Chapter 9
Quantum Mechanics and Electronic Structure

Abstract Quantum mechanics provides the basis for the description of matter on the atomic scale. Developed in conjunction with progress in spectroscopy, it explains phenomena such as the photoelectric effect, molecular spectra, electronic structure, and the chemical bond. Challenging and at the same time fascinating, the predictions of quantum mechanics are beyond direct everyday perception. (To some extent this is in contrast to thermodynamics and changes of state (Chap. 3) where experience from everyday perception is a reasonable criterion for assessing the soundness of predictions.) The basic concepts introduce the postulates of quantum mechanics. Aside from problems dealing with black body radiation, wave-packet propagation, and the hydrogen atom, applications of operator calculus and the variational principle are highlights that show perspectives with regard to tackling advanced problems in this field.

9.1 Basic Concepts

John Dalton's atomic model of matter is successful in the quantitative description of chemical reactions outlined in Chap. 2. From the beginning of the twentieth century, however, material science made tremendous progress in obtaining increasing insight into the structure of matter. Joseph John Thomson discovered the negatively charged *cathode rays* and deduced from his discovery the existence of the electron as an elementary particle. He developed a more precise atomic model, based on positive and negative charge being distributed in the atom. Ernest Rutherford deduced from scattering experiments that the entire positive charge and nearly the complete mass of the atom is concentrated in the nucleus. At the beginning of the twentieth century, thermodynamics and electrodynamics were fully developed theories, but they failed to explain the structure and stability of the atom. Moreover, they could not explain the structure of emission and absorption spectra of atoms investigated by Joseph Fraunhofer and others. At this time, Pieter Zeeman had already observed the splitting of characteristic spectral lines of sodium in an external magnetic field. These discoveries, however, revealed the necessity of a new description of the properties of matter in terms of quantum mechanics. It is thus obvious that the development of quantum mechanics is closely related to discoveries in the field of spectroscopy.

Quantum mechanics makes use of complex numbers (see Sect. A.3.4). In the following, it is thus assumed that the reader is familiar with the basic rules for complex number calculus.

9.1.1 Failure of Classical Mechanics: Key Experiments

9.1.1.1 Photoelectric Effect

If a cathode material is irradiated in a vacuum with light of wavelength λ, electrons are emitted if the wavelength is below a certain threshold wavelength λ_0 characteristic for the material. The kinetic energy of the electrons can be determined by applying a negative stopping potential between the irradiated material and an anode material. This necessary stopping potential U, which results in zero photo current, depends linearly on the light frequency $\nu = \frac{c}{\lambda}$:

$$U(\nu) = \frac{h}{e}\,(\nu - \nu_0) \tag{9.1}$$

From the slope of the function $U(\nu)$, the fundamental constant h can be determined, which is called **Planck's constant**.

If the frequency of the light irradiating the cathode is below the threshold frequency ν_0, no electrons are detected, no matter how high the light intensity. The interpretation of the photoelectric effect given by Albert Einstein is that the energy of light is mediated in discrete portions, *quanta*, with the energy

$$E = h\nu \tag{9.2}$$

The associated particle with zero mass called *photon* moves at the speed of light c, and has the momentum

$$p = \frac{h}{\lambda}. \tag{9.3}$$

The resulting wave-particle duality was extended by Louis-Victor de Broglie to electrons and other massive particles. In this context, Eq. (9.3) is called the de Broglie equation and λ **de Broglie wavelength**.

9.1.1.2   Black Body Radiation

If a piece of matter is heated to a high temperature, it starts to glow. This phenomenon was intensively studied at the end of the nineteenth century, and it was found that classical thermodynamics and the theory of electrodynamics could not fully explain the emission characteristics. *Black body* absorbs all electromagnetic radiation in the complete frequency spectrum. If it is in thermal equilibrium with its surroundings, it also emits electromagnetic radiation, and the spectral energy density depends only on temperature. The radiation emitted through a small hole of a cavity is in very good approximation with black body radiation, as all radiation impinging on the hole from the surroundings is absorbed by the atoms of the cavity walls, which are in equilibrium with the radiation field. Electromagnetic theory predicts the **spectral energy density** of such a black body to be:

$$u(v, T) = \frac{8\pi v^2}{c^3} \langle E_{\text{osc}} \rangle \tag{9.4}$$

Here, $\langle E_{\text{osc}} \rangle$ is the *average oscillator energy* of an atomic oscillator with a frequency v. The classical equipartition theorem predicts $\langle E_{\text{osc}} \rangle = k_B T$. Thus, the spectral energy would diverge to infinity if $v \to \infty$. Max Planck has corrected the expression for $\langle E_{\text{osc}} \rangle$ based on his hypothesis of the quantization of the oscillator energy:

$$E = n h v \qquad n = 0, 1, 2, \ldots \tag{9.5}$$

In Problem 9.1, we show that Planck's assumption leads to the correct expression for the energy density of a black body:

$$u(v, T) = \frac{8\pi h v^3}{c^3} \frac{1}{e^{\frac{hv}{k_B T}} - 1} \tag{9.6}$$

The power P emitted by a black body with a total area A depends only on its temperature and is given by the **Stefan-Boltzmann law**:

$$P = \sigma A T^4 \tag{9.7}$$

Here,

$$\sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2} = 5.670373 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \tag{9.8}$$

is the Stefan-Boltzmann constant.

9.1.2   Wave Mechanics

9.1.2.1   Postulates of Quantum Mechanics

Quantum mechanics, as it appears adequate for providing a description of systems on the atomic and molecular scale, can be summarized by a few postulates[1]:

Postulate 1:   To every state of a system there is a complex function ψ ascribed to and defining the state.
Comments: (1) For one particle this function is $\psi(x, t)$. (2) According to Max Born, $|\psi(x, t)|^2 \, dx$ is the (quantum mechanical) probability of finding the particle in a region between x and $x + dx$. (3) Dirac's abstract generalization of the wave function is a **ket-vector** $|\psi\rangle$.

Postulate 2:   The wave functions form a complex vector space. If ψ_1 and ψ_2 are two possible wave functions, then $\psi = \alpha\psi_1 + \beta\psi_2$ (where α and β are complex numbers) is also a possible wave function.
Comment: This is the **superposition principle**.

Postulate 3:   The *scalar product* of two wave functions ψ_1 and ψ_2 is:

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{+\infty} \psi_1^*(x, t)\psi_2(x, t) \, dx \tag{9.9}$$

Specifically,

$$\langle\psi|\psi\rangle = \int_{-\infty}^{+\infty} |\psi(x, t)|^2 \, dx \tag{9.10}$$

is called the *norm* of the wave function.
Comment: Dirac's notation calls $\langle\psi|$ a **bra-vector**

Postulate 4:   A **Hermitian operator** $\hat{A}$ is one for which

$$\langle\hat{A}\psi_1|\psi_2\rangle = \langle\psi_1|\hat{A}\psi_2\rangle; \tag{9.11}$$

Observables, i.e., measurable quantities with real eigenvalues, are represented by Hermitian operators. Comment: If $\hat{A}$ is an arbitrary operator, then $\hat{A}^+$ is called its **adjoint operator**, and

$$\langle\hat{A}^+\psi_1|\psi_2\rangle = \langle\psi_1|\hat{A}\psi_2\rangle; \tag{9.12}$$

As a consequence, a Hermitian operator is called **self adjoint operator**: $\hat{A}^+ = \hat{A}$.

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[1]The number of postulates differs from textbook to textbook, although they cover the same content.

Postulate 5: If $\hat{A}$ is an arbitrary operator, then $|\psi_n\rangle$ is called eigenfunction or eigenstate of $\hat{A}$, and λ_n eigenvalue, if the following equation holds:

$$\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle \qquad (9.13)$$

If there are several possible eigenstates, then the eigenstates are orthonormal[2]:

$$\langle\psi_m|\psi_n\rangle = \delta_{mn} \qquad (9.14)$$

Comment: This requires the eigenstates to be normalized. The spectrum of possible eigenstates constitutes a complete basis, and an arbitrary state function can be written:

$$|\phi\rangle = \sum_n c_n|\psi_n\rangle.$$

Since

$$\langle\psi_m|\phi\rangle = \sum_n c_n\langle\psi_m|\psi_n\rangle = \sum_n c_n\delta_{nm} = c_m$$

Postulate 6: If the state $|\phi\rangle$ of a system is not an eigenstate of an operator $\hat{A}$, a measurement of its observable provides one of the possible eigenvalues λ_n. The quantum mechanical **expectation value** for this observable is:

$$\langle\hat{A}\rangle = \frac{\langle\phi|\hat{A}|\phi\rangle}{\langle\phi|\phi\rangle} \qquad (9.15)$$

Comment: The probability that the result of the measurement provides the eigenvalue λ_n is: $|c_n|^2$ where $c_n = \langle\psi_n|\phi\rangle$. This follows from:

$$\langle\hat{A}\rangle = \langle\phi|\hat{A}|\phi\rangle = \sum_m\sum_n c_m^*c_n\langle\psi_m|A|\psi_n\rangle = \sum_m\sum_n c_m^*c_n\lambda_n\underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{mn}} = \sum_n|c_n|^2\lambda_n$$

Postulate 7: The state function of a system follows from the solution of the time-dependent **Schrödinger equation**:

$$\boxed{i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle} \qquad (9.16)$$

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[2]The Kronecker delta δ_{mn} is defined as follows: $\delta_{mn} = 1$ if $m = n$, and $\delta_{mn} = 0$ if $m \neq n$.

Comment: The operator $\hat{H}$ is the Hamiltonian whose eigenvalue is the total energy (see Problem 9.6).

9.1.2.2   Commutators

Application of quantum mechanics to special systems and their discussion frequently makes use of the concept of a commutator between two operators $\hat{A}$ and $\hat{B}$:

$$[\hat{A}, \hat{B}] \stackrel{\text{def}}{=} \hat{A}\hat{B} - \hat{B}\hat{A} \qquad (9.17)$$

If $[\hat{A}, \hat{B}] = 0$ then the two operators commute with each other. In this case, the order of these operators does not influence the result. An important consequence is that commuting operators share a common orthonormal system of eigenfunctions.

9.1.2.3   Harmonic Oscillator

The harmonic oscillator problem is defined by the Schrödinger equation of a particle of mass m moving in a harmonic potential that is characterized by the force constant k:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) + \frac{1}{2}kx^2\psi_n(x) = E_n\psi_n(x) \qquad (9.18)$$

The problem can be treated exactly and the solutions can be found in textbooks. The energy eigenvalues are:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right); \quad n = 0, 1, 2, \ldots \qquad (9.19)$$

where the angular frequency ω of the motion is related to the force constant k

$$\omega = \sqrt{\frac{k}{m}}. \qquad (9.20)$$

Even in the ground state $n = 0$, the particle has a zero-point vibrational energy $E_0 = \frac{\hbar\omega}{2}$ (see also Problem 9.2). The first energy levels of the harmonic oscillator and the wave functions are shown in Fig. 9.1. The ground state wave function of the harmonic oscillator is a Gaussian function, excited state wave functions contain Hermite polynomials (see Appendix Sect. A.3.13). The harmonic oscillator problem is the basis for the description of molecular vibrations (see Sect. 10.1.3).
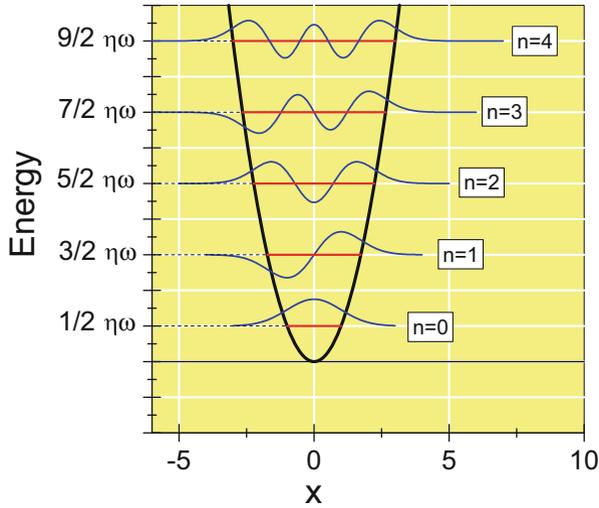
Fig. 9.1 Energy levels and wave functions of the harmonic oscillator. The amplitude of the wave functions was scaled by a factor of 0.5

9.1.3 Atomic Structure

Exact descriptions of the electronic structure of atoms can only be given for the neutral hydrogen atom along with other one-electron systems, such as He^+, Li^{2+}. The textbook results for the energy levels in these systems are:

$$E_{nl} = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} \qquad n = 1, 2, \ldots \tag{9.21}$$

where μ is the effective mass of the two-body system.[3] The number n is the principal quantum number and $l = 0, 1, \ldots, n - 1$ is the quantum number for the orbital angular momentum. The quantity

$$\text{Ry} = \frac{m_e e^4}{8\epsilon_0^2 h^2} = 13.605693 \, \text{eV} \tag{9.22}$$

is the Rydberg energy. As can be seen in Eq. (9.21), there is a *degeneracy* of the energy levels with regard to different values of l. In the absence of external fields a further degeneracy with regard to the magnetic quantum number m occurs, which takes integer values between $-l$ and $+l$. The wave functions for the hydrogen

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[3]If $M \gg m_e$ is the mass of the nucleus, the effective mass $\mu = \frac{M m_e}{M + m_e}$ is close to m_e. In the case of positronium consisting of an electron and a positron of the same mass, however, $\mu = \frac{m_e}{2}$.

problem are a solution of the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi_{nlm}(r,\theta,\phi) = E_{nlm}\psi_{nlm}(r,\theta,\phi) \qquad (9.23)$$

where the Laplacian operator Δ is best expressed in spherical coordinates r, θ and ϕ (see Eq. (A.68) in Sect. A.3.11). The wave function separates into two parts:[4] a radial function $R_{nl}(r)$ and a spherical harmonic $Y_{lm}(\theta,\phi)$:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi) \qquad (9.24)$$

The eigenvalue equation for the angular part is:

$$\hat{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi); \qquad l = 0,1,2\ldots; \ m = -l, -l+1, \ldots, 0, \ldots, l-1, l \qquad (9.25)$$

with $\hat{L}^2$ being the operator of the angular momentum squared, and l is the angular momentum quantum number. A state with $l = 0$ is called an s-state, $l = 1$ is called a p-state, and $l = 2$ a d-state. Explicit expressions for the first spherical harmonics are given in the Appendix in Sect. A.3.14. The eigenvalue equation of the radial function is:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0}r\right]R_{nl}(r) = E_{nl}R_{nl}(r). \qquad (9.26)$$

Its solutions are tabulated in the Appendix Sect. A.3.15 for hydrogen ($Z = 1$).

The spatial shape of some orbital wave functions is shown in Fig. 9.2.

9.1.4 Atomic Units

In atomic and molecular structure theory, it is common to introduce *atomic units* (a.u.). This involves setting:

$$\hbar = e = m_e = 4\pi\epsilon_0 = 1. \qquad (9.27)$$

As a result, the atomic energy unit is 1 E_h (Hartree)$=27.211386$ eV, which is twice the Rydberg energy. The atomic unit of length is $1a_0 = 0.52917721092(17)\times 10^{-10}$ m, i.e., 1 bohr radius.

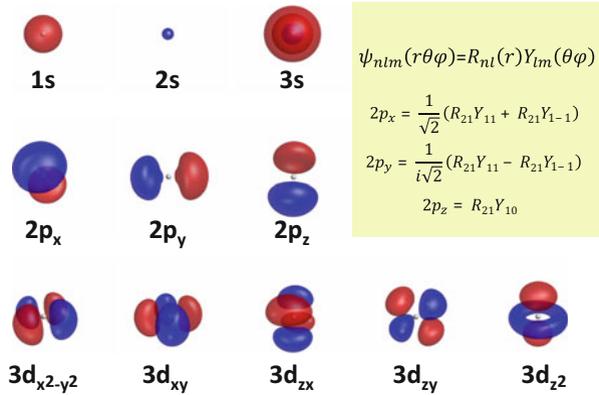[4]For explicit expressions of $R_{nl}(r)$ and $Y_{lm}(\theta,\phi)$ see Sects. A.3.14 and A.3.15.

Fig. 9.2 Spacial geometry of some orbitals of the hydrogen atom. The surface of the constant contour value ± 0.05 of the orbital wave functions is shown. The *inset* demonstrates the construction of (real) $2p_x$, $2p_y$ and $2p_z$ functions from radial functions and (complex) spherical harmonics

9.2   Problems

Problem 9.1 (Derivation of the Average Oscillator Energy) Given the possible energy values of an oscillator,

$$E_n = E_0 + nh\nu, \quad n = 0, 1, \ldots, \tag{9.28}$$

and a Boltzmann distribution for the average occupation number,

$$\langle n \rangle = \sum_n^\infty n \exp(-\alpha n), \quad \alpha = \frac{h\nu}{k_B T}, \tag{9.29}$$

derive Planck's equation for the average oscillator energy

$$\langle E_{\text{osc}} \rangle = E_0 + \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}. \tag{9.30}$$

E_0 is an arbitrary constant energy that is determined in Problem 9.2.

Solution 9.1   In this exercise, we deal with the average oscillator energy introduced in Sect. 9.1.1.2. Doing so, we understand an essential part of Planck's law for the radiation density of a black body. Before entering the calculation, it is useful
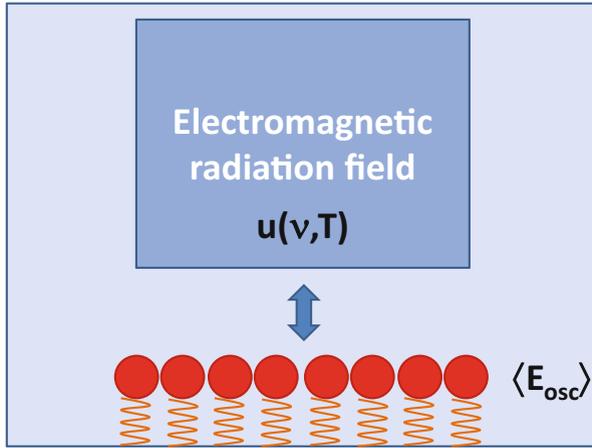
Fig. 9.3 Thermal equilibrium between the electromagnetic radiation field within a cavity coupled with absorption and emission to atomic oscillators at the cavity walls (schematic)

to reflect on the nature of the oscillators for which we calculate the average energy. Following Planck, we can assume a thermal equilibrium between the electromagnetic radiation field within a cavity and the atoms at the cavity walls. The equilibrium is established by absorption and emission processes of quanta of energy $h\nu$. The scenario is sketched schematically in Fig. 9.3. Experimentally, it has been found that the spectral energy density of a black body is independent of its composition, chemical nature, and structure. The simple model representing the atoms of the cavity wall is thus an ensemble of so-called *Lorentz-oscillators*, spring mass systems vibrating at a frequency ν. We have seen how such an ensemble of oscillators can be treated by means of statistical thermodynamics in Sect. 8.1.2.

According to Planck's assumption, the energy values of an oscillator of frequency ν is:

$$E_n = E_0 + n\,h\nu \qquad\qquad n = 0, 1, 2\ldots \qquad\qquad (9.31)$$

Here, n counts the number of quanta by which the oscillator is excited. Next, the concept of probability and statistics is introduced: we express the expectation value of the oscillator energy, $\langle E_{\mathrm{osc}}\rangle$, by the average number of quanta, $\langle n\rangle$:

$$\langle E_{\mathrm{osc}}\rangle = \langle n\rangle\,h\nu \qquad\qquad (9.32)$$

For $\langle n\rangle$ we use a *Boltzmann-Ansatz*:

$$\langle n\rangle = \frac{\sum_n^\infty n\,\exp\left(-\frac{E_n}{k_B T}\right)}{\sum_n^\infty \exp\left(-\frac{E_n}{k_B T}\right)} = \frac{\sum_n^\infty n\,\exp\left(-\alpha n\right)}{\sum_n^\infty \exp(-\alpha n)}; \qquad \alpha = \frac{h\nu}{k_B T} \qquad (9.33)$$

Note that the factor α compares the quantum energy of the oscillator with the thermal energy at a given temperature T. The rest is clever mathematics. The sums in the last equation can be expressed by a geometrical series (see Eq. (A.57) in the Appendix):

$$\sum_n^\infty e^{-\alpha n} = \frac{1}{1 - e^{-\alpha}},$$ (9.34)

and

$$\sum_n^\infty n\, e^{-\alpha n} = -\frac{\partial}{\partial \alpha} \sum_n^\infty e^{-\alpha n} = -\frac{\partial}{\partial \alpha} \frac{1}{1 - e^{-\alpha}} = \frac{e^{-\alpha}}{(1 - e^{-\alpha})^2}.$$ (9.35)

Putting the last three equations together, we obtain:

$$\langle n \rangle = \frac{e^{-\alpha}(1 - e^{-\alpha})}{(1 - e^{-\alpha})^2} = \frac{1}{e^\alpha - 1}$$ (9.36)

Hence, by resubstitution, the average energy of a harmonic oscillator at a temperature of T is

$$\langle E_{\text{osc}} \rangle = E_0 + \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T} - 1\right)}$$ (9.37)

leading to the correct expression for the spectral energy density of black body radiation, Eq. (9.6). Interestingly, Max Planck went a slightly different route, focusing on the average oscillator entropy [1].

Problem 9.2 (The Zero Point Energy) *Hint: It is assumed that you have dealt with Problem 9.1.* The constant E_0 in Problem 9.1 is the quantum mechanical zero point energy. From the condition $h\nu \ll k_B T$ and the average oscillator energy given in Problem 9.1, prove that $E_0 = \frac{h\nu}{2}$.

Solution 9.2 Although the zero point energy of an oscillator would follow from a rigorous quantum mechanical treatment of the harmonic oscillator based on the Schrödinger equation, the same result has already been obtained from consideration of the so-called *correspondence principle*, proposed by Niels Bohr [2]: Each quantum system should behave like a classical system in the limit where classical mechanics applies. Classically, one expects an ensemble of oscillators at a finite temperature to have an average oscillator energy of $k_B T$. This value should be reproduced by the quantum mechanical treatment; if high quantum numbers n are occupied, i.e., if the average energy of the oscillator consists of so many energy

portions $h\nu$ that the discrete nature of the excitation spectrum becomes negligible: this is the limit $h\nu \ll k_B T$. Therefore, we start with the oscillator energy in Eq. (9.30) and make use of the power series expansion Eq. (A.58) found in the Appendix,

$$\frac{\alpha}{e^\alpha - 1} = 1 - \frac{\alpha}{2} + B_1 \frac{\alpha^2}{2!} - B_2 \frac{\alpha^4}{4!} + \cdots$$

where $B_1 = \frac{1}{6}$ and $B_2 = \frac{1}{30}$ are the first Bernoulli numbers. With $\alpha = \frac{h\nu}{k_B T}$ we write

$$\langle E_{\text{osc}} \rangle = E_0 + k_B T \frac{\alpha}{e^\alpha - 1} = E_0 + k_B T \left(1 - \frac{\alpha}{2} + B_1 \frac{\alpha^2}{2!} - B_2 \frac{\alpha^4}{4!} + \cdots \right)$$

$$\langle E_{\text{osc}} \rangle = E_0 + k_B T - \frac{h\nu}{2} + \frac{1}{12} k_B T \left(\frac{h\nu}{k_B T} \right)^2 - \frac{1}{720} k_B T \left(\frac{h\nu}{k_B T} \right)^4 + \cdots$$

In the limit $h\nu \ll k_B T$, the terms containing powers of $\frac{h\nu}{k_B T}$ can be ignored and thus the correspondence principle requires

$$\lim_{h\nu \ll k_B T} \langle E_{\text{osc}} \rangle = E_0 + k_B T - \frac{h\nu}{2} \overset{!}{=} k_B T,$$

from which the zero point energy

$$E_0 = \frac{h\nu}{2} = \frac{\hbar\omega}{2} \tag{9.38}$$

follows.

