma^+(\boldsymbol{k}+\boldsymbol{q})c_{\sigma'}^+(\boldsymbol{k}')c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q})c_\sigma(\boldsymbol{k})$ also amounts to an electron-electron attraction. Compare (19.103) with the simplified expression for free fermion operators,

$$H' = \Lambda \sum_{\sigma,\sigma'} \int d^3\boldsymbol{q} \int d^3\boldsymbol{k} \int d^3\boldsymbol{k}'\, c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k}).$$

In $\boldsymbol{x}$ space this becomes

$$H' = (2\pi)^3 \Lambda \sum_{\sigma,\sigma'} \int d^3\boldsymbol{x}\, \psi_\sigma^+(\boldsymbol{x}) \psi_{\sigma'}^+(\boldsymbol{x}) \psi_{\sigma'}(\boldsymbol{x}) \psi_\sigma(\boldsymbol{x}),$$

which is an attractive interaction for $\Lambda < 0$ and repulsive otherwise.

The possible instability of Fermi surfaces against phonon-induced energetically favored correlations between electrons, and the ensuing suppression of electron scattering, had been identified in the 1950s as the mechanism for low temperature superconductivity[14]. Please consult [5, 17, 22, 25] for textbook discussions of low temperature superconductivity.

19.8 Problems

19.1. Suppose we are using the Born-Oppenheimer approximation for the hydrogen atom, i.e. we treat the proton as fixed at location $\boldsymbol{X}_p = \boldsymbol{0}$. This would yield the same energy levels and energy eigenfunctions that we had found in the exact solution in Chapter 7, *except* that the reduced mass $\mu = m_e m_p/(m_e + m_p)$ would be replaced by the electron mass m_e in the result for the Bohr radius a, and therefore also in the energy eigenvalues and the wave functions.

Show that the corresponding change in the mass value $\delta\mu = m_e - \mu$ satisfies $\delta\mu/\mu = m_e/m_p$. Show also that in the center of mass frame, the neglected kinetic energy of the proton is related to the kinetic energies of the electron and of the relative motion according to

$$K_p = \frac{m_e}{m_p} K_e = \frac{m_e}{m_e + m_p} K_r.$$

Expand the ground state wave function in the Born-Oppenheimer approximation in first order in m_e/m_p in terms of the exact energy eigenstates from Chapter 7.

[14] J. Bardeen, L.N. Cooper, J.R. Schrieffer, Phys. Rev. 108, 1175 (1957); see also H. Fröhlich, Phys. Rev. 79, 845 (1950) and J. Bardeen, D. Pines, Phys. Rev. 99, 1140 (1955).

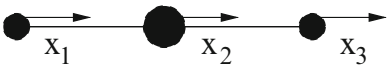

Fig. 19.8 Three particles with masses m and M. It is supposed that the particles can only move along the line connecting them

19.2. Show that the hermitian symmetric matrix $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ (19.80) with eigenvalues $\omega_I^2(\boldsymbol{k}) \geq 0$ and corresponding normalized eigenvectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ has square roots $\underline{\tilde{\Omega}}(\boldsymbol{k})$,

$$\underline{\tilde{\Omega}^2}(\boldsymbol{k}) = \underline{\tilde{\Omega}}^2(\boldsymbol{k}).$$

Hint: The column vectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ can be used to form a unitary matrix $\underline{Q}(\boldsymbol{k})$. The matrix $\underline{Q}(\boldsymbol{k})$ transforms $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ into diagonal form, or in turn can be used to generate $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ from its diagonal form $\mathrm{diag}(\omega_1^2(\boldsymbol{k}), \ldots, \omega_{3N}^2(\boldsymbol{k}))$. Use this observation to construct all the possible square roots $\underline{\tilde{\Omega}}(\boldsymbol{k})$ in terms of $\underline{Q}(\boldsymbol{k})$ and $\mathrm{diag}(\pm\omega_1(\boldsymbol{k}), \ldots, \pm\omega_{3N}(\boldsymbol{k}))$.

19.3. Suppose the three particles with masses m and M in Figure 19.8 can only move in one dimension.

The potential energy of the system is

$$V = \frac{K}{2}(x_1 - x_2)^2 + \frac{K}{2}(x_2 - x_3)^2.$$

Calculate the eigenvibrations and the eigenfrequencies of the system.

Solution. The potential in matrix notation is

$$V = \frac{K}{2}(x_1, x_2, x_3)\begin{pmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix},$$

and we have to find the eigenvectors of the corresponding matrix

$$\underline{\Omega^2} = K\begin{pmatrix} \frac{1}{m} & -\frac{1}{\sqrt{mM}} & 0 \\ -\frac{1}{\sqrt{mM}} & \frac{2}{M} & -\frac{1}{\sqrt{mM}} \\ 0 & -\frac{1}{\sqrt{mM}} & \frac{1}{m} \end{pmatrix}, \tag{19.104}$$

cf. 19.62.

