

Physical Chemistry of Ionic Materials Ions and Electrons in Solids

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Preface

The book that you are about to read is, in a broad sense, concerned with the physical chemistry of solids. More specifically, it deals with the ionic and electronic charge carriers in ionic solids. The latter species are the major players in the game when one attempts a detailed understanding or deliberate tuning of kinetic properties. The charge carriers that we refer to are not necessarily identical with the charged particles that constitute the solid, but rather with the effective particles that transport charge, i.e. in the case of ionic crystals the ionic point defects, in addition to excess electrons and holes. These ionic and electronic charge carriers constitute the redox and acid–base chemistry in the same way as is the case for aqueous solutions, they permit charge and matter transport to occur, and are also reactive centres in the sense of chemical kinetics. This explains the central role of defect chemistry in this book.

The more classical introductory chapters on chemical bonding, phonons, and thermodynamics of the perfect solid may, on one hand, be considered as preparation for the key chapters which deal with thermodynamics of the real solid, as well as with kinetics and electrochemistry — both being unthinkable without the existence of defects; on the other hand, they provide the complement necessary for the book to serve as a textbook of physical chemistry of solids. (In fact the different chapters correspond to classical fields of physical chemistry but referred to the solid state.)

The structure of the book is expected to be helpful in view of the heterogeneity of the potential readership: This addresses chemists who traditionally consider solids from a static, structural point of view and often ignore the “internal life” enabled by defect chemistry, physicists who traditionally do not take pertinent account of composition as a state parameter, and materials scientists who traditionally concentrate on materials properties and may not adequately appreciate the basic role of electrochemistry.

Of course the book cannot fully cover the materials space or the world of properties. If the reader is a chemist, he or she may miss special chapters on covalent and disordered solids (e.g. polymers); the physicist will certainly find electronic properties under-represented (e.g. metals), and the materials scientist may have expected a detailed consideration of mechanical and thermal properties. Nonetheless the author is convinced — and this is based on lectures on Physical Chemistry and Materials Science given to very different audiences in Cambridge (USA), Tübingen and Stuttgart (Germany) and Graz (Austria) — that he made a germane selection to highlight the physical chemistry of charge carriers in solids. A certain preference

for examples stemming from the working group of the author is not the result of slothfulness or vanity; rather, it is based on the endeavour to concentrate on a few model materials.

The many cross-references are meant to facilitate reading; proofs or remarks that would disturb the flow of reading and belong to a different level are put into footnotes, and they should be considered when reading the text a second time.

Compared to the German version which appeared earlier (*Festkörper – Fehler und Funktion, Prinzipien der Physikalischen Festkörperchemie*; B. G. Teubner Stuttgart, 2000), the English text is — apart from a few modifications and hopefully a smaller concentration of “defects” — essentially a 1:1 translation.

I am indebted to D. Bonnell, W. B. Eberhardt, K. Funke, O. Kienzle, M. Martin, M. Rühle, E. Schönherr and A. Simon for discussions and the courtesy of providing valuable figures.

I would like to thank my co-workers and colleagues for critical remarks. In particular I appreciate helpful discussion with Jürgen Fleig, Janez Jamnik, Klaus-Dieter Kreuer, Rotraut Merkle and Roger de Souza. To Dr de Souza I am also indebted for his great help in the process of translating the German version into English. I would like to thank Barbara Reichert for the unremitting editorial assistance. Sofia Weiglein and M. Trieloff deserve thanks for their help as regards many tiny things (infinity times zero might be a very significant number). Harry Tuller (MIT Cambridge) and Werner Sitte (TU Graz) provided the hospitality, and my wife Eva the additional free time, without which this book would have never been completed. Many thanks to them.

Stuttgart, January 2004

Joachim Maier

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1 Introduction

1.1 Motivation

It may seem odd to ask the reader in the first sentence of the book he or she has just opened to put it down for a moment (naturally with the intention of picking it up and reading it again with greater motivation). Consider, however, your environment objectively for a moment. The bulk of it is (as we ourselves are to a large degree) made up of solid matter. This does not just apply to the materials, from which the house in which you live is built or the chair in which you may be seated is made, it also applies to the many technical products which make your life easier, and in particular to the key components that are hidden from your eyes, such as the silicon chip in the television set, the electrodes in the radio battery, and the oxide ceramics in the oxygen sensors of modern automobiles. It is the rigidity of solids which endows them with characteristic, advantageous properties: The enduring structure of our world is inconceivable without solid matter, with its low diffusion coefficients at least for one component (the reader may like to consider for a moment his or her surroundings being in spatial equilibrium, i.e. with all diffusion barriers having been removed). In addition and beyond the mere mechanical functionality, solids offer the possibility of subtly and reproducibly tailoring electromagnetic, chemical and thermal functions.