Problem 9.3 (Electron Impact Heating, see Fig. 9.4) In the ultrahigh vacuum technique, electron impact heating is often used to heat a sample to high temperature. Consider a thin sample with a cross-sectional area of $1\,\text{cm}^2$ grounded to earth potential. Its initial temperature of $300\,\text{K}$ is that of the surroundings. A tungsten wire emits electrons with an emission current of $1.5\,\text{mA}$. Under the assumption that the sample is a black body and that radiation is the only heat transfer mechanism, calculate the potential between the tungsten wire and the sample to achieve a sample temperature of $1{,}200\,\text{K}$.

Solution 9.3 Cathode rays discovered by J.J. Thomson have practical applications in science and technology. The impact of electrons is a very effective way of heating
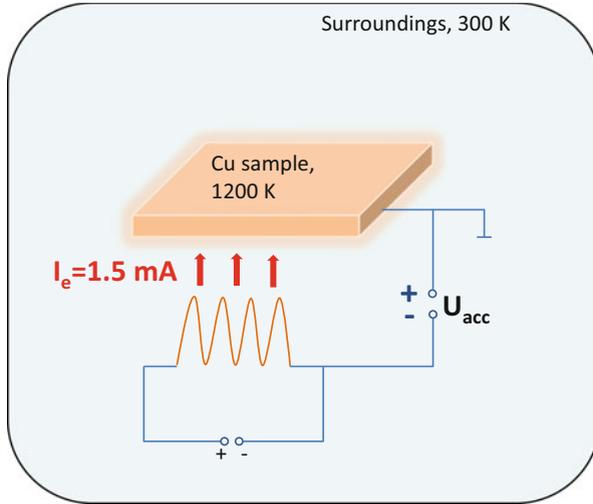
Fig. 9.4 Principle of electron impact heating. U_{acc} is the high voltage, by which emitted electrons are accelerated toward the copper sample

a sample to a high temperature.[5] Under ultrahigh vacuum conditions at a pressure below 10^{-5} Pa, heat transfer from the sample to the surroundings is predominantly radiative; if heat losses across the sample mounting can be ignored.[6] Assuming the copper sample to be a black body, the total radiation power emitted can be estimated using the Stefan Boltzmann law (Eq. (9.7)). If we additionally account for the temperature of the surroundings $T_{surr.}$, the net thermal power emitted by the sample at a given temperature T_{sample} is

$$P_{thermal} = A\sigma \left(T_{sample}^4 - T_{surr.}^4 \right)$$

where A is the total area of the copper sample, i.e., twice the cross-sectional area. To determine the necessary acceleration voltage, we equate this thermal power with the electrical power as the product of U_{acc} and the electron current I_e impinging on the sample. Hence,

$$P_{el.} = U_{acc}I_e \tag{9.39}$$

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[5]Sample heating to high temperature, also called tempering, is, for example, needed to obtain well-defined, clean and crystalline materials.

[6]In Problem 7.4 we have seen that heat conduction mediated by particle collisions is largely suppressed under ultrahigh vacuum conditions.

and solving for U_{acc} we obtain

$$U_{acc} = \frac{A\sigma}{I_e} \left(T_{sample}^4 - T_{surr.}^4 \right)$$

$$= \frac{2 \times 10^{-4} \, m^2 \times 5.670373 \times 10^{-8} \, W \, m^{-2} \, K^{-4}}{0.0015 \, A} \left((1200 \, K)^4 - (300 \, K)^4 \right)$$

$$= 15,616 \, V.$$

We thus need high-voltage acceleration to reach the requested sample temperature. In this context, it is worth mentioning another practical application: generation of X-rays . Electrons impinging on the sample surface with an energy in the keV range produce a certain amount of X-ray radiation.[7]

Problem 9.4 (Photoelectric Effect) Different cathode materials are irradiated with LASER light at a wavelength of $\lambda = 633 \, nm$:

Cathode material	Al	Ba	Ba on WO_3	Cd	Cs	K
Work function (eV)	4.30	2.52	0.30	4.04	1.94	2.22

a. Which of the cathode materials show the photoelectric effect?
b. The intensity of the LASER radiation is continuously increased. Does this alter the number of cathode materials showing the photoelectric effect?

Solution 9.4 The photoelectric effect is the basis of several important experimental methods such as X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS, ESCA[8]). On the other hand, a simple setup (Fig. 9.5) to demonstrate the photoelectric effect is possible so that the experiment can be regularly performed on high-school physics courses. A cathode on ground potential is irradiated with monochromatic LASER light of wavelength λ. In our case, it is a helium neon LASER with $\lambda = 633 \, nm$. The associated quantum energy is:

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \, J \, s \times 2.99792 \times 10^8 \, m \, s^{-1}}{633 \times 10^{-9} \, m}$$

$$= 3.14 \times 10^{-19} \, J = 1.96 \, eV. \tag{9.40}$$

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[7] See Problem 10.1 and Table 10.1 at page 300.
[8] XPS X-ray photoelectron spectroscopy, UPS ultraviolet photoelectron spectroscopy, ESCA electron spectroscopy for chemical analysis.
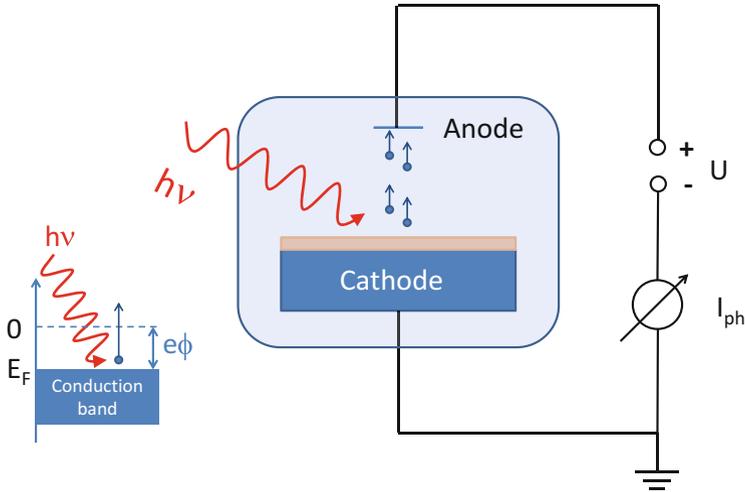
Fig. 9.5 Experimental setup to measure the photoelectric effect from cathode materials. The *inset* on the *left* illustrates the photo effect in the energy band model of a metal. The work function $e\phi$ is the difference in energy of the Fermi energy E_F and the vacuum potential level

If the quantum energy exceeds the work function $e\phi$ of the cathode material, a photo electron excited from the *Fermi level* may escape into the vacuum and be extracted to the anode, the latter being on a positive potential level. Thus, only if the LASER light generates photoelectrons is a photocurrent I_{ph} measured. Our task in **subproblem (a)** is to check which of the cathode materials have a work function energy smaller than or equal to the quantum energy of our LASER. This is the case for barium on tungsten oxide (Ba on WO_3) and for cesium (Cs). In the latter case the quantum energy exceeds the work function only by $0.02\,eV$. In all other cases, the quantum energy of the LASER is not sufficient to generate photo electrons. In **subproblem (b)**, we are asked if an increase of LASER intensity could induce a photoelectric effect in the other cathode materials, too. This is not the case. The excitation of a photoelectron appears to be an elementary process requiring an energy of at least $e\phi$. The number of light quanta, i.e., the intensity of the LASER beam, is not decisive for the photoelectric effect to occur.

Problem 9.5 (Lithium Atom and Quantum Defect)

a. The ionization energy of Lithium ($Z = 3$) is $5.39\,eV$. Assume that the model of the hydrogen atom can be applied to lithium and calculate the effective charge Z_{eff} of the nucleus as a result of the shielding by the 1s electrons.

Fig. 9.6 Atomic energy
levels of the element lithium

Fig. 9.6 Atomic energy levels of the element lithium
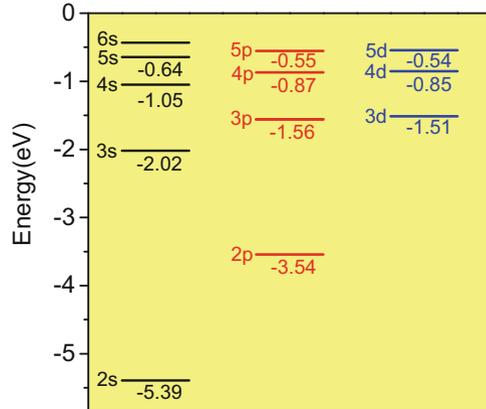

Problem 9.5 (continued)

b. Figure 9.6 shows the energy levels of the Li atom (L.J. Radziemski et
   al., Phys. Rev. A **52** (1995), 4462). Use the result of subproblem (a) to
   calculate the energy levels of the lithium atom. Compare the result with
   the experimental data and describe the differences.

c. An improved approximative model for hydrogen-like atoms makes use of
   the so-called quantum defects δ_l ($l = s, p, \dots$), which modify the formula
   for the energy levels according to:

$$E_{n,l} = -\frac{\mathrm{Ry}}{(n - \delta_l)^2}. \tag{9.41}$$

Use the data in Fig. 9.6 and determine the parameters δ_l for lithium.

Solution 9.5 Although the quantum mechanical models give a very concise picture
for atoms and ions with one single electron, systems with more than one electron can
only be treated in an approximate fashion. Here, we shall consider the lithium atom
with three electrons and the ground state configuration $1s^2 2s^1$. If the atom undergoes
a process of ionization, the 2s electron is removed. The situation is shown in Fig. 9.7.
In the simple picture of the Bohr model, the two 1s electrons lead to a shielding
of nuclear charge. If the shielding were complete, the 2s electron would *see* an
effective charge of $+e$. For all transitions in which only the 2s electron is involved,
an approximative treatment on the basis of an adapted model for the hydrogen atom
can be applied.

Fig. 9.7 Simple picture of the lithium atom within the Bohr model. The charge of the nucleus is partially shielded by the 1s electrons
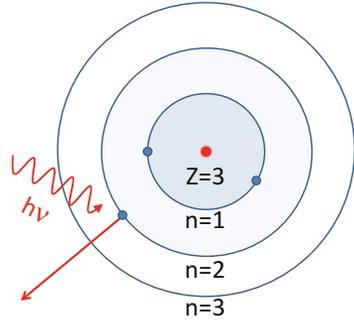
In **subproblem (a)**, we apply the simplest adaption and consider an effective nuclear charge $Z_{\text{eff}}e$ replacing the charge Ze of the "naked" nucleus:

$$\Delta E = E_f - E_i = Z_{\text{eff}}^2 \frac{m_e e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \tag{9.42}$$

If the model is reasonable, we expect Z_{eff} close to 1. In the ionization process ($n_i = 2$ and $n_f \to \infty$), the last equation yields:

$$E_{\text{ion}} = Z_{\text{eff}}^2 \text{Ry} \left(\frac{1}{4} - 0 \right)$$

and thus

$$Z_{\text{eff}} = \sqrt{\frac{4E_{\text{ion}}}{Ry}} = 1.26$$

The result is in fact close to 1, but it also indicates that the shielding of the nuclear charge by the 1s electrons is not complete.

Further, in **subproblem (b)**, we deal with the lithium atom and refine the treatment of its electronic structure to some extent. Alkali metals (Li, Na, K, ...) have a single valence electron and the electronic excitations of the atom are governed by transitions of this valence electron in excited states. The energy levels of such states are given in Fig. 9.6. At first, we investigate how well the effective nuclear charge $Z_{\text{eff}} = 1.26$ can reproduce this term diagram. The energy levels depend only on the quantum number n and are calculated using:

$$E_n = \frac{Z_{\text{eff}}^2 \text{Ry}}{n^2} \tag{9.43}$$

We obtain $E_2 = -4.28\,\text{eV}$, $E_3 = -1.90\,\text{eV}$, $E_4 = -1.07\,\text{eV}$, and $E_5 = -0.69\,\text{eV}$. We notice that the lithium energy levels E_{nl} depend markedly on the angular

momentum quantum number l, which is not reproduced by our simple formula. Our result for E_2 lies between the 2s level ($-5.39\,\text{eV}$), and the 2p level ($-3.54\,\text{eV}$). Similarly, our result for E_3 falls between 3s ($-2.02\,\text{eV}$) and 3d ($-1.51\,\text{eV}$). Our value E_4 is fairly close to the energy of the 4s state ($-1.05\,\text{eV}$), the same is true for E_5, which is close to the energy of the 5s state ($-0.64\,\text{eV}$). In summary, we can conclude that the higher the principal quantum number n, the better the prediction based on the effective nuclear charge. For $n = 2$, the agreement is worse and the model cannot explain the observed splitting between 2s and 2p, for example. Is an improved treatment possible?

In **subproblem (c)**, we follow an alternative treatment that goes back to the work of Rydberg and Schrödinger [3], who introduced the quantum defect δ_l. We use Eq. (9.41) and determine δ_l from the energy levels in Fig. 9.6. We could carry out a trial and error procedure or nonlinear fitting to determine δ_s from the values for 2s, 3s, 4s, and 5s. Alternatively, we solve for δ_l and obtain:

$$\delta_l = n - \sqrt{-\frac{\text{Ry}}{E_{n,l}}} \tag{9.44}$$

We obtain $\delta_s = 0.412$ (2s), 0.405 (3s), 0.401 (4s), and 0.390 (5s). All values are close to each other. We take the average value of 0.402 δ_s and obtain the energy levels shown in Table 9.1. With the same method, we obtain $\delta_p = 0.040$ and $\delta_d = 0.000$. The agreement between experimental and calculated energies is good.

Because of its simplicity the quantum defect model has been popular and is still used to describe highly excited atoms, the so-called Rydberg atoms.

Table 9.1 Comparison of energy levels in the lithium atom (see Fig. 9.6) and calculated energies based on the quantum defect approximation with Eq. (9.41)

State	2s	3s	4s	5s
Experiment	−5.39	−2.02	−1.05	−0.64
Calculated ($\delta_s = 0.402$)	−5.33	−2.01	−1.05	−0.64
State	2p	3p	4p	5p
Experiment	−3.54	−1.56	−0.87	−0.55
Calculated ($\delta_p = 0.040$)	−3.54	−1.55	−0.87	−0.55
State		3d	4d	5d
Experiment		−1.51	−0.85	−0.54
Calculated ($\delta_d = 0.000$)		−1.51	−0.85	−0.54

Problem 9.6 (Schrödinger Equation)

a. What is the classical relation between the kinetic energy E_{kin} of a particle of mass m and its momentum p? What is the *Hamilton function*? Give the classical trajectory of the particle.
b. Consider a particle moving in x direction in a constant potential V. For a quantum mechanical description, use a plane wave:

$$\psi(x,t) = \psi_0 \, e^{\frac{i}{\hbar}(px - Ht)} \tag{9.45}$$

where H is the total energy of the particle, and p its momentum. Apply the following operators to the free particle wave function:

$$i\hbar \frac{\partial}{\partial t} \qquad \frac{\hbar}{i} \frac{\partial}{\partial x} \qquad -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Use the classical relationship from subproblem (a) and identify the differential equation, which is satisfied by the plane wave description of the free particle.

Solution 9.6 In this problem, we familiarize ourselves with the foundations of quantum mechanics by considering the simple problem of a single particle moving without forces in space. The laws of quantum mechanics as a theory describing matter on the atomic scale cannot be derived in a strict way. Instead, even the interpretation of the wave function must be based on the comparison with experimental results. As a result of this comparison, the laws of quantum mechanics are formulated as *postulates*[9] (see Sect. 9.1.2). According to the famous *correspondence principle*, the predictions of quantum mechanics must meet the prediction of classical mechanics within the macroscopic limit, or, otherwise, within the fictive limit $h \to 0$, i.e., if Planck's constant were zero, and thus no quantization would occur. In **subproblem (a)**, we first look at the classical mechanics of a free particle of mass m and momentum p. Its kinetic energy is given by:

$$E_{kin} = \frac{1}{2}mv^2 = \frac{p^2}{2m}. \tag{9.46}$$

In theoretical mechanics there are two functions on which the equations of motion of a classical mechanical system are based: one is the *Hamilton function*, or the Hamiltonian H, which is the total kinetic energy plus the total potential energy of

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[9] An extensive discussion can be found in the book by David Bohm [4].

the system[10]:

$$H = E_{\text{kin}} + V \tag{9.47}$$

In the case of a single particle moving freely, the potential V takes a constant value. In general, however, V may vary with the location of the particle. If V also depended on time, we would be dealing with a nonconservative system. If the Hamiltonian of a system is known, the equations of motion follow from:

$$\dot{x}_i = \frac{\partial H}{\partial p_i} \tag{9.48}$$

$$\dot{p}_i = -\frac{\partial H}{\partial x_i} \tag{9.49}$$

Here, p_i is the momentum of the ith particle and x_i is its position. In our case of a one-particle system, the equations of motion are thus:

$$\dot{x} = \frac{p}{m} \tag{9.50}$$

and

$$\dot{p} = 0 \tag{9.51}$$

The momentum of the particle is constant, and its position is obtained by integration. If $x(0)$ is the position at $t = 0$, then:

$$\int_{x(0)}^{x(t)} dx = \int_0^t \frac{p}{m}\, dt \Leftrightarrow x(t) = x(0) + vt \tag{9.52}$$

where $v = \frac{p}{m}$ is the constant velocity of the particle. Thus, the classical trajectory is well-defined by classical mechanics.

In **subproblem (b)**, we switch to a quantum mechanical description using the one-particle wave function Eq. (9.45). This choice is not mandatory, but note that – provided that the superposition principle holds in quantum mechanics – any arbitrary complex wave function can be represented by a superposition of plane waves. Another strong argument is the analogy with optics and electromagnetic wave theory, which in a vacuum makes use of a plane wave representation of the electric and the magnetic field vector, which is a solution of the wave equation. What sort of wave equation does Eq. (9.45) satisfy? We check this by taking the

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[10]The other function is the Lagrangian $L = E_{\text{kin}} - V$

partial derivative in time:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = i\hbar \frac{\partial}{\partial t} \psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = H\psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = H\psi(x, t) \tag{9.53}$$

Thus, the special *operator* $i\hbar \frac{\partial}{\partial t}$ applied to the wave function reproduces the latter, and multiplies it with the total energy. In mathematical terms, Eq. (9.53) is an *eigenvalue problem*. The plane wave is an eigenfunction of the special operator $i\hbar \frac{\partial}{\partial t}$. We call this operator the *Hamiltonian operator* $\hat{H}$, as its eigenvalue is simply the total energy (see subproblem (a)). The same arithmetic can be performed using the other operators. For the partial derivative in x, we obtain:

$$\frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x, t) = \frac{\hbar}{i} \frac{\partial}{\partial x} \psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = p\psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = p\psi(x, t) \tag{9.54}$$

Thus, we identify the special operator $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ as the momentum operator (in x-direction), and the wave function also proves to be an eigenfunction of $\hat{p}$, and p is its eigenvalue. It is straightforward now to seek an *operator of the kinetic energy*, $\frac{\hat{p}^2}{2m}$, which is the third operator we apply. We obtain:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = \frac{p^2}{2m} \psi_0 \, e^{\frac{i}{\hbar}(px-Ht)} = E_{\text{kin}} \psi(x, t) \tag{9.55}$$

Moreover, we recognize that there is a second way of expressing the Hamiltonian operator as the sum of the operator of the kinetic energy and the constant potential:

$$\hat{H}\psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \psi(x, t) = \left(\frac{p^2}{2m} + V \right) \psi(x, t) = H\psi(x, t) \tag{9.56}$$

Thus, if we combine Eq. (9.53) with Eq. (9.56), we obtain the wave equation sought, which is satisfied by the plane wave:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \psi(x, t) \tag{9.57}$$

This is the Schrödinger equation of a massive particle for the special case of a constant potential. Note that derivatives in space (second order) and in time (first order) differ, whereas the wave equation describing electromagnetic waves in a vacuum contains second-order derivatives in space and time, as the textbooks show. In summary, using the plane wave description of a particle moving in a constant potential, we have identified the wave equation describing the motion of the particle. Moreover, we have seen that the physical observables total energy H, kinetic energy E_{kin}, and momentum p are associated with special operators. This concept can be generalized to an arbitrary observable O and its associated operator $\hat{O}$.

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Problem 9.7 (Wave Packets and Uncertainty Principle)
The wave function of a localized particle can be described as a superposition
of plane waves with different momentum:

$$\psi(x) = \int_{-\infty}^{+\infty} B(p) \exp\left(\frac{i}{\hbar}px\right) dp \tag{9.58}$$

where $B(p)$ is the distribution function for the momentum. Consider the
special distribution function:

$$B(p) = \begin{cases} 0 & p < (p_0 - \Delta p) \\ A & (p_0 - \Delta p) \leq p \leq (p_0 + \Delta p) \\ 0 & p > (p_0 + \Delta p) \end{cases}$$

a. Give the expression for the probability density $w(x) = |\psi(x)|^2$ to find the
   particle within x and $x + dx$. Note that A follows from the normalization
   of the wave function. Sketch the probability density for an electron with
   average kinetic energy $E_0 = 100\,\text{eV}$ and $\Delta p = 2.5 \times 10^{-3} p_0$.
b. Express the uncertainty Δx defined as the distance x from the center of
   $w(x)$, where the probability density has fallen to half of its maximum value.
   Calculate the product $\Delta p \, \Delta x$ and give an interpretation of the result.

Solution 9.7 According to the superposition principle in quantum mechanics (see
Sect. 9.1.2), an arbitrary function can be written as a superposition of plane waves.
Although a single plane wave has a well-defined momentum and energy, a wave
packet constructed by the superposition of many plane waves is characterized
by a momentum distribution, thus involving the statistical aspect of the wave
function. Quantum mechanics assumes that the wave function $\psi(x, t)$ contains all
the information about the particle, and $|\psi(x)|^2 = \psi^*(x)\psi(x)\,dx$ is the probability of
finding the particle between x and $x + dx$. Note that the rules dealing with complex
numbers are summarized in the Appendix, Sect. A.3.4.