Rather than trying to solve

$$\det(\underline{\Omega^2} - \omega^2\underline{\mathbf{1}}) = 0,$$

we can infer two eigenmodes from the translation and reflection symmetry of the system.

Invariance of the potential under translations $x_1 = x_2 = x_3$ implies that one eigenvector of $\underline{\Omega^2}$ has the form

$$\hat{\boldsymbol{Q}}_{\omega_1=0} = \frac{1}{\sqrt{2m+M}} \begin{pmatrix} \sqrt{m} \\ \sqrt{M} \\ \sqrt{m} \end{pmatrix}.$$

Reflection symmetry also suggests an eigenmode $x_1 = -x_3$, $x_2 = 0$,

$$\hat{\boldsymbol{Q}}_{\omega_2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix},$$

and application of $\underline{\Omega^2}$ yields the corresponding eigenvalue

$$\omega_2^2 = \frac{K}{m}.$$

The remaining eigenvector follows from orthogonality on $\hat{\boldsymbol{Q}}_{\omega_1}$ and $\hat{\boldsymbol{Q}}_{\omega_2}$,

$$\hat{\boldsymbol{Q}}_{\omega_3} = \frac{1}{\sqrt{2(2m+M)}} \begin{pmatrix} \sqrt{M} \\ -2\sqrt{m} \\ \sqrt{M} \end{pmatrix},$$

and application of $\underline{\Omega^2}$ confirms that this is an eigenmode with frequency

$$\omega_3^2 = \frac{K}{m} + \frac{2K}{M}.$$

For the actual eigenvibration we have to go back to the amplitude vector $\boldsymbol{a}_{\omega_2}$ (19.60), because different masses participate in the oscillation. The normalized amplitude vector (19.65) is

$$\hat{\boldsymbol{a}}_{\omega_3} = \frac{1}{\sqrt{2mM(2m+M)}} \begin{pmatrix} M \\ -2m \\ M \end{pmatrix}.$$

The eigenvibrations $\boldsymbol{a}_{\omega_2}$ and $\boldsymbol{a}_{\omega_3}$ are shown in Figure 19.9.

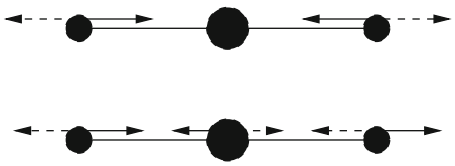

Fig. 19.9 The eigenvibrations $\boldsymbol{a}_{\omega_2}$ and $\boldsymbol{a}_{\omega_3}$

19.4. Calculate the positive semi-definite square root of the matrix $\underline{\Omega^2}$ in equation (19.104). Use the hint from Problem 2.

Answer.

$$\underline{\Omega} = \frac{\sqrt{K}}{2\sqrt{mM(2m+M)}} \times \begin{pmatrix} M+\sqrt{M(2m+M)} & -2\sqrt{mM} & M-\sqrt{M(2m+M)} \\ -2\sqrt{mM} & 4m & -2\sqrt{mM} \\ M-\sqrt{M(2m+M)} & -2\sqrt{mM} & M+\sqrt{M(2m+M)} \end{pmatrix}.$$

19.5. The electron-phonon interaction Hamiltonian (19.99) is very similar to the electron-photon interaction Hamiltonian in the representation (18.92),

$$H_{e-\gamma} = \frac{e\hbar c}{m_e}\sqrt{\frac{\hbar\mu_0}{(2\pi)^3}}\sum_{\sigma,\alpha}\int\frac{d^3\boldsymbol{q}}{\sqrt{2\omega(\boldsymbol{q})}}\int d^3\boldsymbol{k}\,\boldsymbol{k}\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q}) \times\left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q})a_\alpha(\boldsymbol{q})c_\sigma(\boldsymbol{k}) + c_\sigma^+(\boldsymbol{k})a_\alpha^+(\boldsymbol{q})c_\sigma(\boldsymbol{k}+\boldsymbol{q})\right]. \quad (19.105)$$

Which effective electron-electron interaction Hamiltonian $H_{e-e}^{(\gamma)}$ would you get if you eliminate the photon operators through a unitary transformation $|\Phi\rangle \to |\Phi'\rangle = \exp(A)|\Phi\rangle$ similar to the transformation that we performed to transform H_{e-q} into $H_{e-e}^{(q)}$ (19.103)?