In **subproblem (a)**, we calculate the probability density $w(x) = |\psi(x)|^2$ for the
wave packet Eq. (9.58). In the first step, we seek the spatial representation of the
wave function:

$$\psi(x) = \int_{-\infty}^{+\infty} B(p) \exp\left(\frac{i}{\hbar}px\right) dp = A \int_{p_0-\Delta p}^{p_0+\Delta p} \exp\left(\frac{i}{\hbar}px\right) dp \tag{9.59}$$

Here, we have inserted the special momentum distribution function $B(p)$ which
states that within a certain interval $2\Delta p$ around the average momentum p_0, all values
of p have the same weight characterized by the quantity A, which we will determine

later. The integral can be solved using the integral table in the Appendix. We obtain:

$$\psi(x) = A \left[\frac{e^{\frac{i}{\hbar}px}}{\frac{i}{\hbar}x} \right]_{p_0-\Delta p}^{p_0+\Delta p} = A \frac{\hbar}{i} e^{\frac{i}{\hbar}p_0 x} \frac{e^{\frac{i}{\hbar}\Delta px} - e^{-\frac{i}{\hbar}\Delta px}}{x} \tag{9.60}$$

If we use Euler's formula $e^{i\phi} = \cos\phi + i\sin\phi$ (see Eq. (A.11)), we can further simplify and obtain:

$$\psi(x) = A \frac{\hbar}{i} \frac{2i\sin\left(\frac{\Delta px}{\hbar}\right)}{x} e^{\frac{i}{\hbar}p_0 x} = 2A\hbar \frac{\sin\left(\frac{\Delta px}{\hbar}\right)}{x} e^{\frac{i}{\hbar}p_0 x} \tag{9.61}$$

The wave function has a complex phase factor $e^{\frac{i}{\hbar}p_0 x}$ which is enveloped by an amplitude function describing spatial variations depending on Δp. The spatial probability density function is the square of the wave function:

$$w(x) = \psi^*(x)\psi(x) = 4A^2\hbar^2 \frac{\sin^2\left(\frac{\Delta px}{\hbar}\right)}{x^2} \tag{9.62}$$

We determine A from the normalization of $w(x)$:

$$\int_{\infty}^{+\infty} w(x)\,dx \overset{!}{=} 1 = 4A^2\hbar^2 \int_{\infty}^{+\infty} \frac{\sin^2\left(\frac{\Delta px}{\hbar}\right)}{x^2}\,dx \overset{\text{Eq. (A.51)}}{=} 4A^2\hbar^2 \pi \frac{\Delta p}{\hbar} \tag{9.63}$$

Solving for A, we get

$$A = \sqrt{\frac{1}{4\pi \Delta p\hbar}} \tag{9.64}$$

and thus the probability density function is

$$w(x) = |\psi(x)|^2 = \frac{\hbar}{\pi \Delta p} \frac{\sin^2\left(\frac{\Delta px}{\hbar}\right)}{x^2} \tag{9.65}$$

Note that the point $x = 0$ requires special treatment because of the pole. Using the rule of l'Hôspital, we verify that $w(0) = \frac{\Delta p}{\pi\hbar}$. Next, we consider the concrete example of an electron with an energy of 100 eV. This is a typical energy measurement of electrons in low-energy electron diffraction (LEED) experiments probing a crystalline surface. An ideal electron gun emits a monochromatic electron beam. Using Eq. (9.46), the momentum of such a perfectly monochromatic electron

Fig. 9.8 Probability density function $w(x) = |\psi(x)|^2$ of a particle with *boxcar* momentum distribution. The *blue line* marks the half width $2\Delta x$
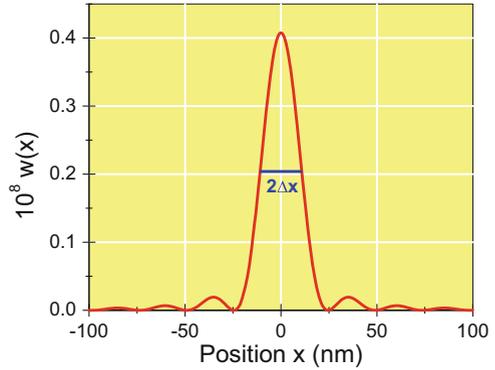
wave would be:

$$p_0 = \sqrt{2m_e E_{\text{kin}}} = \sqrt{2 \times 9.1094 \times 10^{-31}\,\text{kg} \times 100 \times 1.6022 \times 10^{-19}\,\text{J}}$$
$$= 5.4 \times 10^{-24}\,\text{kg m s}^{-1}. \tag{9.66}$$

A real electron gun, however, emits electrons with a certain energy spread and thus the momentum scatters around the average momentum. In our case, $\Delta p = 2.5 \times 10^{-3} = 1.35 \times 10^{-26}\,\text{kg m s}^{-1}$. Using this information, we can plot $w(x)$. The result is shown in Fig. 9.8. The function has a central principle maximum around $x = 0$ and several weak side maxima. Repeated measurements of the electron's position would localize it statistically within a range of several nanometers from the center. In **subproblem (b)**, we quantify this resulting uncertainty in position, defining Δx as the distance from the center where the probability density drops to 50% of the maximum value. The condition for the uncertainty Δx is thus

$$w(\Delta x) \overset{!}{=} \frac{1}{2}w(0) = \frac{1}{2}\frac{\Delta p}{\pi \hbar} \tag{9.67}$$
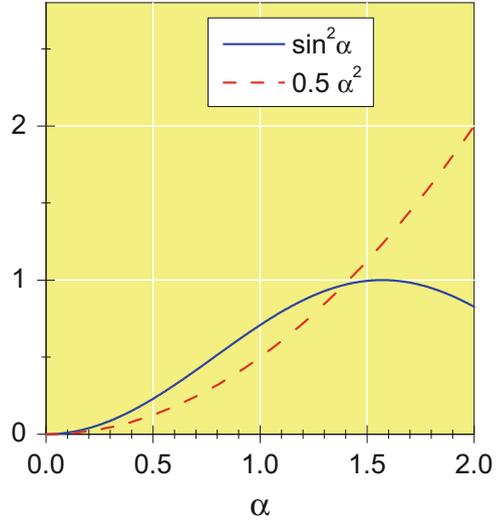
and

$$\frac{\hbar}{\pi \Delta p}\frac{\sin^2\left(\frac{\Delta p \Delta x}{\hbar}\right)}{\Delta x^2} = \frac{\Delta p}{2\pi \hbar} \tag{9.68}$$

which can be written in the following way:

$$\sin^2\left(\frac{\Delta p\, \Delta x}{\hbar}\right) = \frac{1}{2}\left(\frac{\Delta p\, \Delta x}{\hbar}\right)^2 \tag{9.69}$$

Fig. 9.9 Graphical solution
of the nonlinear equation
$\sin^2 \alpha = \frac{1}{2}\alpha^2$

If we define $\alpha = \frac{\Delta p \, \Delta x}{\hbar}$ we must solve the transcendental equation

$$\sin^2 \alpha = \frac{1}{2}\alpha^2 \tag{9.70}$$

This can be done graphically by seeking the intersection point, which is at $\alpha \approx 1.39$ (see Fig. 9.9). We therefore find the following relation between the uncertainties in momentum and position:

$$\Delta p \, \Delta x = 1.39\hbar \tag{9.71}$$

Note that our result is consistent with Heisenberg's uncertainty principle [4]:

$$\Delta p \, \Delta x \geq \hbar \tag{9.72}$$

The uncertainties in position and momentum are mutually related. An increase in Δp leads to a decrease in Δx and vice versa. Applied to the concrete example of diffraction experiments, this has concrete implications: a highly monochromatic gun with small Δp guarantees a large Δx, which is advantageous in diffraction experiments where constructive and destructive interference of large wave trains is needed. An electron gun with a large energy spread and thus large Δp, in contrast, would result in small values of Δx and interference between atomic layers at a crystal surface would be hampered. Note that typical atomic layer distances in a crystal are within the range of a few tenths of a nanometer.

Problem 9.8 (Gaussian Wave Packet Propagation)

a. Prove that the Gaussian wave packet

$$\psi(x,t) = N\left(\frac{1}{\alpha + i\beta t}\right)^{\frac{1}{2}} e^{i(k_0 x - \omega_0 t)} e^{-\frac{(x - v_g t)^2}{4(\alpha + i\beta t)}} \tag{9.73}$$

is a solution of the time-dependent Schrödinger-equation of a free particle of mass m. N is a normalization constant, the parameter α is the initial variance σ_x^2 of the wave packet, $\omega_0 = \frac{\hbar k_0^2}{2m}$, $\beta = \frac{\hbar}{2m}$, the group velocity $v_g = \frac{\hbar k_0}{m}$.

b. Determine the normalization constant N in Eq. (9.73).

c. Give an interpretation of Eq. (9.73) by plotting the probability density $\psi^\star \psi$ for $t = 0\,\text{s}$, $t = 2 \times 10^{-14}\,\text{s}$, and $t = 5 \times 10^{-14}\,\text{s}$ for a ballistic electron with a group velocity of $10^6\,\text{m s}^{-1}$. The electron is initially located within $10^{-9}\,\text{m}$ at $x(t = 0) = 0$.

Solution 9.8 Few textbooks deal with explicit solutions of the *time-dependent* Schrödinger equation. Here, we consider the ballistic movement of a free particle in one spatial dimension with time. The probability of locating the particle within a certain interval between x and $x + dx$ is determined by the absolute square of the wave function, $|\psi(x,t)|^2$.

In **subproblem (a)**, we prove that Eq. (9.73) is a solution of the time-dependent Schrödinger equation. The straightforward, but somewhat tedious way is to calculate the derivatives of $\psi(x,t)$ in x and t and to show that $i\hbar \frac{\partial}{\partial t}\psi(x,t)$ equals $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)$. Making use of the chain rule, the first derivative in x is

$$\frac{\partial \psi}{\partial x} = N\sqrt{\frac{1}{\alpha + i\beta t}}\,(ik_0)\,e^{i(k_0 x - \omega_0 t)} e^{-\frac{(x - v_g t)^2}{4(\alpha + i\beta t)}}$$

$$+ N\sqrt{\frac{1}{\alpha + i\beta t}}\,e^{i(k_0 x - \omega_0 t)} e^{-\frac{(x - v_g t)^2}{4(\alpha + i\beta t)}}\left(-\frac{2(x - v_g t)}{4(\alpha + i\beta t)}\right)$$

and thus

$$\frac{\partial \psi}{\partial x} = \psi(x,t)\left(ik_0 - \frac{2(x - v_g t)}{4(\alpha + i\beta t)}\right).$$

To form the second derivative, we use the chain rule on the last equation again and obtain

$$\frac{\partial^2 \psi}{\partial x^2} = \psi(x,t)\left(\left(ik_0 - \frac{2(x-v_g t)}{4(\alpha+i\beta t)}\right)^2 - \frac{2}{4(\alpha+i\beta t)}\right)$$

$$= \psi(x,t)\left(-k_0^2 - \frac{4ik_0(x-v_g t)+2}{4(\alpha+i\beta t)} + \frac{4(x-v_g t)^2}{16(\alpha+i\beta t)^2}\right) \qquad (9.74)$$

The time derivative is:

$$\frac{\partial \psi}{\partial t} = \left(-\frac{i\beta}{2(\alpha+i\beta t)}\right) N \sqrt{\frac{1}{\alpha+i\beta t}} e^{i(k_0 x-\omega_0 t)} e^{-\frac{(x-v_g t)^2}{4(\alpha+i\beta t)}}$$

$$+ N\sqrt{\frac{1}{\alpha+i\beta t}}(-i\omega_0)e^{i(k_0 x-\omega_0 t)} e^{-\frac{(x-v_g t)^2}{4(\alpha+i\beta t)}}$$

$$+ \left(\frac{2(x-v_g t)v_g}{4(\alpha+i\beta t)} + \frac{(x-v_g t)^2 4i\beta}{16(\alpha+i\beta t)^2}\right) N\sqrt{\frac{1}{\alpha+i\beta t}} e^{i(k_0 x-\omega_0 t)} e^{-\frac{(x-v_g t)^2}{4(\alpha+i\beta t)}}$$

After sorting and multiplication with $i\hbar$ we obtain:

$$i\hbar\frac{\partial \psi}{\partial t} = \psi(x,t)\left(\hbar\omega_0 + \frac{2\hbar\beta}{4(\alpha+i\beta t)} + \frac{2i\hbar v_g(x-v_g t)}{4(\alpha+i\beta t)} - \frac{4\hbar\beta(x-v_g t)^2}{16(\alpha+i\beta t)^2}\right).$$

If we take into account that $\hbar\beta = \frac{\hbar^2}{2m}$, $\hbar v_g = \frac{\hbar^2 2k_0}{2m}$, and $\hbar\omega_0 = \frac{\hbar^2 k_0^2}{2m}$, we obtain:

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\psi(x,t)\left(-k_0^2 - \frac{2}{4(\alpha+i\beta t)} - \frac{4ik_0(x-v_g t)}{4(\alpha+i\beta t)} + \frac{4(x-v_g t)^2}{16(\alpha+i\beta t)^2}\right)$$

$$\stackrel{\text{Eq. (9.74)}}{=} -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2}$$

Thus, the wave packet satisfies the time-dependent Schrödinger equation. In **subproblem (b)**, we determine the normalization constant N. We also check if the total probability integrated over the whole one-dimensional space remains constant with time. If this were not the case, Eq. (9.73) would not describe a physically meaningful situation. Normalization requires the unit probability of finding the particle of between $x = -\infty$ and $x = +\infty$. Hence,

$$1 \stackrel{!}{=} \int_{-\infty}^{+\infty} \psi^\star(x,t)\psi(x,t)\,dx = N^2\sqrt{\frac{1}{\alpha-i\beta t}}\sqrt{\frac{1}{\alpha+i\beta t}}\int_{-\infty}^{+\infty} e^{-\frac{(x-v_g t)^2}{4(\alpha-i\beta t)}} e^{-\frac{(x-v_g t)^2}{4(\alpha+i\beta t)}}\,dx$$

As

$$\frac{1}{\alpha + i\beta t}\frac{1}{\alpha - i\beta t} = \frac{1}{\alpha^2 + \beta^2 t^2}$$

and

$$\frac{1}{\alpha + i\beta t} + \frac{1}{\alpha - i\beta t} = \frac{2\alpha}{\alpha^2 + \beta^2 t^2}$$

both the prefactors and the integral can be simplified:

$$1 \overset{!}{=} N^2 \sqrt{\frac{1}{\alpha^2 + \beta^2 t^2}} \int_{-\infty}^{+\infty} e^{-\frac{2\alpha\left(x - v_g t\right)^2}{4(\alpha^2 + \beta^2 t^2)}} \, dx$$

The integral can be evaluated using a definite integral from the integral table (see Eq. (A.46)):

$$\int_{-\infty}^{+\infty} e^{-a^2 u^2} \, du = \frac{\sqrt{\pi}}{a}.$$

After the substitution $u = x - v_g t$ and $a = \left(\frac{\alpha}{2(\alpha^2 + \beta^2 t^2)}\right)^{\frac{1}{2}}$ we obtain

$$1 \overset{!}{=} N^2 \sqrt{\frac{1}{\alpha^2 + \beta^2 t^2}} \sqrt{\frac{2\pi(\alpha^2 + \beta^2 t^2)}{\alpha}}$$

and thus the normalization constant is independent of time: $N = \left(\frac{\alpha}{2\pi}\right)^{\frac{1}{4}}$. According to our calculations, the probability density of the particle is

$$w(x, t) = \psi^\star(x, t)\psi(x, t) = \left(\frac{\alpha}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{\alpha^2 + \beta^2 t^2}\right)^{\frac{1}{2}} e^{-\frac{\alpha\left(x - v_g t\right)^2}{2(\alpha^2 + \beta^2 t^2)}} \tag{9.75}$$

It is a Gaussian distribution centered around $x(t) = v_g t$, i.e., the wave packet moves with the group velocity v_g as time proceeds. At the same time, however, the wave packet also spreads over time. By comparison with Eq. (A.64), defining the normal distribution, we identify the time-dependent variance of the wave packet:

$$\sigma^2(t) = \alpha\left(1 + \frac{\beta^2 t^2}{\alpha^2}\right). \tag{9.76}$$

This spreading of the wave packet is illustrated in **subproblem (c)**. We consider an electron with velocity $v_g = 10^6 \, \mathrm{m\,s^{-1}}$. This corresponds to a wave vector $k_0 =$

Fig. 9.10 Movement and spreading of the Gaussian wave packet with time. The *blue dashed line* marks the classical trajectory of the particle according to Eq. (9.52) moving with the group velocity v_g. The center of the Gaussian wave packet follows the classical trajectory
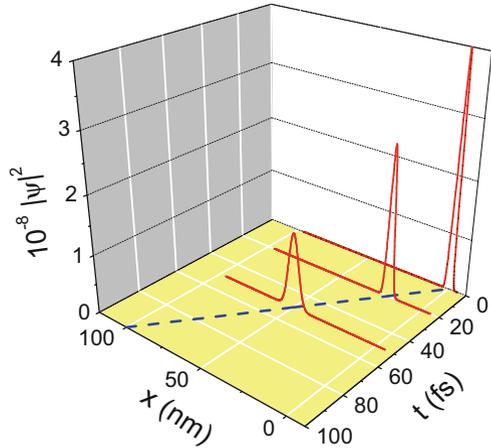
$\frac{mv_g}{\hbar} = 8.6 \times 10^9 \, \text{m}^{-1}$, and to a kinetic energy of $E = \frac{\hbar^2 k_0^2}{2m} = 4.55 \times 10^{-19} \, \text{J}$, or 2.8 eV. The electron could, for example, have been emitted after an interaction of a photon with an atom. We assume that the electron is initially confined to a spatial dimension of 1 nm. Therefore, $\alpha = 10^{-18}$ m. The parameter β has the dimension of a velocity and has a value of $5.7884 \times 10^{-5} \, \text{m s}^{-1}$. This determines the density of the electron's wave packet according to Eq. (9.75). In Fig. 9.10, the wave packet is plotted for the time $t = 0$, 20 fs, and 50 fs (1 fs $= 10^{-15}$ s). Within this time, the electron classically travels 20 nm and 50 nm respectively. The classical trajectory (blue dashed line) is calculated according to Eq. (9.52). Although the center of the wave packet follows this classical trajectory, the spreading of the wave packet over time is evident. After 50 fs, the width of the wave packet is about three times the initial width.

Problem 9.9 (Conservation of the Norm of the Wave Function)
If $|\psi(t_0)\rangle$ is the initial state of a quantum system at time t_0 and $\hat{H}$ its time-independent Hamiltonian, the state of the system at time $t_0 + \tau$ is:

$$|\psi(t_0 + \tau)\rangle = \exp\left(-\frac{i}{\hbar}\hat{H}\tau\right)|\psi(t_0)\rangle \qquad (9.77)$$

a. Prove Eq. (9.77). *Hint:* Use a Taylor series expansions of the exponential function and $|\psi(t)\rangle$.
b. Using Eq. (9.77), prove that if $\psi(t)$ is normalized at $t = t_0$, then it is normalized at arbitrary t.

Solution 9.9 The probability interpretation of quantum mechanics is frequently doubted by students, perhaps as often as the validity of the second law of thermodynamics. The interpretation of $|\psi|^2$ as a probability density in fact requires the total probability, i.e., the norm, to be conserved. It is our task in this problem to rigorously show this on the basis of the postulates of quantum mechanics (Sect. 9.1.2). Apart from the Hamiltonian $\hat{H}$ and the wave function at $t = t_0$, no further specifications are made about the system. The problem is an occasion to deal with the numerous postulates of quantum mechanics found in Sect. 9.1.2.1.

In **subproblem (a)**, we consider a special operator acting on the wave function, namely the *propagator*

$$\hat{U}(\tau) = \exp\left(-\frac{i}{\hbar}\hat{H}\tau\right). \tag{9.78}$$

We show that $\hat{U}$ applied to wave function at t_0 yields the wave function at a later time $t > t_0$. As a hint, it was recommended to expand $\hat{U}$ and $|\psi(t)\rangle$. We thus start with a Taylor series expansion of the wave function (see Eq. (A.54) in the Appendix):

$$|\psi(t_0 + \tau)\rangle \overset{\text{Eq. (A.54)}}{=} \sum_{n=0}^{\infty} \frac{\tau^n}{n!}\frac{\partial^n}{\partial t^n}|\psi(t = t_0)\rangle \tag{9.79}$$

The sum on the right-hand side, however, can be written in a compact form using an exponential operator acting on the state $|\psi(t)\rangle$ at time $t = t_0$:

$$\sum_{n=0}^{\infty} \frac{\tau^n}{n!}\frac{\partial^n}{\partial t^n}|\psi(t = t_0)\rangle \overset{\text{Eq. (A.55)}}{=} \exp\left(\tau\frac{\partial}{\partial t}\right)|\psi(t = t_0)\rangle \tag{9.80}$$

This exponential operator thus *shifts* the wave function forward in time by a value τ, which justifies the terminus propagator:

$$|\psi(t_0 + \tau)\rangle = \exp\left(\tau\frac{\partial}{\partial t}\right)|\psi(t_0)\rangle \tag{9.81}$$

What is left is to replace the time derivative with the Hamiltonian. Using $\hat{H} = i\hbar\frac{\partial}{\partial t}$ (see Eq. (9.16)), we find

$$|\psi(t_0 + \tau)\rangle = \exp\left(\tau\frac{\hat{H}}{i\hbar}\right)|\psi(t_0)\rangle = \hat{U}(\tau)|\psi(t_0)\rangle \tag{9.82}$$

which proves Eq. (9.77).

As an application of the postulates of quantum mechanics in Sect. 9.1.2.1, it is worth looking at the special properties of $\hat{U}$: Because of

$$|\psi(t_0)\rangle = \underbrace{\hat{U}(-\tau)\,\hat{U}(\tau)}_{=1}\,|\psi(t_0)\rangle = \hat{U}^{-1}(\tau)\,\hat{U}(\tau)|\psi(t_0)\rangle$$

the *inverse* of $\hat{U}(\tau)$ is $\hat{U}(-\tau)$. The inverse of $\hat{U}$, however, is also the adjoint operator of $\hat{U}$, and thus:

$$\hat{U}(-\tau) = \exp\left(+\frac{i}{\hbar}\hat{H}\tau\right) = \exp\left(-\frac{i}{\hbar}\hat{H}\tau\right)^{*} = \hat{U}^{+}(\tau).$$

As a consequence,

$$\hat{U}^{+} = \hat{U}^{-1} \Leftrightarrow \hat{U}^{+}\hat{U} = 1. \tag{9.83}$$

An operator satisfying Eq. (9.83) is called **unitary operator**, and the transformation Eq. (9.82) is thus called a **unitary transformation**. This leads us to **subproblem (b)**, where we prove that the wave function, if normalized at $t = t_0$, is also normalized at $t > t_0$, e.g., at $t = t_0 + \tau$. The norm is the *scalar product*

$$\langle\psi(t_0)|\psi(t_0)\rangle = \langle\psi(t_0)|\,\underbrace{\hat{U}^{+}(\tau)\,\hat{U}(\tau)}_{1}\,\psi(t_0)\rangle = \langle\left(\hat{U}^{+}(\tau)\right)^{+}\psi(t_0)|\hat{U}(\tau)\psi(t_0)\rangle$$

$$\tag{9.84}$$

Because of $\left(\hat{U}^{+}\right)^{+} = \hat{U}$, we can thus write:

$$\langle\psi(t_0)|\psi(t_0)\rangle = \langle\hat{U}(\tau)\psi(t_0)|\hat{U}(\tau)\psi(t_0)\rangle = \langle\psi(t_0 + \tau)|\psi(t_0 + \tau)\rangle \tag{9.85}$$

which was to be proven. The conservation of the norm of the wave function is thus the consequence of the unitary transformation of the wave function using the propagator $\hat{U}$. In Problem 9.8 the conservation of the probability was shown for the special case of a wave packet. The wave packet depicted in Fig. 9.10 broadens over time, but the total probability density remains constant. In this exercise, we have seen that this property of the wave function is general. The conservation of the norm would hold even in a more complex situation, e.g., if a wave packet would be partially reflected at a wall.

Problem 9.10 (Operators I)
Hint: It is recommended that you have already dealt with Problem 9.6. For the treatment of the harmonic oscillator problem the creation and annihilation operators

$$\mathbf{a}^+ = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) \tag{9.86}$$

$$\mathbf{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right) \tag{9.87}$$

are introduced, where $\hat{x}$ and $\hat{p}$ are the operators of position and momentum of the particle of mass m. The particle moves in a harmonic potential $V(x) = \frac{m\omega^2 x^2}{2}$ at an angular frequency ω.

a. Prove the commutation relations

$$[\hat{x}, \hat{p}] = -\frac{\hbar}{i} \tag{9.88}$$

$$\left[\mathbf{a}, \mathbf{a}^+\right] = 1 \tag{9.89}$$

$$\left[\mathbf{N}, \mathbf{a}^+\right] = \mathbf{a}^+ \tag{9.90}$$

$$[\mathbf{N}, \mathbf{a}] = -\mathbf{a} \tag{9.91}$$

where the number operator is defined by means of $\mathbf{N} = \mathbf{a}^+\mathbf{a}$.

b. Show that the Hamiltonian of the harmonic oscillator problem can be written:

$$\hat{H} = \hbar\omega\left(\mathbf{N} + \frac{1}{2}\right). \tag{9.92}$$

c. If $|n\rangle$ is the state function of the harmonic oscillator in its nth excited state, prove and interpret the following relations:

$$\mathbf{N}\,\mathbf{a}|n\rangle = (n-1)\mathbf{a}|n\rangle \tag{9.93}$$

$$\mathbf{N}\,\mathbf{a}^+|n\rangle = (n+1)\mathbf{a}^+|n\rangle \tag{9.94}$$

Solution 9.10 In this exercise, we become more familiarized with operator calculus in quantum mechanics. We acquire an insight into how this can be advantageously used for the description of the harmonic oscillator model, which is of key importance, e.g., in vibrational spectroscopy.

The momentum operator of a particle moving in one dimension has already been introduced in Problem 9.6:

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{9.95}$$

We use $\hat{p}$ together with the position operator $\hat{x}$ to formulate the operators $\mathbf{a}^+$ and $\mathbf{a}$ according to Eqs. (9.86) and (9.87). These are called creation and annihilation operator and it is our goal to clarify their significance. In **subproblem (a)**, we prove commutation relations for $\mathbf{a}$, $\mathbf{a}^+$, and a third operator called the number operator:

$$\mathbf{N} = \mathbf{a}^+\mathbf{a} \tag{9.96}$$

The commutator of two operators has been defined in Eq. (9.17). The significance of the commutator becomes clear if we realize that two mathematical objects do not necessarily obey the commutative law. If the order of two operators acting on a wave function does influence the result, then they have a non-zero commutator. An example is the operators of position of momentum, where the order does in fact matter: if we consider the expressions

$$\hat{x}\hat{p}\psi(x) = \hat{x}\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x) = \frac{\hbar}{i}x\frac{\partial \psi(x)}{\partial x}$$

and

$$\hat{p}\hat{x}\psi(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}(\hat{x}\psi(x)) = \frac{\hbar}{i}\psi(x) + \frac{\hbar}{i}x\frac{\partial \psi(x)}{\partial x}$$

we notice that

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = -\frac{\hbar}{i} \tag{9.97}$$

which is the first of the commutator expressions that was meant to be shown.

It is straightforward to apply Eq. (9.17) to $\mathbf{a}^+$ and $\mathbf{a}$:

$$\begin{aligned}
\left[\mathbf{a}, \mathbf{a}^+\right] &= \mathbf{a}\mathbf{a}^+ - \mathbf{a}^+\mathbf{a} \\
&= \frac{m\omega}{2\hbar}\left[\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) - \left(\hat{x} - \frac{i}{m\omega}\hat{p}\right)\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)\right] \\
&= \frac{m\omega}{2\hbar}\left[-\frac{2i}{m\omega}(\hat{x}\hat{p} - \hat{p}\hat{x})\right] \\
&= -\frac{i}{\hbar}[\hat{x}, \hat{p}] \overset{\text{Eq. (9.97)}}{=} 1
\end{aligned} \tag{9.98}$$

This was shown. Note that after expansion of the terms in the first line of Eq. (9.98), the terms containing $\hat{x}^2$ and $\hat{p}^2$ cancel each other out. To prove Eq. (9.90), we can use Eq. (9.89):

$$\left[\mathbf{N}, \mathbf{a}^+\right] \overset{\text{Eq. (9.96)}}{=} \mathbf{a}^+\mathbf{a}\mathbf{a}^+ - \mathbf{a}^+\mathbf{a}^+\mathbf{a} = \mathbf{a}^+\left[\mathbf{a}, \mathbf{a}^+\right] \overset{\text{Eq. (9.89)}}{=} \mathbf{a}^+ \tag{9.99}$$

In the same fashion, Eq. (9.91) is shown:

$$\left[\mathbf{N}, \mathbf{a}\right] \overset{\text{Eq. (9.96)}}{=} \mathbf{a}^+\mathbf{a}\mathbf{a} - \mathbf{a}\mathbf{a}^+\mathbf{a} = -\left[\mathbf{a}, \mathbf{a}^+\right]\mathbf{a} \overset{\text{Eq. (9.89)}}{=} -\mathbf{a} \tag{9.100}$$

To understand the meaning of these operators we move on to **subproblem (b)**, where we show that the Hamiltonian of the harmonic oscillator problem can be rewritten in a simpler form containing the number operator. From the Schrödinger equation of the harmonic oscillator Eqs. (9.18) and (9.20) we may extract the Hamiltonian in the form:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \tag{9.101}$$

where we have considered Eq. (9.95). In this form, the relation to the classic Hamiltonian $H = E_{\text{kin}} + V$ is obvious. To prove Eq. (9.92) it is best to show that the right-hand side of this equation is equivalent to Eq. (9.101):

$$
\begin{aligned}
\hbar\omega\left(\mathbf{N} + \frac{1}{2}\right) &= \hbar\omega\left(\mathbf{a}^+\mathbf{a} + \frac{1}{2}\right) \\
&= \hbar\omega\left(\frac{m\omega}{2\hbar}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right)\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right) + \frac{1}{2}\right) \\
&= \frac{m\omega^2}{2}\left(\hat{x}^2 - \frac{i}{m\omega}\underbrace{(\hat{p}\hat{x} - \hat{x}\hat{p})}_{-[\hat{x},\hat{p}]} + \frac{1}{m^2\omega^2}\hat{p}^2\right) + \frac{\hbar\omega}{2} \\
&\overset{\text{Eq. (9.97)}}{=} \frac{m\omega^2}{2}\hat{x}^2 - \frac{m\omega^2}{2}\frac{i}{m\omega}\frac{\hbar}{i} + \frac{\hat{p}^2}{2m} + \frac{\hbar\omega}{2} \\
&= \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \overset{\text{Eq. (9.101)}}{=} \hat{H}
\end{aligned}
\tag{9.102}
$$

Here, it is worth comparing this special form of the Hamiltonian with the expression for the energies of the harmonic oscillator, Eq. (9.19). It is obvious that $\left[\hat{H}, \mathbf{N}\right] = 0$ and thus the number operator and the Hamiltonian operator are commuting operators, meaning that they share the same spectrum of eigenfunctions. In the form

$$\hbar\omega\left(\mathbf{N} + \frac{1}{2}\right)\psi_n = \hbar\omega\left(\mathbf{n} + \frac{1}{2}\right)\psi_n \tag{9.103}$$

the significance of **N** now becomes very clear: it yields the number of quanta, n, by which the oscillator is excited. In a notation with ket vectors,

$$\mathbf{N}|n\rangle = n|n\rangle. \tag{9.104}$$

Moving on to **subproblem (c)**, we show further relations revealing the significance of the operators **a** and $\mathbf{a}^+$. Employing the commutator relations Eqs. (9.90) and (9.91) we first consider the expression:

$$\mathbf{Na}|n\rangle \overset{\text{Eq. (9.91)}}{=} (\mathbf{aN} - \mathbf{a})\,|n\rangle = \mathbf{a}\,(\mathbf{N} - 1)\,|n\rangle \overset{\text{Eq. (9.104)}}{=} \mathbf{a}(n-1)|n\rangle = (n-1)\mathbf{a}|n\rangle. \tag{9.105}$$

which proves Eq. (9.93)

Using the same trick with the commutator relation Eq. (9.90) we obtain:

$$\mathbf{Na}^+|n\rangle \overset{\text{Eq. (9.90)}}{=} \mathbf{a}^+\,(\mathbf{N} + 1)\,|n\rangle \overset{\text{Eq. (9.104)}}{=} \mathbf{a}^+(n+1)|n\rangle = (n+1)\mathbf{a}^+|n\rangle. \tag{9.106}$$

Our interpretation of these expressions is based on the number operator: If it is applied to the state $\mathbf{a}^+|n\rangle$, it yields $n + 1$ quanta. Moreover, a state $\mathbf{a}|n\rangle$ contains $n-1$ quanta. That is, $\mathbf{a}^+$ increases n by 1; it creates a quantum, whereas $\mathbf{a}$ decreases n by 1, it annihilates a quantum. Further analysis would in fact show that

$$\mathbf{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle \tag{9.107}$$

and

$$\mathbf{a}|n\rangle = \sqrt{n}|n-1\rangle \tag{9.108}$$

At the end of this exercise, we reflect on the use of this concept, for example, in conjunction with spectroscopy. A very important application is the derivation of **selection rules** for the harmonic oscillator,[11] as these operators describe transitions between harmonic oscillator states. In addition, if the harmonic oscillator model is applied to the case of electromagnetic waves and the photon picture of light, the raising and lowering operators describe the creation and annihilation of photons in elementary interaction processes with matter. Moreover, we use these operators in Problem 9.17 to solve the quantum double well.

---

[11] See Eq. (10.18) in Chap. 10.

Problem 9.11 (Operators II)

For the description of two-level systems the **Pauli spin matrices**

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (9.109)$$

are introduced.

a. Verify that the Pauli spin matrices satisfy the commutation rules for the angular momentum apart from a constant factor.
b. Consider a two-level system with a ground state $|g\rangle$ and an excited state $|e\rangle$. A general state of the system is:

$$\alpha|e\rangle + \beta|g\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \qquad (9.110)$$

Use the Pauli spin matrices to construct *ladder* operators σ_+ and σ_- with the following properties:

$$\sigma_+|g\rangle = |e\rangle; \quad \sigma_-|e\rangle = |g\rangle; \quad \sigma_+|e\rangle = 0; \quad \sigma_-|g\rangle = 0 \qquad (9.111)$$

c. What is the effect of σ_z acting on ground and excited states?

Solution 9.11 This second exercise on operator calculus focuses on Pauli spin matrices and their use in conjunction with the description of spin and two-level systems in general. In **subproblem (a)**, we verify that the Pauli spin matrices defined in Eq. (9.109) satisfy the angular momentum commutation rules apart from a constant factor. Here, we must recapitulate at first these rules for examinations in spectroscopy or advanced physical chemistry with which we should be very familiar. Given a system with angular momentum vector $\mathbf{J} = (J_x, J_y, J_z)$ and the related angular momentum operators $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$, the three components of the angular momentum cannot be measured at the same time with arbitrary precision, because they do not commute:

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z \qquad (9.112)$$

$$[\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x \qquad (9.113)$$

$$[\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y \qquad (9.114)$$

The square of the angular momentum, $J^2 = J_x^2 + J_y^2 + J_z^2$ and the z-component is usually chosen to define the state of angular momentum. The respective operators commute with each other:

$$[\hat{J}^2, \hat{J}_z] = 0 \qquad (9.115)$$

Matrices (see Sect. A.3.16 in the Appendix) are mathematical objects that do not necessarily follow the commutative law. It is straightforward to check this for the Pauli spin matrices:

$$[\sigma_x, \sigma_y] = \sigma_x\sigma_y - \sigma_y\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\sigma_z \qquad (9.116)$$

In the same way, we obtain:

$$[\sigma_y, \sigma_z] = \sigma_y\sigma_z - \sigma_z\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} = 2i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 2i\sigma_x \qquad (9.117)$$

and

$$[\sigma_z, \sigma_x] = \sigma_z\sigma_x - \sigma_x\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} - \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = 2i\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = 2i\sigma_y \qquad (9.118)$$

In summary, the Pauli spin matrices follow the commutation rules

$$[\sigma_x, \sigma_y] = 2i\sigma_z \qquad [\sigma_y, \sigma_z] = 2i\sigma_x \qquad [\sigma_z, \sigma_x] = 2i\sigma_y. \qquad (9.119)$$

A comparison with Eq. (9.114) shows that, apart from a factor $\frac{\hbar}{2}$, the Pauli spin matrices σ_x, σ_y, and σ_z follow the same commutation rules as the operators of the three angular momentum components J_x, J_y, and J_z. For completeness, we may also construct the matrix:

$$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2$$

$$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 3\mathbf{I}_2 \qquad (9.120)$$

with $\mathbf{I}_2$ the (2,2) unit matrix. It is obvious that each of the Pauli spin matrices commutes with the unit matrix. Thus, the commutation rule Eq. (9.115) also finds

its analogy in:

$$[\sigma^2, \sigma_z] = 0. \tag{9.121}$$

In **subproblem (b)**, we focus on the use of the Pauli spin matrices for the description of a quantum mechanical two-level system. This may describe, for example, a proton or an electron with spin $\frac{1}{2}$ in an external magnetic field. Depending on the orientation, the spin with regard to the magnetic field, the energy of the particle splits into two states (Zeeman effect). Two-level systems, however, are also important in spectroscopy for the treatment of the fundamental interaction between light and matter: absorption, emission, and induced emission (see Chap. 10). Here, the two-level system represents an atom or molecule with an initial state $|i\rangle$ and a final state $|f\rangle$, whereas the electromagnetic field is described in the model of a harmonic oscillator with quantum energy $\hbar\omega$ matching the energy difference between the states $|i\rangle$ and $|f\rangle$. In the literature, such a model is known as a Jaynes Cummings model. The latter makes use of Pauli spin matrices to describe the transitions of the two-level system. In the present problem, we consider the ground state denoted $|g\rangle$ and an excited state $|e\rangle$, as illustrated in Fig. 9.11. A general *mixed* state of the system is given according to Eq. (9.110) where the absolute values of the two complex numbers α and β give the probability of finding the system in the pure states $|e\rangle$ and $|g\rangle$ respectively. This two-level system can be represented mathematically by vectors where the ground and the excited state are given as:

$$|g\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \qquad |e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{9.122}$$
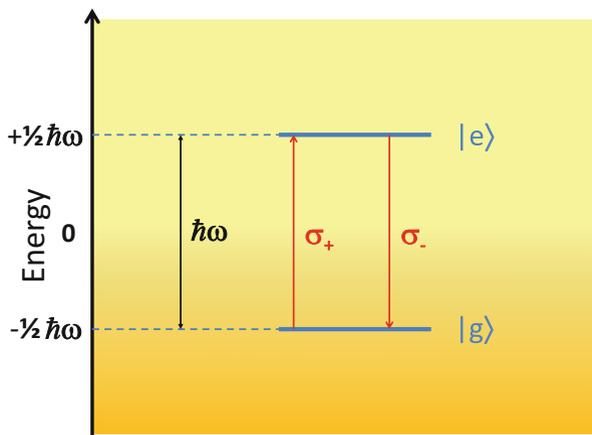

Fig. 9.11 A quantum mechanical two-level system of a ground and an excited state with an energy difference $\hbar\omega$. Ladder operators σ_+ and σ_- mediate transitions between the two states

Our task is to find ladder operators describing the transitions between these two states. According to the problem text, these ladder operators can be constructed from the Pauli spin matrices. There are two possibilities of finding these operators: guessing is of course possible for the student, with mathematical intuition. We follow the second, systematic way. Starting with σ_+, we assume that this operator can be written as a linear combination of the Pauli spin matrices:

$$\sigma_+ = a\sigma_x + b\sigma_y + c\sigma_z = \begin{pmatrix} c & a - ib \\ a + ib & -c \end{pmatrix} \tag{9.123}$$

According to Eq. (9.111), we can set up two equations to determine the coefficients a, b, and c:

$$\begin{pmatrix} c & a - ib \\ a + ib & -c \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} a - ib \\ -c \end{pmatrix} \overset{!}{=} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{9.124}$$

and

$$\begin{pmatrix} c & a - ib \\ a + ib & -c \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} c \\ a + ib \end{pmatrix} \overset{!}{=} \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{9.125}$$

From these equations, it is immediately clear that $c = 0$. For a and b we have two equations:

$$a - ib = 1 \tag{9.126}$$

and

$$a + ib = 0 \tag{9.127}$$

The addition of Eqs. (9.126) and (9.127) yields the result $a = \frac{1}{2}$, whereas subtraction gives $b = \frac{i}{2}$. We reinsert these values in Eq. (9.123) and obtain the result:

$$\sigma_+ = \frac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{9.128}$$

For the second ladder operator σ_- we can proceed in exactly the same way. The result is:

$$\sigma_- = \frac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{9.129}$$

In **subproblem (c)**, we examine the effect of σ_z on the states of the two-level system. We have:

$$\sigma_z|g\rangle = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -1|g\rangle \tag{9.130}$$

and

$$\sigma_z|e\rangle = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = +1|e\rangle \tag{9.131}$$

We can interpret this in the following way: in a two-level system with spin, σ_z projects out the spin orientation. In subproblem (a), we have seen that the Pauli matrices need to be multiplied by a factor of $\frac{\hbar}{2}$ to obtain the spin operators. Thus,

$$\hat{S}_z|-\tfrac{1}{2}\rangle = \frac{\hbar}{2}\sigma_z|-\tfrac{1}{2}\rangle = -\frac{\hbar}{2}|-\tfrac{1}{2}\rangle \tag{9.132}$$

and

$$\hat{S}_z|+\tfrac{1}{2}\rangle = \frac{\hbar}{2}\sigma_z|+\tfrac{1}{2}\rangle = \frac{\hbar}{2}|+\tfrac{1}{2}\rangle \tag{9.133}$$

In a general two-level system, σ_z can be used to determine the energy of the state. If the energy of the ground state is $-\frac{\hbar\omega}{2}$ and that of the excited state $+\frac{\hbar\omega}{2}$ (see Fig. 9.11), then the Hamiltonian of this system is apparently:

$$\hat{H} = \frac{\hbar\omega}{2}\sigma_z, \tag{9.134}$$

and

$$\hat{H}|g\rangle = -\frac{\hbar\omega}{2}|g\rangle; \quad \hat{H}|e\rangle = +\frac{\hbar\omega}{2}|e\rangle \tag{9.135}$$

In summary, we have seen how a special type of matrix as a concrete representation of operators can be used to describe transitions in a two-level system. We were able to formulate the Hamiltonian of such a system, which, as mentioned above, is the basis for the Jaynes Cummings model used in optics and spectroscopy.

Fig. 9.12 The model of an electron, which is free to move on a ring with a radius of r
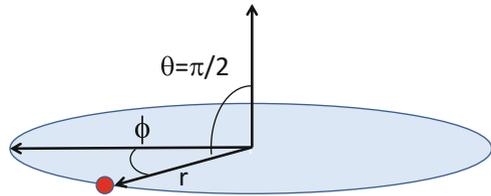
Problem 9.12 (Quantization: The Electron on a Ring)
An electron may freely move on a ring with a radius r (see Fig. 9.12). The Schrödinger equation for this problem is:

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2}\psi(\phi) = E\psi(\phi) \tag{9.136}$$

where the azimuthal angle ϕ characterizes the position of the electron.

a. Can you motivate Eq. (9.136)?
b. A general form of the wave function is

$$\psi(\phi) = A\,e^{iM\phi}. \tag{9.137}$$

   Show that Eq. (9.137) is a solution of Eq. (9.136).
c. Determine the constants A and M from the assumption that the wave function is normalized and unique, i.e., $\psi(\phi + 2\pi) = \psi(\phi)$. What is the relationship between the energy and M?

Solution 9.12 The electron on the ring is an instructive example of how quantization results as a consequence of boundary conditions. An application of this simple model to electronic excitations in the benzene molecule is shown below in Problem 9.13. In **subproblem (a)**, we derive the Schrödinger equation Eq. (9.136) for the wave function $\psi(\phi)$. As stated in the problem text, the electron moves freely, i.e., it moves in a constant potential that can be set to zero. The general form of the Schrödinger equation is thus:

$$-\frac{\hbar^2}{2m}\Delta\psi = E\psi. \tag{9.138}$$

As can be seen in Fig. 9.12, the azimuthal angle ϕ is the only degree of freedom left to the electron forced onto the ring. The movement of the electron is best described in spherical coordinates in which the Laplace operator in the general Schrödinger equation reads (see Eq. (A.68)):

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\phi^2} \tag{9.139}$$

We choose the origin of the coordinate system in the center of the ring, and we can assume that the ring plane is aligned to the equator $\theta = \frac{\pi}{2}$. Hence, $\sin \theta = 1$. Because θ and the radial coordinate r are constant, the first two terms in Eq. (9.139) are zero and the Laplacian reduces to:

$$\Delta = \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}.$$

Therefore, the Schrödinger equation for the electron on the ring is given by Eq. (9.136).

In **subproblem (b)**, we seek general solutions by inserting the ansatz $\psi(\phi) = Ae^{iM\phi}$ in Eq. (9.136). As

$$\frac{\partial \psi}{\partial \phi} = iMAe^{iM\phi} = iM\psi(\phi)$$

and therefore

$$\frac{\partial^2 \psi}{\partial \phi^2} = -M^2 Ae^{iM\phi} = -M^2 \psi(\phi),$$

we see that Eq. (9.137) satisfies Eq. (9.136):

$$\frac{\hbar^2 M^2}{2mr^2} \psi(\phi) = E\psi(\phi)$$

As a consequence, the energy of the electron is related to the parameter M via $E = \frac{\hbar^2 M^2}{2mr^2}$.

In **subproblem (c)**, we further narrow the wave function by applying suitable boundary conditions. The uniqueness of the wave function requires $\psi(\phi + 2\pi) = \psi(\phi)$, i.e., like the angle ϕ also the wave function must be periodic in multiples of 2π. Thus, $A\exp(iM\phi) \overset{!}{=} A\exp(iM\phi + 2\pi i)$ which is satisfied if M is integral. Therefore,

$$E = \frac{\hbar^2 M^2}{2mr^2}; \qquad M = 0, \pm 1, \pm 2, \ldots \tag{9.140}$$

A discrete spectrum of energy levels is a consequence of the special boundary conditions. Finally, we exploit the normalization condition. The total probability of finding the electron on the ring is 1. Therefore,

$$\int_0^{2\pi} \psi^\star \psi \, d\phi = \int_0^{2\pi} Ae^{-iM\phi} Ae^{iM\phi} \, d\phi = A^2 \int_0^{2\pi} d\phi = 2\pi A^2 \overset{!}{=} 1$$

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{iM\phi}; \qquad M = 0, \pm 1, \pm 2, \ldots \tag{9.141}$$
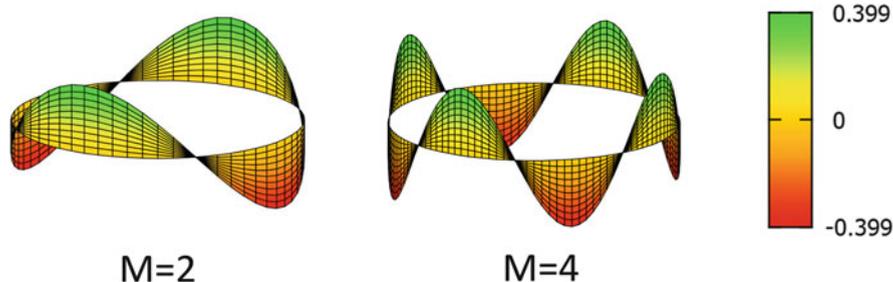
M=2   M=4

Fig. 9.13 Illustration of the solutions for the electron on the ring in a quantum mechanical treatment. The real part of the complex wave functions is shown for the quantum numbers $M = 2$ and $M = 4$

The real part of the complex wave function is illustrated in Fig. 9.13 for $M = 2$ and $M = 4$. Note that according to Eq. (9.141) the ground state wave function ($M = 0$) has a constant value across the ring, whereas excited states exhibit a harmonic behavior, where the number of full oscillations across the ring is an integer.

Problem 9.13 (Electronic Excitation of the Benzene Molecule)
Hint: This problem assumes that you have dealt with Problem 9.12.
    The electron on the ring (Problem 9.12) is a simple model system for the six delocalized π electrons in the benzene molecule C_6H_6. Assume a ring radius of 140 pm.

a. Calculate the energies of the states $M = 0, \pm1, \pm2$ and make a term diagram.
b. Distribute the six π electrons for the collective ground state. Assume that empty states with the lowest energy are occupied and the maximum occupation of a state with quantum number M is 2.
c. What is the configuration for the first collective excited state? Calculate the excitation energy from the ground state. Compare your results with the spectroscopic result, according to which the transition from the electronic ground state to the first excited state of benzene is observed at a wave length of 253 nm.

Solution 9.13 Electronic excitations involving delocalized π-electrons, so-called $\pi \to \pi^*$ transitions, are highly important in relation to **chromophores**, i.e., groups of atoms within a material responsible for its color. Benzene (Fig. 9.14) is one of the prime examples of a molecule with delocalized π electrons. In this problem, we apply the simple model of the electron on the ring (Problem 9.12) to the electronic properties of this molecule. We assume that the six π electrons of benzene move independently from each other across the ring. Moreover, any interaction with
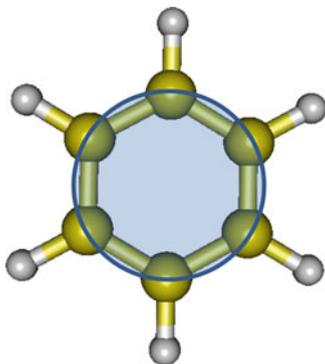
Fig. 9.14 The benzene molecule C_6H_6 with its cyclic structure. The six π electrons are delocalized over the hexagonal ring. The radius of the ring (*blue*) is approximately identical to the carbon-carbon distance of 140 pm
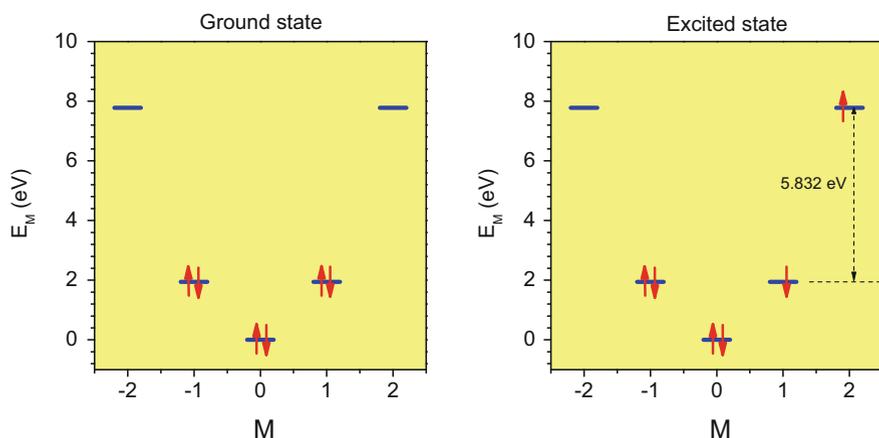

Fig. 9.15 Term scheme characterizing the electronic states of benzene. The *arrows* pointing upward and downward represent π-electrons with opposite spin

atomic cores is neglected altogether. The crudeness of this approximation has the advantage of simplicity.

In **subproblem (a)**, we model the electronic ground state by distributing the six π electrons on the one electron state resulting from Eq. (9.140). With the mass of the electron $m = 9.10939 \times 10^{-31}$ kg, $r = 1.4 \times 10^{-10}$ m and $\hbar = 1.054572 \times 10^{-34}$ J s we obtain:

$$E_M = M^2 \times 1.944 \, \text{eV}$$

The resulting energy for $M = 0$ is thus 0 eV, for $M = \pm 1$ it is $E_{\pm 1} = 1.944$ eV, and for $M = \pm 2$ it is $E_{\pm 2} = 7.776$ eV. These energy levels are outlined in Fig. 9.15.

Based on the one-electron states characterized by the quantum number M, we now construct the configuration for the electronic ground state in **subproblem (b)**. As the ground state has the lowest total energy, we occupy the lowest levels first. Taking account of the Pauli principle, only two electrons with opposite spin orientation can occupy one state of quantum number M. Therefore, as illustrated in the left diagram in Fig. 9.15, the ground state configuration is characterized by filled levels of $M = 0$ and $M = \pm 1$.

In **subproblem (c)**, we consider the first excited state. The latter is reached if one electron from a state $M = \pm 1$ is removed and brought into a state with $M = \pm 2$, as shown in the right-hand diagram of Fig. 9.15. In our approximation of non-interacting electrons, we can assume that the energy difference between the excited state and the ground state is simply the difference between the levels $M = \pm 1$ and $M = \pm 2$, which is the excitation energy

$$E_{\text{ex}} = \frac{\hbar^2}{2mr^2} \left(2^2 - 1^2\right) = \frac{3\hbar^2}{2mr^2} = 5.832 \, \text{eV}.$$

The transition can be mediated by a photon of wave length $\lambda = \frac{hc}{E_{\text{ex}}} = 213 \, \text{nm}$. This result is quite close to the experimental value of 253 nm within the ultraviolet spectral range. We conclude that, despite its simplicity, the model of the electron on the ring predicts the correct order of magnitude for the electronic excitation of the benzene molecule. Analogous models exist for chain-like molecules containing delocalized π-electrons, such as the butadiene molecule. In this case, the simple quantum mechanical model is the particle in a one-dimensional box. A practical application of ultraviolet spectroscopy is discussed in Problem 10.3.

Problem 9.14 (Hydrogen 1s Wave Function)

a. Show that the ground state wave function of the hydrogen atom,

$$\psi_{n=1, l=0}(r, \theta, \phi) = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} \exp\left(-\frac{r}{a_0}\right), \tag{9.142}$$

is normalized.
b. Calculate the expectation value of the radial coordinate r of the electron in its ground state.
c. Calculate the probability that the electron is located within a sphere of radius 10^{-15} m; in other words, the probability of finding the electron in the hydrogen nucleus.

Solution 9.14 This problem is a straightforward application of quantum mechanical rules and integration. We deal with the ground state solution of the hydrogen problem and prove in **subproblem (a)** that the 1s wave function is normalized, i.e.,

we must show that:

$$\int |\psi_{n=1,l=0}(r,\theta,\phi)|^2 dV = 1 \tag{9.143}$$

In spherical coordinates (see Sect. A.3.11 in the Appendix), the integral is:

$$\int_{r=0}^{\infty} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a_0^3} \underbrace{\int_{r=0}^{\infty} r^2 \exp\left(-\frac{2r}{a_0}\right) dr}_{\frac{a_0^3}{4}, \text{ see Eq. (A.45)}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{2} = 1$$

Thus, the 1s wave function is indeed normalized.

In **subproblem (b)**, we calculate the expectation value for the radial coordinate in this state (see postulate 6 in Sect. 9.1.2.1),

$$\langle r \rangle = \int \psi_{1s}^* r \psi_{1s} \, dV. \tag{9.144}$$

The definite integral Eq. (A.45), $\int_0^\infty x^n e^{-ax} = \frac{n!}{a^{n+1}}$ can be used for the calculation of integrals with arbitrary powers of the radial coordinate. The integration over the angles yields the same result as in subproblem (a). Hence,

$$\langle r \rangle = \frac{4\pi}{\pi a_0^3} \int_0^\infty r^3 \exp\left(-\frac{2r}{a_0}\right) = \frac{4}{a_0^3} \frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{3}{2} a_0 \tag{9.145}$$

This result may look astonishing at first sight. We must not confuse it with the *most probable* radius of the electron, which is given by the maximum of the probability density function $w(r) = |\psi_{1s}|^2 r^2$ shown in Fig. 9.16. Its maximum is at $r = a_0$, i.e., the most probable distance of the electron in the ground state is identical to the Bohr radius. The expectation value for r we have just computed is at $1.5a_0$. As can be seen in Fig. 9.16, the probability density decreases steeply for large distances, and also for small distances of the electron from the nucleus. In **subproblem (c)**, we calculate the probability of finding the electron within the nucleus. The notion of finding the electron in the nucleus may seem strange at first. However, such a calculation is of importance for the estimation of the probability of a certain type of elementary particle reaction predicted in the year 1935 by Hideki Yukawa:

$$\mathrm{p} + \mathrm{e}^- \rightarrow \mathrm{n} + \nu_e \tag{9.146}$$

Fig. 9.16 Probability density function of the radial coordinate in the 1s ground state of the hydrogen atom. The maximum and thus the most probable distance of the electron is at $r = a_0 \approx 0.529 \times 10^{-10}$ m. The *red line* marks the expectation value calculated in subproblem (b)
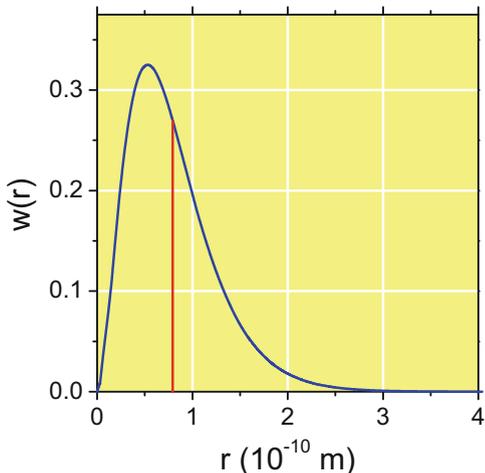
The so-called K-capture of some isotopes such as $^{37}_{18}$Ar is the reaction of an electron of the electron shell (most likely the K-shell) with a proton of the nucleus, converting the latter into a neutron and an electron neutrino ν_e. Therefore, what is the probability of finding the electron within the hydrogen nucleus? We assume a radius of the nucleus of $r_N = 10^{-15}$ m. Obviously, this probability is:

$$p = \int_{r=0}^{r_N} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right) r^2 \sin\theta \, dr \, d\theta \, d\phi \qquad (9.147)$$

The difference from our calculation in subproblem (a) is that we have to integrate from $r = 0$ to $r = r_N$. From the integral table in the Appendix we use Eq. (A.44) and obtain:

$$p = \frac{4\pi}{\pi a_0^3} \int_0^{r_N} r^2 \exp\left(-\frac{2r}{a_0}\right) dr$$

$$= \frac{4}{a_0^3} \left[\exp\left(-\frac{2r}{a_0}\right) \left(-\frac{a_0 r^2}{2} - \frac{2r a_0^2}{4} - \frac{2a_0^3}{8}\right) \right]_0^{r_N}$$

$$= \exp\left(-\frac{2r_N}{a_0}\right) \left(-\frac{2r_N^2}{a_0^2} - \frac{2r_N}{a_0} - 1\right) - (-1)$$

$$= 1 - e^{-2\left(\frac{r_N}{a_0}\right)} \left(1 + 2\left(\frac{r_N}{a_0}\right) + 2\left(\frac{r_N}{a_0}\right)^2\right) = 9 \times 10^{-15} \qquad (9.148)$$

Hence, the probability of finding the electron within the nucleus is only about 10^{-14}. Given one mole of hydrogen atoms, there are, nevertheless, about 6 billion atoms in which the electron is located within the nucleus.
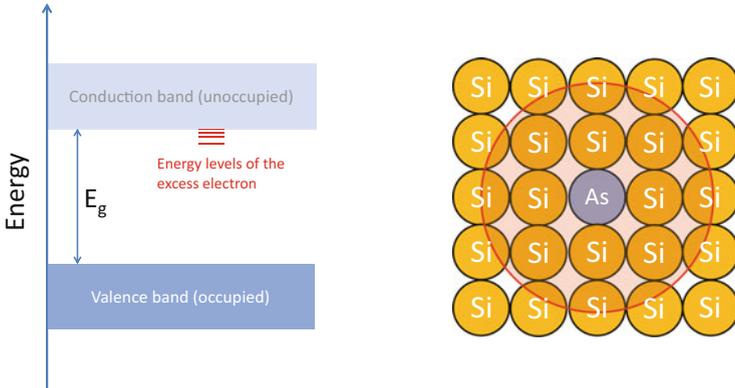
Fig. 9.17 *Left*: Band model of n-doped silicon. *Right*: Incorporation of arsenic into a silicon crystal lattice (schematic)

Problem 9.15 (Hydrogen   Problem   Applied   to   Semiconductor Technology)

The properties of pure and doped silicon are of high importance in semiconductor technology. Silicon is a semiconductor with a *band gap* of $1.12\,\text{eV}$ between the valence band and the conduction band. At room temperature, the electric conductivity of silicon is weak. Why? To increase its conductivity, arsenic (n-doping) or boron (p-doping) is incorporated into the silicon crystal (see Fig. 9.17). Arsenic has an excess valence electron that can be approximately treated using a modified hydrogen problem.

a. Calculate the three lowest energies of the excess electron. Assume an *effective mass m** $= 0.3\,m_e$ of this electron and a dielectric constant of $\epsilon = 11.7$ for the surrounding medium silicon. Calculate the ionization energy of this excess electron. Explain why n-doped silicon has considerably increased room-temperature conductivity.

b. What is the distance to the excess electron from the arsenic core? How many Si atoms are within the sphere, defined by the Bohr radius of the excess electron? The density of silicon is $2.34\,\text{g}\,\text{cm}^{-3}$.

c. The above description can only be realistic for small concentrations of As, i.e., if a mutual interaction between defects can be neglected. Estimate a critical As concentration above which the electron orbits of neighboring As defects penetrate each other. Using the band structure of silicon, can you explain the consequences for the defect states?

Solution 9.15 This exercise includes an adaption of Bohr's atom model to a special problem in semiconductor physics. We characterize the spectrum of energy levels of

an n-doped Si crystal. Such a simple treatment already provides essential features without becoming too involved in the details of solid state physics. Silicon is a semiconductor, i.e., under ambient conditions it is neither an electric insulator nor is it a real conductor. The reason for this can be explained using a simplified band model as shown in Fig. 9.17 (left-hand diagram). Electric conduction requires free charge carriers in the conduction band. To excite an electron from the filled valence band to the conduction band, however, the energy of the *band gap* $E_g = 1.12\,\text{eV}$ is needed at least. At room temperature, the thermal energy $k_B T$ is only 26 meV. Hence, a thermal excitation is unlikely and free charge carriers are not available under room temperature conditions.

In **subproblem (a)** we consider an isolated arsenic atom embedded in the silicon crystal lattice. The latter is described as a continuum with a dielectric constant of $\epsilon = 11.7$. Compared with silicon with electron configuration [Ne]$3s^2 3p^2$, arsenic with electron configuration [Ar]$4s^2 4p^3$ has an excess valence electron. We treat this excess electron using the hydrogen problem (Eq. (9.21)) with the following modifications: (1) we assume an effective charge of the ion core[12] of $Z_{\text{eff}} e = 1e$. (2) we assume an *effective mass*[13] of the excess electron $m^* = 0.3$. Taken together, the modified Rydberg formula for the energy levels of the excess electron is:

$$E_n = -\frac{m^* e^4}{8\epsilon^2 \epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{0.3}{\epsilon^2} \frac{\text{Ry}}{n^2}; \qquad n = 1, 2, \ldots \qquad (9.149)$$

with Ry being 13.606 eV (see Eq. (9.22)). The first three energy levels are thus $E_1 = -29.8\,\text{meV}$, $E_2 = -7.5\,\text{meV}$, $E_3 = -3.3\,\text{meV}$ relative to the lower edge of the conduction band. Note that ionization of the arsenic atom ($n \to \infty$) causes the generation of one free charge carrier. The ionization energy for this process is just thus 29.8 meV, which is close to the thermal energy at room temperature. As a consequence, according to this simple model, doping of silicon crystals with arsenic increases its room temperature conductivity.

In **subproblem (b)**, we scrutinize the plausibility of the model. Bohr's formula for the radius of the electron orbit according to the above modifications is:

$$r_n = \frac{4\pi\epsilon\epsilon_0 \hbar^2}{m^* e^2} n^2 = \frac{\epsilon}{0.3} \frac{4\pi\epsilon_0 \hbar^2}{e^2} n^2 = \frac{\epsilon}{0.3} a_0 n^2 \qquad n = 1, 2, \ldots \qquad (9.150)$$

with $a_0 = 0.5292 \times 10^{-10}$ m. The radius r_1 of the excess electron in its ground state is thus 21×10^{-8} cm. A sphere with this radius has a volume of $V = \frac{4\pi}{3} r_1^3 = $

---

[12] See also Problem 9.5, where, for the lithium atom, we estimated an effective charge of 1.26 based on the experimental value of the ionization energy.

[13] The justification of an effective mass in solid state physics is based on the fact that the motion of an electron in the crystal is not free. While maintaining the expression for the kinetic energy, $E_{\text{kin}} = \frac{\hbar^2 k^2}{2m^*}$, the effective mass can be derived from the curvature of electron bands at special points in the crystal's reciprocal k-space.

$3.9 \times 10^{-20} \, \text{cm}^3$. Using the given density of $\rho = 2.34 \, \text{g cm}^{-3}$ and the molar mass of silicon $M_{\text{Si}} = 28.09 \, \text{g mol}^{-1}$, the number of silicon atoms within this sphere is $\frac{N_A \rho V}{M_{\text{Si}}} \approx 2000$. Hence, the continuum treatment of the silicon crystal as a dielectricum seems plausible.

Finally, in **subproblem (c)**, we consider the case in which the arsenic defects are no longer isolated. In our simple model, we estimate the critical concentration of arsenic atoms where the orbits of the excess electrons penetrate each other. If we consider a cube with an edge length $2r_1 = 42 \times 10^{-8}$ cm, the orbits of neighboring arsenic defects would touch each other. This cube has a volume of $(2r_1)^3 = 7.4 \times 10^{-20} \, \text{cm}^3$ with one arsenic defect at each of its corners, contributing $\frac{1}{8}$ of its sphere. Hence, within such a cube, there is $8 \times \frac{1}{8} = 1$ arsenic defect and the critical defect density is thus:

$$\mathcal{N}_{\text{crit.}} = \frac{1}{(2r_1)^3} = 1.3 \times 10^{19} \, \text{cm}^{-3}. \tag{9.151}$$

The consequences for the band structure are shown in Fig. 9.18. Although the energy levels of isolated excess electrons are sharply defined, the mutual perturbation of neighboring defects leads to a splitting of these levels into a quasi-continuum of possible defect states and thus the formation of a *band tail* located beneath the lower edge of the conduction band.

Problem 9.16 (Variational Method)
According to the variational principle, an estimation E_0 of the ground state energy of a system characterized by its Hamiltonian $\hat{H}$ can be obtained by a minimization of the energy functional
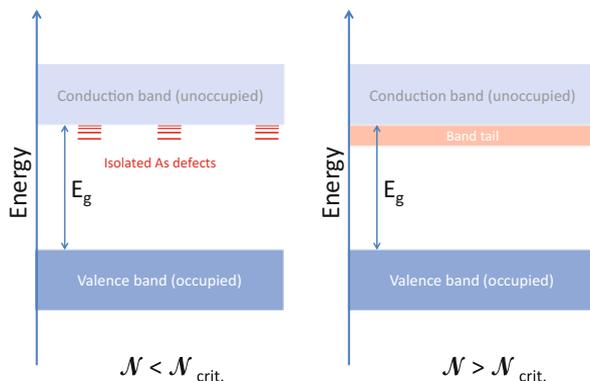
(continued)

Fig. 9.18 Effect of defect concentration on the band structure (schematic)

Problem 9.16 (continued)

$$\bar{H} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \overset{!}{=} \text{min.} \tag{9.152}$$

$|\psi\rangle$ is an appropriate test function depending on one or more optimization parameters that are varied during the minimization process. With this test function $E_0 = \bar{H}$ is the best approximation of the ground state energy that can be obtained.

a. Consider the Hamiltonian of the hydrogen atom and use the Gaussian function

$$\psi(r) = N e^{-\alpha r^2} \tag{9.153}$$

with the normalization constant N and the variational parameter α as a test function to determine E_0 as an estimation of the ground state energy. Compare your result with the exact ground state energy. *Hint: It is convenient to introduce atomic units.*

b. Repeat the calculation with the two-parameter function

$$\psi(r) = c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \tag{9.154}$$

where $\alpha_1 = 2.87$ and $\alpha_2 = 0.28$ are fixed exponents and c_1 and c_2 are the variational parameters. *Hints: Write the energy functional in the form*

$$\bar{H} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}} = \frac{N}{D}, \tag{9.155}$$

Transform the equations for the minimum condition in a system of equations for the coefficients c_1 and c_2. Exploit the condition that the denominator D is 1 if ψ is normalized.

Solution 9.16 In this exercise, we deal with approximative methods for the solution of the time-independent Schrödinger equation. The variational principle is the basis of many methods in quantum chemistry. Concepts such as the effective charge we have dealt with in Problem 9.5 may be quite useful. However, there is no systematic way of improving the results. Of high value in atomic and molecular structure theory are concepts that may be systematically improved – even if the improvement leads to an increase in computational costs. Starting from a suitable test function with one or more adjustable parameters, the energy functional $\bar{H}$ is calculated and minimized by variation of the parameter set. The minimum provides the best estimation for the ground state energy with the chosen test function. Here, we apply a method to the hydrogen atom, a system for which we know the exact result of the ground

state energy, the negative Rydberg constant (see Eq. (9.22)), or $E_{\text{exact}} = -0.5\,E_h$ in atomic units.

In **subproblem (a)**, we consider a single Gaussian to be a test function given in Eq. (9.153). At first sight, it may seem artificial to treat the hydrogen problem using a Gaussian function. However, because of their properties, Gaussian functions are widely used in quantum chemistry to construct wave functions. Hence, our problem is instructive. We start by writing down the Hamiltonian of the hydrogen problem. In the ground state (1s state, $l = 0$), the effective Hamiltonian in atomic units (Sect. 9.1.4) is:

$$\hat{H} = \underbrace{-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)}_{\hat{T}} \underbrace{-\frac{1}{r}}_{V} \tag{9.156}$$

where $\hat{T}$ is the operator of the kinetic energy of the electron. V is its potential energy, i.e., the attractive Coulomb potential with the core. Our goal is to calculate Eq. (9.152). We start with the denominator, where we assume that our test function is normalized (see Problem 9.14), i.e.

$$\langle \psi | \psi \rangle = 4\pi \int_0^\infty N e^{-\alpha r^2} N e^{-\alpha r^2} \, r^2 dr \overset{!}{=} 1 \tag{9.157}$$

Thus,

$$\langle \psi | \psi \rangle = 4\pi N^2 \int_0^\infty e^{-2\alpha r^2} \, r^2 dr \overset{\text{Eq. (A.49)}}{=} 4\pi N^2 \frac{1}{4}\sqrt{\frac{\pi}{(2\alpha)^3}} = 1 \tag{9.158}$$

and the normalization constant is therefore:

$$N^2 = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}}. \tag{9.159}$$

The numerator splits into two parts, one with the kinetic energy, and one with the potential energy:

$$\bar{H} = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | V | \psi \rangle \tag{9.160}$$

The second term is:

$$
\begin{aligned}
\langle \psi | V | \psi \rangle &= -4\pi \int_0^\infty N e^{-\alpha r^2} \frac{1}{r} N e^{-\alpha r^2} \, r^2 dr \\
&= -\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} 4\pi \int_0^\infty e^{-2\alpha r^2} \, r\, dr \\
&\overset{\text{Eq. (A.48)}}{=} -\left(\frac{8\alpha}{\pi}\right)^{\frac{1}{2}}.
\end{aligned} \tag{9.161}
$$

Because

$$\frac{\partial}{\partial r}e^{-\alpha r^2} = -2\alpha r e^{-\alpha r^2} \tag{9.162}$$

and

$$\frac{\partial^2}{\partial r^2}e^{-\alpha r^2} = \frac{\partial}{\partial r}\left(-2\alpha e^{-\alpha r^2}\right) = \left(4\alpha^2 r^2 - 2\alpha\right)e^{-\alpha r^2} \tag{9.163}$$

the kinetic energy term is:

$$\langle\psi|\hat{T}|\psi\rangle = 4\pi \int_0^\infty Ne^{-\alpha r^2}\left(-2\alpha^2 r^2 + \alpha + 2\alpha\right)Ne^{-\alpha r^2}\,r^2\,dr$$

$$= \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} 4\pi \left[-2\alpha \underbrace{\int_0^\infty e^{-2\alpha r^2}r^4\,dr}_{\frac{3}{8}\sqrt{\frac{\pi}{(2\alpha)^5}}} + 3\alpha \underbrace{\int_0^\infty e^{-2\alpha r^2}r^2\,dr}_{=\frac{1}{4}\sqrt{\frac{\pi}{(2\alpha)^3}}}\right] \tag{9.164}$$

where we have again used the integral table in the Appendix (Eq. (A.49)). This expression reduces to:

$$\langle\psi|\hat{T}|\psi\rangle = -\frac{3\alpha}{2} + 3\alpha = \frac{3\alpha}{2} \tag{9.165}$$

Using Eqs. (9.160), (9.161), and (9.165), we obtain the expression for the energy functional:

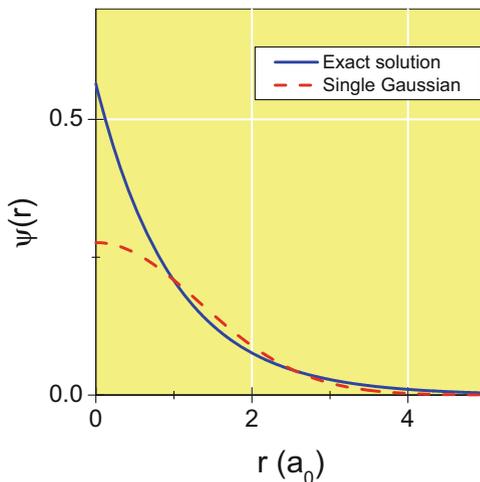$$\bar{H} = \frac{3}{2}\alpha - \left(\frac{8\alpha}{\pi}\right)^{\frac{1}{2}} \tag{9.166}$$

Now, we can minimize the functional by setting the first derivative to zero:

$$\frac{\partial\bar{H}}{\partial\alpha} = \frac{3}{2} - \frac{1}{2}\left(\frac{8}{\pi}\right)^{\frac{1}{2}}\alpha_{\min}^{-\frac{1}{2}} \overset{!}{=} 0 \tag{9.167}$$

Solving for $\alpha_{\min}$, we obtain:

$$\alpha_{\min} = \frac{8}{9\pi} = 0.2829 \tag{9.168}$$

Fig. 9.19 Comparison
between the exact 1s wave
function of the hydrogen
atom (*solid line*) and a
Gaussian test function with
exponent $\alpha = 0.2829$
(*dashed line*)

Reinserting the optimal exponent into Eq. (9.166), we obtain an estimation of the ground state energy:

$$E_0 = -\frac{4}{3\pi} = -0.4244\,E_h = -11.51\,\text{eV}. \tag{9.169}$$

The use of a single Gaussian as a test function reaches about 85% of the true ground state energy E_{exact}. The optimized test function is shown in Fig. 9.19 together with the exact ground state wave function.[14] Both functions are quite different, both in the core region and at larger distances from the core, where the exact wave function decays more rapidly than the Gaussian function. As mentioned above, the variational principle offers the possibility of arriving at an improved result if we use a more flexible test function. This is examined in **subproblem (b)**, which, however, is quite tedious. Our test function has now two fixed primitive Gaussian functions. The exponent $\alpha_2 = 0.28$ is essentially the optimal value obtained in subproblem (a), whereas the Gaussian function with $\alpha_1 = 2.87$ is more pronounced in the near-core region. We begin by constructing the energy functional, which should be written in

---

[14]We have dealt with the exact solution in Problem 9.14 on page 257. In the literature, atomic orbital functions with exponential decay in the region far from the core are also called Slater functions.

the form given in Eq. (9.155). Using Eq. (9.154) the denominator is:

$$
\begin{aligned}
\langle \psi | \psi \rangle &= 4\pi \int_0^\infty \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) r^2 \, dr \\
&= 4\pi \left[c_1^2 \int_0^\infty e^{-2\alpha_1 r^2} r^2 \, dr + 2c_1 c_2 \int_0^\infty e^{-(\alpha_1+\alpha_2) r^2} r^2 \, dr \right. \\
&\quad \left. + c_2^2 \int_0^\infty e^{-2\alpha_2 r^2} r^2 \, dr \right] \\
&\overset{\text{Eq. (A.49)}}{=} 4\pi \left[c_1^2 \frac{1}{4} \sqrt{\frac{\pi}{(2\alpha_1)^3}} + 2c_1 c_2 \frac{1}{4} \sqrt{\frac{\pi}{(\alpha_1+\alpha_2)^3}} + c_2^2 \frac{1}{4} \sqrt{\frac{\pi}{(2\alpha_2)^3}} \right] \\
&= c_1^2 \left(\frac{\pi}{2\alpha_1} \right)^{\frac{3}{2}} + 2c_1 c_2 \left(\frac{\pi}{\alpha_1+\alpha_2} \right)^{\frac{3}{2}} + c_2^2 \left(\frac{\pi}{2\alpha_2} \right)^{\frac{3}{2}} \\
&= c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22} \tag{9.170}
\end{aligned}
$$

The coefficients S_{11}, S_{12}, and S_{22} depend only on the given exponents $\alpha_1 = 2.87$ and $\alpha_2 = 0.28$. Their values are $S_{11} = 0.40491$, $S_{12} = 0.99600$, and $S_{22} = 13.28749$. Later, we exploit the fact that the expression Eq. (9.170), which is the norm of the test wave function, is unity. The numerator of the energy functional $\langle \psi | \hat{H} | \psi \rangle$ consists of two terms, the kinetic energy and the potential energy. For the latter, we have:

$$
\begin{aligned}
\langle \psi | V | \psi \rangle &= 4\pi \int_0^\infty \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) \left(-\frac{1}{r} \right) \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) r^2 \, dr \\
&= -4\pi \left[c_1^2 \int_0^\infty e^{-2\alpha_1 r^2} r \, dr + 2c_1 c_2 \int_0^\infty e^{-(\alpha_1+\alpha_2) r^2} r \, dr \right. \\
&\quad \left. + c_2^2 \int_0^\infty e^{-2\alpha_2 r^2} r \, dr \right] \\
&\overset{\text{Eq. (A.48)}}{=} -4\pi \left[c_1^2 \frac{1}{4\alpha_1} + 2c_1 c_2 \frac{1}{2(\alpha_1+\alpha_2)} + c_2^2 \frac{1}{4\alpha_2} \right] \\
&= -\left[c_1^2 \frac{\pi}{\alpha_1} + 2c_1 c_2 \frac{2\pi}{(\alpha_1+\alpha_2)} + c_2^2 \frac{\pi}{\alpha_2} \right] \\
&= c_1^2 V_{11} + 2c_1 c_2 V_{12} + c_2^2 V_{22} \tag{9.171}
\end{aligned}
$$

where $V_{11} = -1.09463$, $V_{12} = -1.99466$, and $V_{22} = -11.21997$ respectively. The kinetic energy term is:

$$
\langle \psi | \hat{T} | \psi \rangle = 4\pi \int_0^\infty \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) \left(-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} \right) \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) r^2 \, dr
$$

$$
= 4\pi \int_0^\infty \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) \left(-2\alpha_1^2 r^2 + 3\alpha_1 \right) c_1 e^{-\alpha_1 r^2} r^2 \, dr
$$

$$
+ 4\pi \int_0^\infty \left(c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} \right) \left(-2\alpha_2^2 r^2 + 3\alpha_2 \right) c_2 e^{-\alpha_2 r^2} r^2 \, dr \qquad (9.172)
$$

Here, we have made use of Eqs. (9.162) and (9.163). Further evaluation yields:

$$
\langle \psi | \hat{T} | \psi \rangle = 4\pi c_1^2 \left[-2\alpha_1^2 \int_0^\infty e^{-2\alpha_1 r^2} r^4 \, dr + 3\alpha_1 \int_0^\infty e^{-2\alpha_1 r^2} r^2 \, dr \right]
$$

$$
+ 4\pi c_1 c_2 \left[-2 \left(\alpha_1^2 + \alpha_2^2 \right) \int_0^\infty e^{-(\alpha_1 + \alpha_2) r^2} r^4 \, dr \right.
$$

$$
\left. + 3 \left(\alpha_1 + \alpha_2 \right) \int_0^\infty e^{-(\alpha_1 + \alpha_2) r^2} r^2 \, dr \right]
$$

$$
+ 4\pi c_2^2 \left[-2\alpha_2^2 \int_0^\infty e^{-2\alpha_2 r^2} r^4 \, dr + 3\alpha_2 \int_0^\infty e^{-2\alpha_2 r^2} r^2 \, dr \right] \qquad (9.173)
$$

The integrals are again evaluated using Eq. (A.49) in the Appendix:

$$
\langle \psi | \hat{T} | \psi \rangle = 4\pi c_1^2 \left[-2\alpha_1^2 \frac{3}{8} \sqrt{\frac{\pi}{(2\alpha_1)^5}} + 3\alpha_1 \frac{1}{4} \sqrt{\frac{\pi}{(2\alpha_1)^3}} \right]
$$

$$
+ 4\pi c_1 c_2 \left[-2 \left(\alpha_1^2 + \alpha_2^2 \right) \frac{3}{8} \sqrt{\frac{\pi}{(\alpha_1 + \alpha_2)^5}} + 3 \left(\alpha_1 + \alpha_2 \right) \frac{1}{4} \sqrt{\frac{\pi}{(\alpha_1 + \alpha_2)^3}} \right]
$$

$$
+ 4\pi c_2^2 \left[-2\alpha_2^2 \frac{3}{8} \sqrt{\frac{\pi}{(2\alpha_2)^5}} + 3\alpha_2 \frac{1}{4} \sqrt{\frac{\pi}{(2\alpha_2)^3}} \right] \qquad (9.174)
$$

If we introduce

$$
\langle \psi | \hat{T} | \psi \rangle = c_1^2 T_{11} + 2 c_1 c_2 T_{12} + c_2^2 T_{22} \qquad (9.175)
$$

then the coefficients are

$$T_{11} = \frac{3}{2} \left(\frac{\pi^3}{8\alpha_1} \right)^{\frac{1}{2}} = 1.74313 \tag{9.176}$$

$$T_{12} = \frac{3\pi}{2} \left(\sqrt{\frac{\pi}{\alpha_1 + \alpha_2}} - (\alpha_1^2 + \alpha_2^2) \sqrt{\frac{\pi}{(\alpha_1 + \alpha_2)^5}} \right) = 0.76227 \tag{9.177}$$

$$T_{22} = \frac{3}{2} \left(\frac{\pi^3}{8\alpha_2} \right)^{\frac{1}{2}} = 5.58074 \tag{9.178}$$

The numerator of the energy functional is thus:

$$\langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | V | \psi \rangle$$
$$= c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22} \tag{9.179}$$

where $H_{11} = 0.64850$, $H_{12} = -1.23239$, and $H_{22} = -5.63923$. We have now constructed the energy functional in the form Eq. (9.155). In the next step, $\bar{H}$ must be minimized by variation of the coefficients c_1 and c_2, i.e., by taking the derivatives with regard to c_1 and c_2:

$$\frac{\partial \bar{H}}{\partial c_1} \stackrel{!}{=} 0; \qquad \frac{\partial \bar{H}}{\partial c_2} \stackrel{!}{=} 0 \tag{9.180}$$

A direct evaluation of the resulting equations is tedious, because they can barely be solved for these coefficients. If we consider N as the numerator of the energy functional and D as its denominator, we use the product rule:

$$\frac{\partial \bar{H}}{\partial c_1} = \frac{\partial}{\partial c_1} \frac{N}{D} = \frac{D \frac{\partial N}{\partial c_1} - N \frac{\partial D}{\partial c_1}}{D^2} \tag{9.181}$$

The denominator is nonzero. Thus,

$$\frac{\partial \bar{H}}{\partial c_1} \stackrel{!}{=} 0 \Leftrightarrow D \frac{\partial N}{\partial c_1} - N \frac{\partial D}{\partial c_1} = 0 \Leftrightarrow \frac{\partial N}{\partial c_1} - \bar{H} \frac{\partial D}{\partial c_1} = 0 \tag{9.182}$$

With

$$\frac{\partial N}{\partial c_1} = 2c_1 H_{11} + 2c_2 H_{12}; \qquad \frac{\partial D}{\partial c_1} = 2c_1 S_{11} + 2c_2 S_{12}$$

we obtain the equation

$$\left(H_{11} - \bar{H} S_{11} \right) c_1 + \left(H_{12} - \bar{H} S_{12} \right) c_2 = 0 \tag{9.183}$$

By taking the derivative with regard to c_2, we obtain:

$$\left(H_{22} - \bar{H}S_{22}\right) c_2 + \left(H_{12} - \bar{H}S_{12}\right) c_1 = 0. \tag{9.184}$$

These equations constitute a system of equations for the coefficients c_1 and c_2:

$$\begin{pmatrix} H_{11} - \bar{H}S_{11} & H_{12} - \bar{H}S_{12} \\ H_{12} - \bar{H}S_{12} & H_{22} - \bar{H}S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{9.185}$$

Nontrivial solutions are obtained if the secular determinant is zero:

$$\begin{vmatrix} H_{11} - \bar{H}S_{11} & H_{12} - \bar{H}S_{12} \\ H_{12} - \bar{H}S_{12} & H_{22} - \bar{H}S_{22} \end{vmatrix} = \left(H_{11} - \bar{H}S_{11}\right)\left(H_{22} - \bar{H}S_{22}\right) - \left(H_{12} - \bar{H}S_{12}\right)^2 = 0 \tag{9.186}$$

This is a quadratic equation for the energy functional $\bar{H}$ with the two roots:

$$\bar{H}_{1,2} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \tag{9.187}$$

where $A = S_{11}S_{22} - S_{12}^2$, $B = 2H_{12}S_{12} - H_{11}S_{22} - H_{22}S_{11}$, and $C = H_{11}H_{22} - H_{12}^2$. The two roots are $\bar{H}_1 = 2.47862 \, E_h$, and $\bar{H}_2 = -0.47586 \, E_h$. The first root apparently corresponds to a maximum energy, the second to the minimum energy sought. If we compare it with the result from subproblem (a), $-0.4244 \, E_h$, we conclude that the addition of a second Gaussian improves the estimate for the ground state energy to about 95% of the exact result, $-0.5 \, E_h$. The results are summarized in Table 9.2.

Having obtained the optimal value for $\bar{H}$, our next goal is the determination of the variational parameters c_1 and c_2 for the negative solution. We insert $\bar{H}_2$ in Eq. (9.183). This yields:

$$c_2 = -\frac{H_{11} - \bar{H}_2 S_{11}}{H_{12} - \bar{H}_2 S_{12}} c_1 \tag{9.188}$$

The second condition is the normalization of the test wave function:

$$c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22} \stackrel{!}{=} 1 \tag{9.189}$$

Table 9.2 Estimated ground state energies of the hydrogen problem based on the variational principle in comparison with the exact result

Wave function	1 Gaussian	2 Gaussians	Exact (Slater function)
E_0 (Hartree units)	-0.4244	-0.4759	-0.50

Fig. 9.20 Comparison of the exact 1s wave function of the hydrogen atom (*solid line*) with the optimized test functions with two Gaussian functions (*dashed line*)
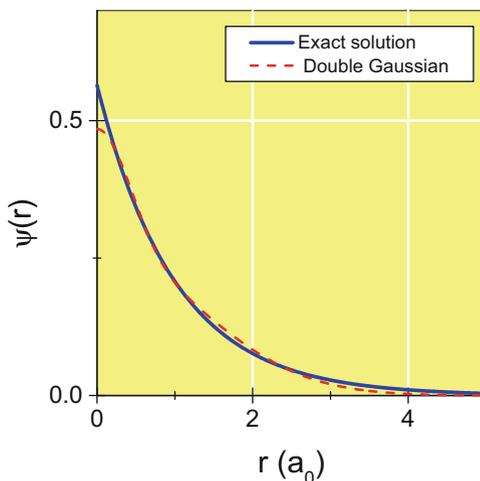
Substituting c_2 and solving for c_1 we obtain:

$$c_1 = \left(S_{11} + \left(\frac{H_{11} - \bar{H}_2 S_{11}}{H_{12} - \bar{H}_2 S_{12}}\right)^2 S_{22} - 2\frac{H_{11} - \bar{H}_2 S_{11}}{H_{12} - \bar{H}_2 S_{12}} S_{12}\right)^{-\frac{1}{2}} = 0.22963$$

(9.190)

and for the second coefficient $c_2 = 0.25472$. The resulting optimized test function is shown in Fig. 9.20 in comparison with the exact wave function (solid line). The optimized double Gaussian test function is quite close to the exact function, with deviations in the near-core and in the far-core region, where the test function takes a steeper course. We conclude that the use of a more flexible double Gaussian test function not only improves the result for the ground state energy, it better resembles the shape of the exact wave function compared with the single Gaussian test function shown in Fig. 9.19. It is worth looking at the remaining deviations in more detail by plotting the radial probability density $w(r) = 4\pi|\psi(r)|^2 r^2$, i.e., the probability of finding the electron between r and $r + dr$. This is done in Fig. 9.21. In this representation, the remaining deviations in the far core region appear more pronounced. Note that the accurate description of electronic structure in the far core region is crucial in chemistry. The method we have applied in this problem can be extended to even more flexible test functions. Contemporary quantum chemistry uses **Gaussian basis sets** with a higher number of primitive Gaussian functions. These give a much more accurate description both in the near core region and – important for chemical bonding - in the region far from the core. Of course, these methods rely on the numerical computation of the integrals and the solution of large systems of equations. Looking back on our solution, we have seen how the variational principle is used to obtain an approximative solution to the well-known hydrogen problem. Even a test function that only approximately compares with the
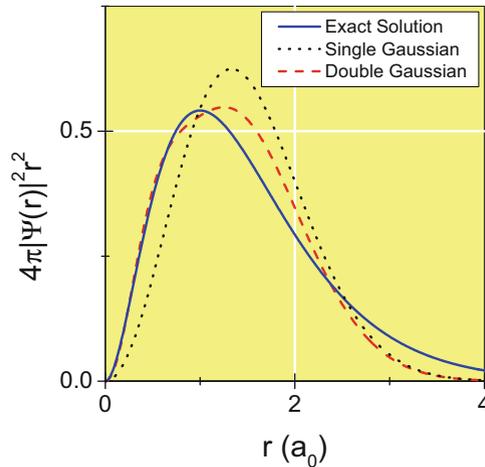
Fig. 9.21 Radial probability density of the exact hydrogen 1s wave function (*solid line*), the optimized double Gaussian function (*dashed line*), and the optimized single Gaussian function (*dotted line*)
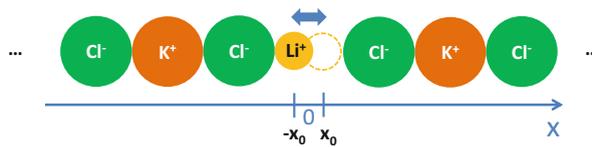

Fig. 9.22 Linear chain of K^+ and Cl^- ions with a vacancy as a model of a lithium doped KCl crystal. Due to the quantum mechanical tunnel effect, the Li^+ ion can switch between the two stable positions

exact solution yields an estimation of the ground state energy that is remarkably close to the exact result.

Problem 9.17 (The Quantum Double Well)

Consider a lithium ion that is free to move in *x*-direction within a K^+ vacancy in an atomic chain of KCl (see Fig. 9.22). Using atomic units, the potential can be approximated by a double-well potential

$$V(x) = \frac{\eta}{x_0^4} \left(x^2 - x_0^2\right)^2 \qquad (9.191)$$

(continued)

Problem 9.17 (continued)

with the two minima at $x = \pm x_0$ ($x_0 = 1.38\, a_0$) and a local maximum $V(0) = \eta = 5 \times 10^{-4}\, E_h$ ($1\, E_h = 27.12\,\text{eV}$, $a_0 = 0.5292\,\text{Å}$).

a. Write down the time-independent Schrödinger equation for the lithium ion.
b. To solve the Schrödinger equation, expand the wave function of the problem in a series of harmonic oscillator functions $\phi_n(x)$:

$$\psi(x) = \sum_{n=0}^{\infty} c_n \phi_n(x) \tag{9.192}$$

Write the Hamiltonian in the form:

$$\hat{H} = \hat{H}_0 + U(x) \tag{9.193}$$

where $\hat{H}_0$ is the Hamiltonian of the harmonic oscillator, and $U(x)$ is an effective potential of the particle.

c. Show that the solution of the Schrödinger equation is equivalent to the solution of the eigenvalue problem

$$H_{mn} c_n = E c_n \qquad n, m = 0, 1, 2, \ldots \tag{9.194}$$

where

$$H_{m,n} = \hbar \omega \left(m + \frac{1}{2} \right) \delta_{mn} + \int_{-\infty}^{+\infty} \phi_m^*(x) U(x) \phi_n(x)\, dx \tag{9.195}$$

d. Use the bra-ket notation and harmonic oscillator algebra introduced in Problem 9.10 and express the matrix elements $H_{m,n}$ in terms of the parameters given.
e. Make a suitable choice for the harmonic oscillator angular frequency ω and use numerical methods to determine at least the energies of the ground state and the first excited state and their wave functions.

Solution 9.17 The context of this quantum mechanical problem is related to solid-state chemistry and physics. More precisely, we deal with a simplified model of lithium-doped potassium chloride (Li:KCl). We have already considered the latter as an example of a system that exhibits a Schottky anomaly (see Problem 8.8). Figure 9.22 shows a linear chain of K^+ and Cl^- ions. Near $x = 0$ one potassium is replaced by a Li^+ cation. As the latter has a smaller ionic radius, it has two stable equivalent positions and the ion can switch between these two positions, either by thermal motion or by means of the quantum mechanical *tunnel effect*. In the latter case, the lithium ion tunnels through the potential barrier between the two positions.

Fig. 9.23 Double-well
model potential of the lithium
ion in the vacancy (*solid
line*). Also shown (*dashed
line*) is the reference
harmonic oscillator potential
used for the solution of the
quantum double well problem
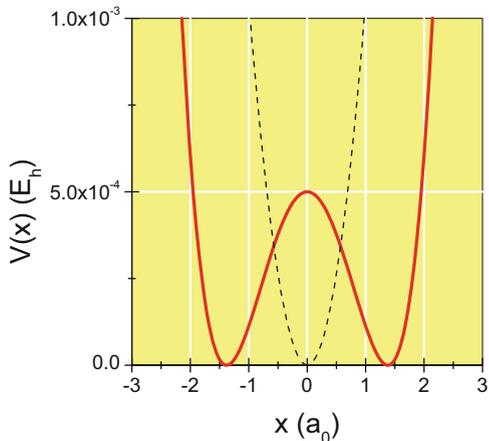
The potential of the lithium in the vacancy, Eq. (9.191), is a symmetric double-well
with minima at $\pm x_0$. It is plotted in Fig. 9.23 using the parameters η and x_0 given in
the problem text. The use of atomic units simplifies the calculations in the following.
Distances are thus defined in multiples of the Bohr radius a_0, energies in multiples
of hartree energy E_h. The form of the potential can be explained by strong repulsive
interaction between Li^+ and Cl^- for $|x| > 2\,a_0$, and electrostatic interaction between
Li^+ and all ions in the chain, which, compared with the interaction at $x = 0$, is
slightly more attractive if the Li^+ moves closer to the neighboring Cl^-. Our goal is
to investigate this system using quantum mechanics. This is highly instructive, not
only because double-well potentials have promising applications such as quantum
dots or quantum antennas. From a mathematical point of view, we learn how to use a
complete orthogonal system of functions to solve the time-independent Schrödinger
equation exactly. Of course, in the end, we must use numerical methods, such as
linear algebra, to obtain solutions. Starting with **subproblem (a)**, we write down the
Schrödinger equation of the time-independent problem characterized by the double-
well potential Eq. (9.191). In atomic units, the Schrödinger equation is:

$$\left[-\frac{1}{2m_{\mathrm{Li}}} \frac{\partial^2}{\partial x^2} + \frac{\eta}{x_0^4} \left(x^2 - x_0^2 \right)^2 \right] \psi(x) = E\psi(x) \tag{9.196}$$

Note that the mass of the lithium ion needs to be provided in multiples of the
electron mass (see Sect. A.1): $m_{\mathrm{Li}} = 6.94\, m_u = 12650.8\, m_e$ where the electron
mass m_e is set to unity in atomic units. There are several possibilities for solving
the Schrödinger equation. One possibility is to define a discrete grid of points along
the x-axis and to discretize the second derivative in addition to the potential and the
wave function. The other possibility is to expand the unknown wave function in a
series of functions that constitute a complete orthogonal set. In this case, we use the
harmonic oscillator functions $\phi_n(x)$ ($n = 0, 1, 2 \dots$) as such a complete set. These

functions[15] are solutions of:

$$\left[-\frac{1}{2m_{\text{Li}}} \frac{\partial^2}{\partial x^2} + \frac{m_{\text{Li}}\omega^2}{2} x^2 \right] \phi_n(x) = E_n \phi_n(x) \tag{9.197}$$

where $E_n = \omega \left(n + \frac{1}{2} \right)$ are the known energy eigenvalues of the harmonic oscillator with an angular frequency ω. The term in brackets in Eq. (9.196) is the Hamiltonian $\hat{H}$ of the quantum double-well.

Following the instruction given in **subproblem (b)**, we rewrite the Hamiltonian as a sum of the harmonic oscillator Hamiltonian $\hat{H}_0$ plus an effective potential $U(x)$:

$$\hat{H} = -\frac{1}{2m_{\text{Li}}} \frac{\partial^2}{\partial x^2} + \frac{m_{\text{Li}}\omega^2}{2} x^2 + \underbrace{\frac{\eta}{x_0^4} \left(x^2 - x_0^2 \right)^2 - \frac{m_{\text{Li}}\omega^2}{2} x^2}_{U(x)}$$

$$= \hat{H}_0 + U(x) \tag{9.198}$$

The new potential function $U(x)$ is simply the difference between the double-well potential and the harmonic oscillator potential, where we are free to choose a suitable value for ω.

In **subproblem (c)**, we use this special form to show that it leads to an eigenvalue problem. Switching to bra-ket notation, the expansion of the unknown wave function in harmonic oscillator states $|n\rangle$ is

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |n\rangle. \tag{9.199}$$

The Schrödinger equation can thus be written

$$\left(\hat{H}_0 + U \right) \sum_{n=0}^{\infty} c_n |n\rangle = E \sum_{n=0}^{\infty} c_n |n\rangle \tag{9.200}$$

The trick is to multiply from the left with $\langle \psi | = \sum_m c_m^* \langle m|$:

$$\sum_{n,m} c_m^* c_n \underbrace{\langle m | \hat{H}_0 + U | n \rangle}_{H_{mn}} = E \sum_{n,m} c_m^* c_n \underbrace{\langle m | n \rangle}_{\delta_{nm}} \tag{9.201}$$

---

[15] Harmonic oscillator wave functions are illustrated in Fig. 9.1. Explicit formulas are provided in the Appendix, Sect. A.3.13.

We thus obtain the eigenvalue equation Eq. (9.194), and because $\hat{H}_0|n\rangle = \omega\left(n + \frac{1}{2}\right)|n\rangle$, the matrix elements H_{mn} are given by:

$$H_{mn} = \omega\left(m + \frac{1}{2}\right)\delta_{mn} + \langle m|U|n\rangle \tag{9.202}$$

which is simply Eq. (9.195) in bra-ket notation. The determination of the matrix elements H_{mn} is our next task in **subproblem (d)**. We could solve the integrals in Eq. (9.195) numerically using explicit forms of the harmonic oscillator wave functions in the Appendix Eq. (A.76) in combination with the recurrence relation Eq. (A.77). Here, however, we can benefit from Dirac's abstract bra-ket notation. We solve the integrals without explicit usage of the harmonic oscillator wave functions, merely by using harmonic oscillator algebra based on creation and annihilation operators introduced in Problem 9.10, Eqs. (9.86) and (9.87). Using these equations, it can be shown that the position operator can be written

$$\hat{x} = \frac{1}{\sqrt{2m_{\text{Li}}\omega}}\left(\mathbf{a}^+ + \mathbf{a}\right) \tag{9.203}$$

The position operator can be inserted into the expression containing the effective potential:

$$U(x) = \frac{\eta}{x_0^4}\left(x^2 - x_0^2\right)^2 - \frac{m_{\text{Li}}\omega^2}{2}x^2$$

$$= \frac{\eta}{x_0^4}\left(x^4 - 2x^2x_0^2 + x_0^4\right) - \frac{m_{\text{Li}}\omega^2}{2}x^2 \tag{9.204}$$

The matrix elements of the effective potential are:

$$\langle m|U(x)|n\rangle = \frac{\eta}{x_0^4}\langle m|x^4|n\rangle - \left(\frac{2\eta}{x_0^2} + \frac{m_{\text{Li}}\omega^2}{2}\right)\langle m|x^2|n\rangle + \eta\underbrace{\langle m|n\rangle}_{\delta_{mn}}. \tag{9.205}$$

Using Eq. (9.203), we obtain:

$$x^2 = \frac{1}{2m_{\text{Li}}\omega}\left(\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a} + \mathbf{a}\mathbf{a}\right) \tag{9.206}$$

and

$$\begin{aligned}
x^4 = \frac{1}{4m_{\text{Li}}^2\omega^2}(&\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}^+\mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}^+\mathbf{a}^+\mathbf{a} + \mathbf{a}^+\mathbf{a}^+\mathbf{a}\mathbf{a} \\
&+ \mathbf{a}\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}\mathbf{a}^+\mathbf{a}\mathbf{a}^+ + \mathbf{a}\mathbf{a}^+\mathbf{a}^+\mathbf{a} + \mathbf{a}\mathbf{a}^+\mathbf{a}\mathbf{a} \\
&+ \mathbf{a}^+\mathbf{a}\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}\mathbf{a}\mathbf{a}^+ + \mathbf{a}^+\mathbf{a}\mathbf{a}^+\mathbf{a} + \mathbf{a}^+\mathbf{a}\mathbf{a}\mathbf{a} \\
&+ \mathbf{a}\mathbf{a}\mathbf{a}^+\mathbf{a}^+ + \mathbf{a}\mathbf{a}\mathbf{a}\mathbf{a}^+ + \mathbf{a}\mathbf{a}\mathbf{a}^+\mathbf{a} + \mathbf{a}\mathbf{a}\mathbf{a}\mathbf{a}).
\end{aligned} \tag{9.207}$$

For the evaluation of the matrix elements $\langle m|x^2|n\rangle$ and $\langle m|x^4|n\rangle$ we insert these operator expressions and consider the relations:

$$\mathbf{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle; \qquad \mathbf{a}|n\rangle = \sqrt{n}|n-1\rangle \tag{9.208}$$

which appeared in Problem 9.10. Using the orthogonality of the harmonic oscillator states, $\langle m|n\rangle = \delta_{m,n}$, we obtain, for example:

$$\langle m|\mathbf{a}^+\mathbf{a}^+|n\rangle = \sqrt{(n+1)(n+2)}\delta_{m,n+2}$$

$$\langle m|\mathbf{a}^+\mathbf{a}|n\rangle = \sqrt{n\,n}\delta_{m,n}$$

$$\langle m|\mathbf{a}^+\mathbf{a}^+\mathbf{a}\mathbf{a}|n\rangle = \sqrt{n(n-1)(n-1)n}\delta_{m,n}$$

$$\langle m|\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+\mathbf{a}|n\rangle = \sqrt{n\,n(n+1)(n+2)}\delta_{m,n+2}$$

Note that the order of the operators in the various terms matters. If we analyze all 20 operator terms in this way, we obtain:

$$
\begin{aligned}
H_{mn} = {} & \omega\left(m+\frac{1}{2}\right)\delta_{m,n} + \eta\delta_{m,n} \\
& + \frac{\eta}{x_0^4}\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{m,n+4} \\
& + \frac{\eta}{x_0^4}\left(\sqrt{(n+1)^3(n+2)} + n\sqrt{(n+1)(n+2)} + (n+3)\sqrt{(n+1)(n+2)}\right. \\
& \left. + \sqrt{(n+1)(n+2)^3}\right)\delta_{m,n+2} \\
& + \frac{\eta}{x_0^4}\left(n(n-1) + (n+1)^2 + 2n(n+1) + n^2 + (n+1)(n+2)\right)\delta_{m,n} \\
& + \frac{\eta}{x_0^4}\left(\sqrt{n(n-1)^3} + (n-2)\sqrt{n(n-1)}\right. \\
& \left. + (n+1)\sqrt{n(n-1)} + \sqrt{n^3(n-1)}\right)\delta_{m,n-2} \\
& + \frac{\eta}{x_0^4}\sqrt{n(n-1)(n-2)(n-3)}\delta_{m,n-4} \\
& - \left(\frac{2\eta}{x_0^2} + \frac{m_{\text{Li}}\omega^2}{2}\right)\left(\sqrt{(n+1)(n+2)}\delta_{m,n+2} + (n+(n+1))\delta_{m,n}\right. \\
& \left. + \sqrt{n(n-1)}\delta_{m,n-2}\right). \tag{9.209}
\end{aligned}
$$

The appearance of the Kronecker deltas $\delta_{m,n}$, $\delta_{m,n\pm2}$, and $\delta_{m,n\pm4}$ indicates that most of the matrix elements H_{mn} are zero. Nonzero matrix elements in the

Fig. 9.24 Sparse occupation
of the Hamiltonian matrix
H_{mn} for the quantum
double-well problem for a
10×10 matrix (schematic).
White fields represent matrix
elements with zero value,
shaded fields represent
elements that are nonzero
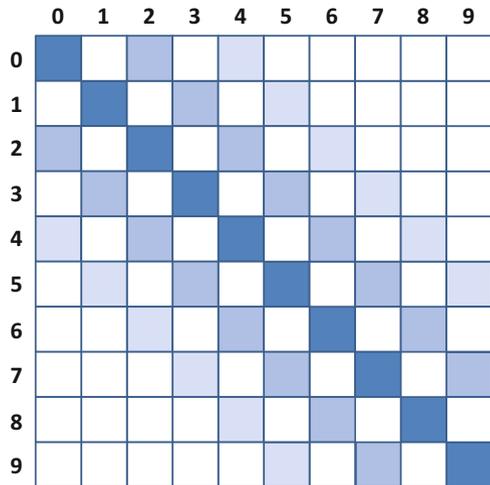
Hamiltonian matrix appear in a band near the diagonal, as illustrated schematically
in Fig. 9.24.

We are now ready to solve the problem numerically in **subproblem (e)**. At first,
we choose the angular frequency ω. In principle, the solution will not depend on
this choice. However, if ω is too large or too small, convergence of the result with
regard to the number of harmonic oscillator states in the calculation may be an
issue. The harmonic oscillator potential should thus approximately fit the double-
well potential and should thus be adapted to the parameters η, the mass m, and x_0.
A possible choice could be:

$$\omega = \sqrt{\frac{8\eta}{m_{\text{Li}}x_0^2}} = 4.07466 \times 10^{-4} \text{ a.u.} \qquad (9.210)$$

The resulting potential of the reference harmonic oscillator is shown in Fig. 9.23
(blue dotted line). A numerical procedure to diagonalize the Hamiltonian matrix
(Eq. (9.209)) can be implemented in various ways, for example, by using mathemat-
ical software or a programming language. In the latter case, powerful linear algebra
libraries are available.[16]

With the above choice for ω it is sufficient to use 20 harmonic oscillator
functions. The resulting eigenvalue spectrum, obtained by diagonalization of the
resulting 20×20 matrix, is shown for the first six states in Fig. 9.25, together
with the double-well potential. Numerical values are also given in Table 9.3. The
ground state and the first excited state are separated by a small splitting of only
$\Delta = 3.32 \times 10^{-6} E_h$ or 0.1 meV. As can be seen in Fig. 9.25, there is also a grouping

---

[16]The most common one is LAPACK, http://www.netlib.org/lapack/.

Fig. 9.25 The first six energy
levels of the quantum
double-well, as obtained from
the solution of Eq. (9.194).
The splitting between the
ground state ($n = 0$) and the
first excited state ($n = 1$) is
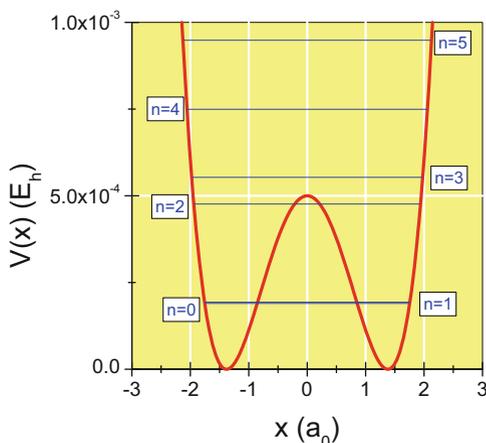very small
($\Delta = 3.4 \times 10^{-6} \, E_h$)

Table 9.3 The first six
energy states of the quantum
double-well obtained from
the solution of Eq. (9.194)

n	E_n ($10^{-4} \, E_h$)
0	1.8996
1	1.9339
2	4.7630
3	5.5326
4	7.4947
5	9.4820

of states $n = 2$ and $n = 3$ with a larger splitting of $77 \times 10^{-6} \, E_h$ discernible. The
energies of these states are close to the potential barrier at $x = 0$.

For the visualization of the wave functions, we use Eq. (9.192) and the eigen-
vectors of the various states. We need the general form of the harmonic oscillator
wave functions Eq. (A.76) and the recurrence relation Eq. (A.77) for the Hermite
polynomials to construct the double-well wave functions. The first six solutions are
shown in Fig. 9.26.

It is striking that states with even n are also even functions, i.e. $\psi_n(x) = \psi(-x)$
for $n = 0, 2, 4$, whereas the states with odd n are asymmetrical: $\psi_n(-x) = -\psi(x)_n$
for $n = 1, 3, 5$. The ground state wave function and the solution for $n = 1$ have a
high amplitude and thus high probability[17] near the stable sites of the Li$^+$ at $x = \pm x_0$. However, for the ground state in particular, there is also a nonzero probability
of finding the Li$^+$ within the potential barrier, and this causes the possibility of
tunneling through the barrier. In contrast, the states $n \geq 2$ with energies comparable
with the energy barrier or higher have a considerable probability in the region of the
barrier, although, by symmetry, odd states have $|\psi_n(0)|^2 = 0$.

---

[17]The probability of finding the Li$^+$ between x and $x + dx$ is $|\psi_n(x)|^2$.
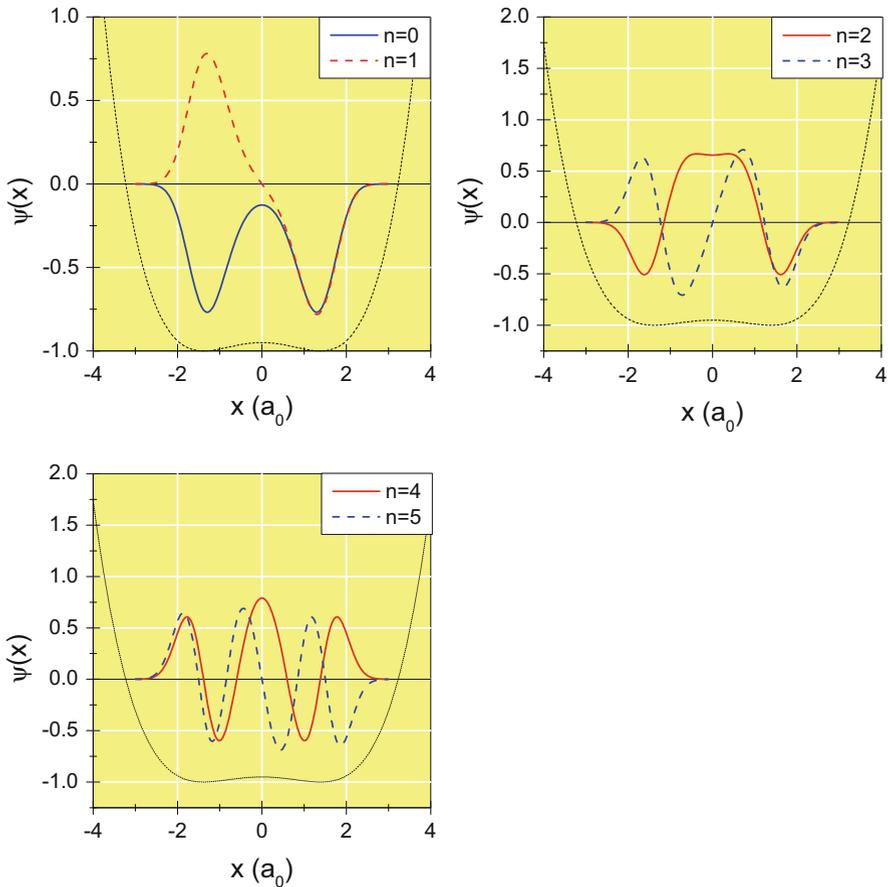
Fig. 9.26 Wave functions in the double-well potential (*short dashed*) of the ground state ($n = 0$) and the first excited states. The wave functions are alternately either symmetrical ($n = 0, 2, 4$) or asymmetrical ($n = 1, 3, 5$)

It is worth mentioning that the model of the one-dimensional atomic chain in Fig. 9.22 can only yield qualitative results for the description of the Li:KCl system. A K^+ vacancy in a KCl crystal has a three-dimensional structure and the potential of a Li^+ ion has not two, but eight local minima. The simple one-dimensional model, however, contains the essential physics to understand the behavior of such multiwell systems. In summary, we have learned how harmonic oscillator wave functions can be used as a complete orthogonal set of functions to solve the Schrödinger equation for the special case of a quantum double-well potential. The method is general and can be used for other potentials, e.g., the asymmetric quantum double-well.

Problem 9.18 (The Chemical Bond)

Hint: It is recommended that the reader has dealt with Problem 9.16.

The simplest chemical system that exhibits a chemical bond between two nuclei is the H_2^+ molecule ion. Use the variational principle (Problem 9.16) to derive approximate analytical solutions for the potential between the two nuclei at rest at positions $\mathbf{R}_1 = \left(0, 0, -\frac{R}{2}\right)$ and $\mathbf{R}_2 = \left(0, 0, +\frac{R}{2}\right)$. As a suitable trial wave function use a linear combination of hydrogen 1s wave functions located at the sites of the nuclei 1 and 2 respectively:

$$\psi(\mathbf{r}) = c_1 \psi_1(r_1) + c_2 \psi_2(r_2) \tag{9.211}$$

where $r_1 = |\mathbf{r} - \mathbf{R}_1|$, $r_2 = |\mathbf{r} - \mathbf{R}_2|$, and ψ_1 and ψ_2 have the form

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}. \tag{9.212}$$

a. Write down the Hamiltonian $\hat{H}$ for the electron, using atomic units.

b. Calculate the *overlap integral*

$$S = \int \psi_1(\mathbf{r}) \, \psi_2(\mathbf{r}) \, dV = \langle \psi_1 | \psi_2 \rangle \tag{9.213}$$

as a function of the internuclear distance R. *Hint*: Introduce the confocal elliptical coordinates

$$\mu = \frac{r_1 + r_2}{R}; \quad \mu \in [1, \infty] \tag{9.214}$$

$$\nu = \frac{r_1 - r_2}{R}; \quad \nu \in [-1, 1] \tag{9.215}$$

and the angle $\phi \in [0, 2\pi]$ defined in Fig. 9.27. The volume element expressed in these coordinates is $dV = \frac{R^3}{8} \left(\mu^2 - \nu^2\right) d\mu \, d\nu \, d\phi$.

c. Use the same integration technique to evaluate the Coulomb integral

$$C = \int \psi_1(\mathbf{r}) \frac{1}{r_2} \psi_1(\mathbf{r}) \, dV = \langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle \tag{9.216}$$

and the exchange integral

$$A = \int \psi_1(\mathbf{r}) \frac{1}{r_1} \psi_2(\mathbf{r}) \, dV = \langle \psi_1 | \frac{1}{r_1} | \psi_2 \rangle \tag{9.217}$$

Fig. 9.27 Geometry of the
H_2^+ molecular ion. The origin
of the molecule-fixed
coordinate system is in the
middle of the connecting line;
nuclei 1 and 2 are at positions
$\left(0, 0, \pm \frac{R}{2}\right)$. The electron at
position **r** and the two nuclei
define a plane that is tilted by
an angle ϕ with regard to the
x-axis
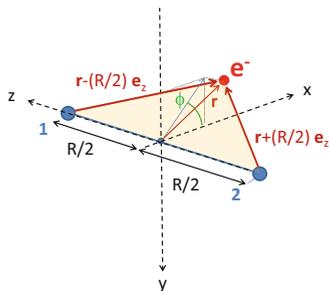
Problem 9.18 (continued)
   as a function of R.
   d. Insert the trial function Eq. (9.212) into the equation

$$\bar{H} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \overset{!}{=} \text{min.} \qquad (9.218)$$

for the variational principle and derive an eigenvalue equation for the
electron energy. Show that one of the two solutions yields to a bonding
of the two nuclei. Determine c_1 and c_2.

Solution 9.18 Perhaps the most important application of quantum mechanics in
chemistry is the explanation of chemical bonds from first principles. Contemporary
methods in quantum chemistry provide accurate descriptions of the electronic
structure of molecules and solids. However, these methods typically require great
numerical effort. Paper and pencil approaches are possible for only the simplest
systems, and, moreover, in an approximate manner. Nevertheless, they allow a
qualitative understanding of the nature of the chemical bond. Here, we deal with the
simplest possible molecular system, the H_2^+ molecular ion. The geometry is shown
schematically in Fig. 9.27. The goal of the exercise is to determine the potential
between the two nuclei as a function of the internuclear distance R. In the electronic
ground state, we expect the potential energy curve

$$V(R) = V_{\text{rep}}(R) + E_{\text{el}}(R) \qquad (9.219)$$

to exhibit a minimum. In atomic units[18], which we use in the following, $V_{\text{rep}} = \frac{+1}{R}$ is
the electrostatic repulsion of the two positively charged nuclei. E_{el} is the electronic
energy acting as an effective potential, calculated at a given bond distance R. The

---

[18]See Sect. 9.1.4. Note that in atomic units the unit length is $1a_0$, and the unit energy is $1\,E_h$.

Schrödinger equation of the electron moving in the Coulomb potential of the two nuclei is:

$$\left[-\frac{1}{2}\Delta - \frac{1}{r_1} - \frac{1}{r_2} \right] \psi(\mathbf{r}) = E_{\text{el}}\psi(\mathbf{r}) \tag{9.220}$$

where $r_1 = |\mathbf{r} - \frac{R}{2}\mathbf{e}_z|$ is the distance of the electron from nucleus 1, and $r_2 = |\mathbf{r} + \frac{R}{2}\mathbf{e}_z|$ is the distance of the electron from nucleus 2 respectively, and $\mathbf{e}_z$ is the unit vector in the z-direction.

The Hamiltonian sought in **subproblem (a)** is thus:

$$\hat{H} = -\frac{1}{2}\Delta - \frac{1}{r_1} - \frac{1}{r_2}. \tag{9.221}$$

It is worth noting that this quantum mechanical problem can be solved precisely by introducing confocal elliptical coordinates [5]. The approximate solution based on the variational principle, however, shows much of the spirit of a quantum chemical treatment. The variational principle was already used in Problem 9.16. The strategy is to use a suitable test function containing a number of adjustable parameters and to minimize the total energy. Improvement of the test function, for example, by increasing the number of parameters, is a systematic approach to the exact solution. In this problem, the test function is a linear combination of hydrogen 1s wave functions centered at the sites of the two nuclei:

$$\psi(\mathbf{r}) = c_1\psi_1(r_1) + c_2\psi_2(r_2) = \frac{1}{\sqrt{\pi}}\left[c_1 e^{-r_1} + c_2 e^{-r_2} \right] \tag{9.222}$$

Apparently, the coefficients c_1 and c_2 are the two adjustable parameters. Note that in the limiting case $R = 0$ where the two nuclei constitute a helium core with a nuclear charge $Ze = 2e$, this test wave function does not coincide with the exact ground state solution of the He$^+$ problem, $\psi_{\text{He}^+} \sim e^{-2r}$.

In **subproblem (b)** and **subproblem (c)**, we deal with three different integrals involved in the treatment of the H$_2^+$ ion. The first integral is the **overlap integral**

$$S(R) = \int \psi_1(\mathbf{r})\psi_2(\mathbf{r})\, dV = \frac{1}{\pi}\int e^{-|\mathbf{r}-\frac{R}{2}\mathbf{e}_z|} e^{-|\mathbf{r}+\frac{R}{2}\mathbf{e}_z|}\, dV = \frac{1}{\pi}\int e^{-(r_1+r_2)}\, dV. \tag{9.223}$$

For the solution we switch to a representation using the confocal elliptical coordinates μ and ν introduced in Eqs. (9.214) and (9.215), in addition to the angle ϕ. It is the angle of the plane defined by the sites of the nuclei and the electron relative to the xz-plane. The significance of the coordinate μ becomes clearer if we imagine that the electron resides on an ellipse, whose two focal points are the sites of the nuclei. As each point on an ellipse leaves constant the sum of distances to the focal points, and because $R\mu = r_1 + r_2$, the coordinate μ has an analog in the radial distance of the electron in the hydrogen problem formulated with spherical coordinates: the

curve of constant μ is an ellipse, as the sphere is an area of constant radial distance. The other coordinate, ν, is related to the difference in the distances between the electron and the nuclear sites. If ν is varied at constant μ, the electron moves on the ellipse. An analogy to the quantity $\cos\theta$ in spherical coordinates is thus established. With the volume element given in the problem text, the overlap integral is thus:

$$S(R) = \frac{1}{\pi} \int_1^\infty d\mu \int_{-1}^{+1} d\nu \int_0^{2\pi} d\phi \, \frac{R^3}{8} \left(\mu^2 - \nu^2\right) e^{-R\mu}. \tag{9.224}$$

Integration over ϕ is trivial and yields a factor 2π. The separation with regard to the other coordinates yields:

$$S(R) = \frac{R^3}{4} \int_1^\infty \mu^2 e^{-R\mu} \, d\mu \underbrace{\int_{-1}^{+1} d\nu}_{=2} - \frac{R^3}{4} \int_1^\infty e^{-R\mu} \, d\mu \underbrace{\int_{-1}^{+1} \nu^2 \, d\nu}_{=\frac{2}{3}}. \tag{9.225}$$

Because

$$\int_1^\infty \mu^2 e^{-R\mu} \, d\mu \overset{\text{Eq. (A.44)}}{=} e^{-R\mu} \left(-\frac{\mu^2}{R} - \frac{2\mu}{R^2} - \frac{2}{R^3}\right)\Bigg|_1^\infty = 0 + e^{-R}\left(\frac{1}{R} + \frac{2}{R^2} + \frac{2}{R^3}\right) \tag{9.226}$$

and

$$\int_1^\infty e^{-R\mu} \, d\mu = -\frac{e^{-R\mu}}{R}\Bigg|_1^\infty = 0 + \frac{e^{-R}}{R} \tag{9.227}$$

the result for the overlap integral is

$$S(R) = e^{-R}\left(\frac{R^2}{3} + R + 1\right). \tag{9.228}$$

$S(R)$ is plotted in Fig. 9.28. The overlap integral diminishes rapidly for increasing R. The second integral is the Coulomb integral Eq. (9.216),

$$C(R) = \int \frac{\psi_1^2(r_1)}{r_2} \, dV = \frac{1}{\pi} \int \frac{e^{-2r_1}}{r_2} \, dV. \tag{9.229}$$

Because $r_1 = \frac{R}{2}(\mu + \nu)$ and $r_2 = \frac{R}{2}(\mu - \nu)$, the introduction of elliptical coordinates yields:

$$C(R) = \frac{1}{\pi} \int_0^{2\pi} d\phi \int_1^\infty d\mu \int_{-1}^{+1} d\nu \, e^{-R(\mu+\nu)} \frac{2}{R} \frac{1}{\mu - \nu} \frac{R^3}{8}\left(\mu^2 - \nu^2\right). \tag{9.230}$$

Fig. 9.28 Overlap integral S, Coulomb integral C, and exchange integral A as a function of the distance between the two hydrogen nuclei
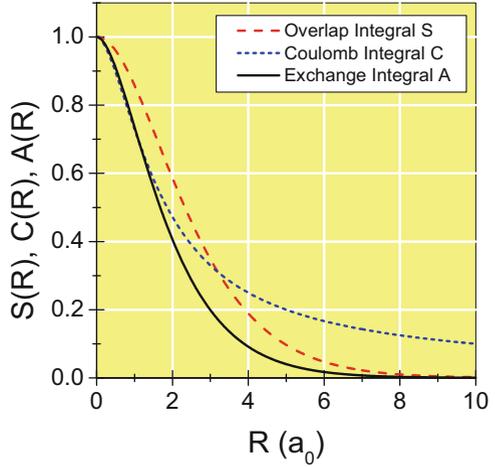
Integration over ϕ is again trivial and further simplification is possible by means of the third binomial formula:

$$C(R) = \frac{R^2}{2} \int_{\mu=1}^{\infty} \int_{v=-1}^{+1} e^{-R(\mu+v)} \left(\mu + v\right) d\mu \, dv. \tag{9.231}$$

Separation of the integrals yields:

$$C(R) = \frac{R^2}{2} \int_{1}^{\infty} e^{-R\mu} \mu \, d\mu \int_{-1}^{+1} e^{-Rv} \, dv + \frac{R^2}{2} \int_{1}^{\infty} e^{-R\mu} \, d\mu \int_{-1}^{+1} e^{-Rv} v \, dv \tag{9.232}$$

where

$$\int_{1}^{\infty} e^{-R\mu} \mu \, d\mu \overset{\text{Eq. (A.43)}}{=} \left. -\frac{e^{-R\mu}}{R^2} \left(R\mu + 1\right) \right|_{1}^{\infty} = \frac{e^{-R}}{R^2} \left(R + 1\right) \tag{9.233}$$

$$\int_{-1}^{+1} e^{-Rv} v \, dv \overset{\text{Eq. (A.43)}}{=} \left. -\frac{e^{-Rv}}{R^2} \left(Rv + 1\right) \right|_{-1}^{+1} = -\frac{e^{-R}}{R^2} \left(R + 1\right) + \frac{e^{-R}}{R^2} \left(1 - R\right) \tag{9.234}$$

$$\int_{-1}^{+1} e^{-Rv} \, dv = \frac{1}{R} \left(e^R - e^{-R}\right). \tag{9.235}$$

With these results, the Coulomb integral is:

$$C(R) = \frac{1}{R} - e^{-2R} \left(1 + \frac{1}{R}\right) \tag{9.236}$$

This function is shown in Fig. 9.28 (short dashed line). At large R, the integral diminishes as R^{-1} and thus has a long range. The calculation of the third integral, called the exchange integral, uses the same methods:

$$A(R) = \int \frac{\psi_1 \psi_2}{r_1} \, dV = \frac{1}{\pi} \int \frac{e^{-(r_1 + r_2)}}{r_1} \, dV \tag{9.237}$$

Introduction of elliptical coordinates and integration over the angle ϕ yields

$$
\begin{aligned}
A(R) &= \frac{R^2}{2} \int_1^\infty \int_{-1}^{+1} e^{-R\mu} \, (\mu - \nu) \, d\mu \, d\nu \\
&= \frac{R^2}{2} \int_1^\infty e^{-R\mu} \mu \, d\mu \underbrace{\int_{-1}^{+1} d\nu}_{=2} - \frac{R^2}{2} \int_1^\infty e^{-R\mu} \, d\mu \underbrace{\int_{-1}^{+1} \nu \, d\nu}_{=1}
\end{aligned} \tag{9.238}
$$

After insertion of Eqs. (9.227) and (9.233), the result for the exchange integral is:

$$A(R) = e^{-R} (1 + R). \tag{9.239}$$

It is also plotted in Fig. 9.28. In **subproblem (d)**, we apply the variational principle. From now on, it is convenient to switch to Dirac's bra-ket notation. We exploit the fact that the hydrogen 1s wave function is normalized, as we have shown in Problem 9.14. Moreover, we assume that the mixing parameters c_1 and c_2 are real. The denominator of the energy functional Eq. (9.218) is thus:

$$
\begin{aligned}
D = \langle \psi | \psi \rangle &= (c_1 \langle \psi_1 | + c_2 \langle \psi_2 |)(c_1 | \psi_1 \rangle + c_2 | \psi_2 \rangle) \\
&= c_1^2 \underbrace{\langle \psi_1 | \psi_1 \rangle}_{=1} + 2 c_1 c_2 \underbrace{\langle \psi_1 | \psi_2 \rangle}_{=S} + c_2^2 \underbrace{\langle \psi_2 | \psi_2 \rangle}_{=1} \\
&= c_1^2 + 2 c_1 c_2 S + c_2^2.
\end{aligned} \tag{9.240}
$$

For the calculation of the nominator of the energy functional we take into account that the Hamiltonian Eq. (9.221) acting on either of the two wave functions yields:

$$\left(-\Delta - \frac{1}{r_1} - \frac{1}{r_2} \right) | \psi_1 \rangle = E_0 | \psi_1 \rangle - \frac{1}{r_2} | \psi_1 \rangle \tag{9.241}$$

and

$$\left(-\Delta - \frac{1}{r_1} - \frac{1}{r_2} \right) | \psi_2 \rangle = E_0 | \psi_2 \rangle - \frac{1}{r_1} | \psi_2 \rangle \tag{9.242}$$

where $E_0 = -0.5\,E_h = -13.605693\,\text{eV}$ is the ground state energy of the hydrogen atom. Thus, the nominator of the energy functional is[19]

$$N = \langle \psi | \hat{H} | \psi \rangle = (c_1 \langle \psi_1 | + c_2 \langle \psi_2 |) \left(-\Delta - \frac{1}{r_1} - \frac{1}{r_2} \right) (c_1 | \psi_1 \rangle + c_2 | \psi_2 \rangle)$$

$$= c_1^2 E_0 \underbrace{\langle \psi_1 | \psi_1 \rangle}_{=1} - c_1^2 \underbrace{\langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle}_{=C} + c_1 c_2 E_0 \underbrace{\langle \psi_1 | \psi_2 \rangle}_{=S} - c_1 c_2 \underbrace{\langle \psi_1 | \frac{1}{r_1} | \psi_2 \rangle}_{=A}$$

$$+ c_1 c_2 E_0 \underbrace{\langle \psi_2 | \psi_1 \rangle}_{=S} - c_1 c_2 \underbrace{\langle \psi_2 | \frac{1}{r_2} | \psi_1 \rangle}_{=A} + c_2^2 E_0 \underbrace{\langle \psi_2 | \psi_2 \rangle}_{=1} - c_2^2 \underbrace{\langle \psi_2 | \frac{1}{r_1} | \psi_2 \rangle}_{=C}$$

$$= c_1^2 (E_0 - C) + 2c_1 c_2 (E_0 S - A) + c_2^2 (E_0 - C) \qquad (9.243)$$

The necessary conditions for a minimum as required in Eq. (9.218) is:

$$\frac{\partial \bar{H}}{\partial c_1} = 0; \qquad \frac{\partial \bar{H}}{\partial c_2} = 0. \qquad (9.244)$$

As shown in Problem 9.16 (Eq. (9.182) on page 269), these conditions are equivalent to:

$$\frac{\partial N}{\partial c_1} - \bar{H} \frac{\partial D}{\partial c_1} = 0 \qquad (9.245)$$

and

$$\frac{\partial N}{\partial c_2} - \bar{H} \frac{\partial D}{\partial c_2} = 0. \qquad (9.246)$$

As a consequence, we arrive at the following system of equations:

$$\left(E_0 - C - \bar{H} \right) c_1 + \left(E_0 S - A - \bar{H}S \right) c_2 = 0 \qquad (9.247)$$

$$\left(E_0 S - A - \bar{H}S \right) c_1 + \left(E_0 - C - \bar{H} \right) c_2 = 0 \qquad (9.248)$$

With the abbreviations $H_{11} = E_0 - C$ and $H_{12} = E_0 S - A$, the system is:

$$\begin{pmatrix} H_{11} - \bar{H} & H_{12} - \bar{H}S \\ H_{12} - \bar{H}S & H_{11} - \bar{H} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad (9.249)$$

---

[19]Note that because of the mathematical form of ψ_1 and ψ_2, $\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle$.

A nontrivial solution requires the secular determinant to be zero:

$$\left(H_{11} - \bar{H}\right)^2 - \left(H_{12} - \bar{H}S\right)^2 = 0 \tag{9.250}$$

This is a quadratic equation:

$$\left(1 - S^2\right) \bar{H}^2 + 2 \left(H_{12}S - H_{11}\right) \bar{H} + H_{11}^2 - H_{12}^2 = 0 \tag{9.251}$$

with two solutions (see Eq. (A.4))

$$\bar{H}_{1/2} = \frac{2 \left(H_{11} - H_{12}S\right) \pm \sqrt{4 \left(H_{11} - H_{12}S\right)^2 - 4 \left(1 - S^2\right) \left(H_{11}^2 - H_{12}^2\right)}}{2 \left(1 - S^2\right)} \tag{9.252}$$

which can be written in compact form

$$\bar{H}_{1/2} = \frac{H_{11} - H_{12}S \pm \left(H_{11}S - H_{12}\right)}{1 - S^2} \tag{9.253}$$

and simplified even further to yield the two solutions:

$$\bar{H}_1 = E_u = \frac{H_{11} - H_{12}}{1 - S} = \frac{E_0 - C - E_0 S + A}{1 - S} = E_0 - \frac{C - A}{1 - S} \tag{9.254}$$

and

$$\bar{H}_2 = E_g = \frac{H_{11} + H_{12}}{1 + S} = \frac{E_0 - C + E_0 S - A}{1 + S} = E_0 - \frac{C + A}{1 + S}. \tag{9.255}$$

The two energy eigenvalues E_g and E_u of the electron can thus be expressed by the integrals, $S(R)$, $C(R)$, $A(R)$, and the ground state energy of the hydrogen atom, E_0. Focusing on the entire system of the H_2^+ ion, we identify these solutions as the electronic contribution E_{el} to the total potential energy according to Eq. (9.219). The resulting potential curves are shown in Fig. 9.29. It is striking that the blue curve related to the energy eigenvalue E_g has a minimum at $R_{min} = 2.5a_0$, whereas the red curve has a monotonic behavior that is thus repulsive at all distances. We have therefore shown that one of the two solutions leads to bonding of the two nuclei. Furthermore, both potential curves have the same long-range behavior:

$$V(R) = \underbrace{+\frac{1}{R}}_{V_{rep}} + E_0 - \frac{C \pm A}{1 \pm S} \xrightarrow{R \to \infty} E_0 = -0.5 \tag{9.256}$$

   This is because the last term compensates for the electrostatic repulsion of the nuclei at long distances due to the long-range behavior of the Coulomb integral (see Eq. (9.236)) whereas the overlap and exchange integrals are negligible at large

Fig. 9.29 Potential between the hydrogen nuclei in the H_2^+ molecular ion, obtained from an approximate solution of the one electron Schrödinger equation using the variational method
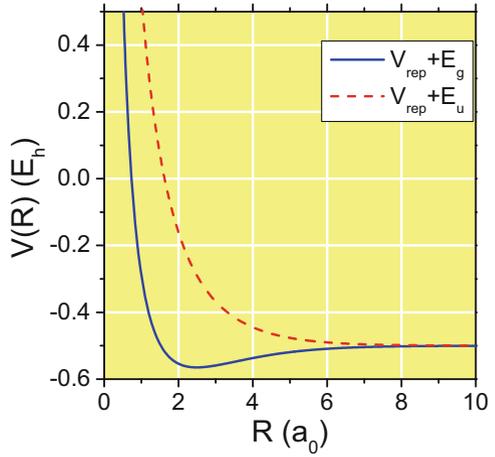
distances. The value $V(R) = -0.5$ at large distances is the total energy of a neutral hydrogen atom and a hydrogen cation. If we neglect the zero-point energy, the formation of a stable H_2^+ molecular ion according to

$$H^+ + H \rightarrow H_2^+ \tag{9.257}$$

involves an energy change $V(R_{min}) - E_0 = -0.065\, E_h = -1.76\,\text{eV}$. To determine the two coefficients, c_1 and c_2, we insert the two solutions for $\bar{H}$ (Eqs. (9.254) and (9.255)) into Eq. (9.249). For the solution with energy E_u, this yields:

$$c_2 = \frac{H_{11} - \bar{H}}{\bar{H}S - H_{12}}c_1 = \frac{H_{11} - \frac{H_{11}-H_{12}}{1-S}}{\frac{H_{11}-H_{12}}{1-S}S - H_{12}}c_1 = -\frac{H_{11}S - H_{12}}{H_{11}S - H_{12}}c_1 = -c_1. \tag{9.258}$$

Moreover, normalization of the total wave function requires:

$$\langle \psi | \psi \rangle = c_1^2 + 2c_1c_2S + c_2^2 = 1. \tag{9.259}$$

Therefore, we obtain:

$$2c_1^2 - 2c_1^2 S = 1 \tag{9.260}$$

and thus

$$c_1 = -c_2 = \frac{1}{\sqrt{2(1-S)}}. \tag{9.261}$$

The wave function is thus:

$$\psi_u(r) = \frac{1}{\sqrt{2\pi\,(1-S)}}\left(e^{-|\mathbf{r}-\mathbf{R}_1|} - e^{-|\mathbf{r}-\mathbf{R}_2|}\right). \tag{9.262}$$

In a completely analogous way, we treat the solution with the eigenvalue E_g. Here, we find

$$c_1 = c_2 = \frac{1}{\sqrt{2\,(1+S)}} \tag{9.263}$$

and, as a consequence, the ground state wave function is:

$$\psi_g(r) = \frac{1}{\sqrt{2\pi\,(1+S)}}\left(e^{-|\mathbf{r}-\mathbf{R}_1|} + e^{-|\mathbf{r}-\mathbf{R}_2|}\right). \tag{9.264}$$

In the terminology of quantum chemistry, ψ_g and ψ_u are molecular orbitals, constructed by a linear combination of the two atomic orbitals ψ_1 and ψ_2 centered at the sites of the nuclei. Both wave functions are plotted for $R = R_{\min} = 2.5a_0$ in Fig. 9.30. Apparently, the ground state ψ_g is symmetrical with regard to an inversion of the molecule, whereas the excited state ψ_u is antisymmetric with regard to inversion. It is worth comparing ψ_g and ψ_u with the ground state ($n = 0$) and the first excited state ($n = 1$) in the quantum double-well problem (Problem 9.17, Fig. 9.26 on page 280). In both problems, the symmetrical solution is energetically favorable compared with the asymmetrical solution. An argument for the bonding nature of the symmetrical solution in the H_2^+ ion is the nonzero electronic charge density among the hydrogen nuclei. In the asymmetrical solution ψ_u, in contrast, the electronic density is repelled from the center of the molecule by symmetry.

In summary, we have applied the variational principle to the simplest molecular system, the H_2^+ ion, containing only one electron. We have shown that ground state electronic energy overcompensates for the electrostatic repulsion of the two hydrogen nuclei at a distance of $R = 2.5a_0$. It is worth noting that the construction of molecular orbitals from atomic orbitals using linear combination is not restricted to 1s orbitals. Extended test wave functions with additional p orbitals, for example, allow polarization effects to be included in the model. The method thus allows a systematic improvement of the solution.
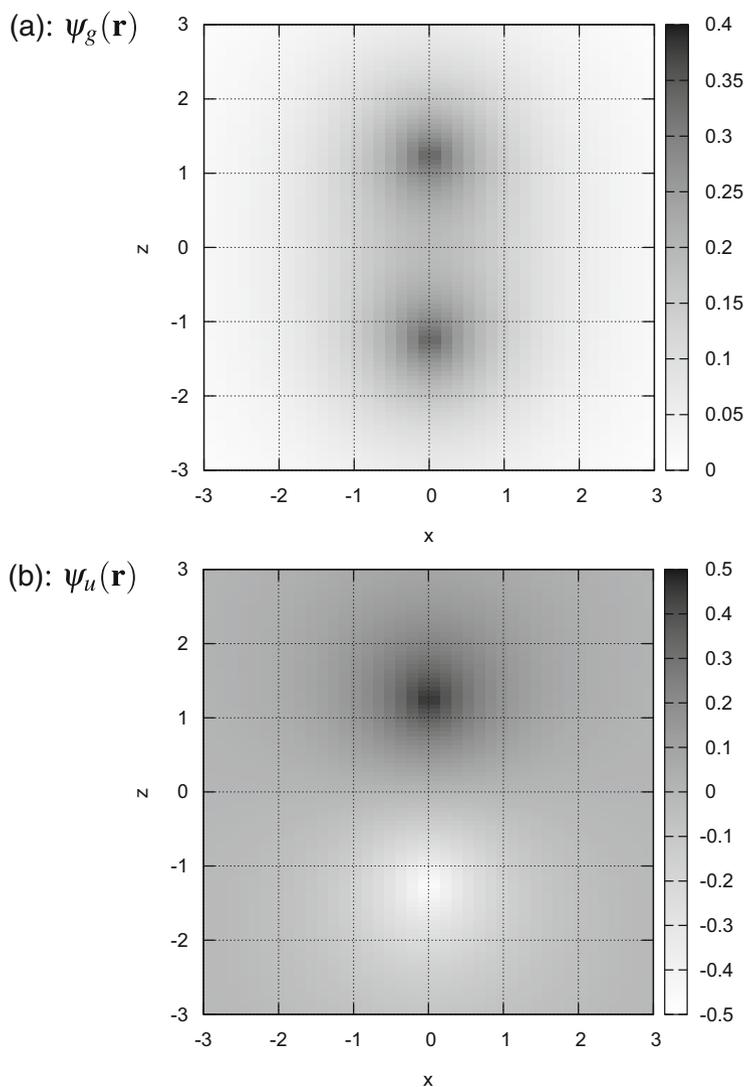
Fig. 9.30 Approximate solutions for the electronic wave functions of the H_2^+ ion based on the variational principle: (**a**) ground state ψ_g according to Eq. (9.264). (**b**) excited state ψ_u according to Eq. (9.262). Using inversion symmetry, ψ_u is characterized by zero electronic density in the center of mass

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