The proportion of functional materials and, in particular, electrical ceramics in daily life is going to increase enormously in the future: Chemical, optical or acoustic sensors will analyse the environment for us, actuators will help us influence it. More or less autonomous systems, controlled by computers and powered by an autarchic energy supply (battery) or by an “electrochemical metabolism” (fuel cell) are by no means visions for the distant future. Wherever it is possible, attempts are being made to replace fluid systems by solid ones, for instance, liquid electrolytes by solid ion conductors. In short: The importance of (inorganic or organic) solids can hardly be overestimated (even if we ignore the crowning functionality of biopolymers, as (almost)¹ done in this book). Furthermore, solid state reactions were not only of importance for and during the creation of our planet, they also constitute a large portion of processes taking place, nowadays, in nature and in the laboratory.

Perhaps you are a chemistry student in the midst of your degree course or a chemistry graduate already with a complete overview of the syllabus. You will then certainly agree that the greater part of a chemist’s education is concerned with liquids and, in particular, with water and aqueous solutions. Solids, when they are considered, are almost always considered from a naive “outer” point of view, i.e. as chemically invariant entities: Interest is chiefly concerned with the perfect structure and chemical bonding; in aqueous solutions it either precipitates or dissolves. Only the surface is considered as a site of chemical reactions. The concept of a solid having an “internal

¹See Section 6.10 of Chapter 6 for systems far from equilibrium.

chemical life”, which makes it possible for us to tailor the properties of a solid, in the same manner that we can those properties of aqueous solutions, sounds — even now — somewhat adventurous.

On the other hand, solid state physicists have influenced the properties of semiconductors such as silicon, germanium or gallium arsenide by defined doping in a very subtle way. If the reader is a physicist, I believe he or she would agree that the role of composition as a parameter is not sufficiently appreciated in physics. Even though internal chemical equilibria are sometimes considered and doping effects are generally taken into account, concentration is still too strongly focused on singular compositions and electronic carriers. In fact, a large number of functional materials are based on binary or multinary compounds, for which stoichiometric effects play an enormous role.

Lastly this text is addressed to materials scientists for whom the mechanical properties frequently and traditionally are of prime interest. Electrochemical aspects are generally not sufficiently considered with respect to their importance for the preparation and durability of the material and optimization of its function. Thus, the fields of ceramics, in general, and electroceramics, in particular, are addressed.

The chemistry and physics of defects play a key role in the following text [1,2]. After all, in the classical examples of water in chemistry and silicon in physics it is not so much the knowledge of the structure or of the chemical bonding that has made it possible to carry out subtle and controllable tuning of properties, but rather the phenomenological knowledge of the nature of relevant particles, such as H_3O^+ ions, OH^- ions or foreign ions in water that determine its acid–base and redox chemistry. In the case of silicon the relevant particles are conduction electrons and electron holes, which, on account of their properties, determine the (redox) chemistry and the electronic properties.

Focusing on such relevant particles leads to the generalized concept of defect chemistry that permits the treatment of internal chemical processes within the solid state (in this context Fig. 1.1 is illustrative). In processes, in which the structure of the

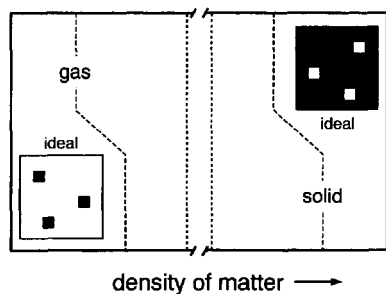


Fig. 1.1: In the same way as the treatment of ideal gases is simple — since the particles are dilute and uncorrelated (l.h.s.) —, the treatment of the solid state becomes equally simple from the viewpoint of the (dilute) defects (r.h.s.). (The portion of matter increases from the left to the right, while the portion of vacancies correspondingly decreases.)

phase does not alter, the perfect state can be regarded as invariant and all the chemical occurrences can then be reduced to the behaviour of the defects, that is, the deviations from the perfect state. The foundation stone of defect chemistry was laid

by Frenkel, Schottky and Wagner [1,2] as early as the 1930s; there is an extensive technical literature covering the field [3–14], but in chemistry and physics it has not yet become an adequate and generally accepted component of our training. In this sense this text is intended to motivate the chemist to deal with the internal chemistry of solid bodies. I hope that the effort will be rewarded with a density of “aha experiences” that will be adequate to compensate for the trouble caused by the physical language which is sometimes necessary. The physicist should be stimulated by the text to examine the internal equilibria of solid materials, changes in their composition and, in particular, the properties of more complex materials. The motivation here ought to be the fact that the formalism of defect chemistry is largely material independent, at least as long as the defect concentrations are sufficiently low, and that it offers a universal phenomenological description in such cases. Finally the text is intended to help the materials scientist to optimize the functional properties of materials, but also to understand the preparation and degradation of structural materials.

If this attempt at motivation is an “attack on open doors”, then the sentences I have written may at least act as a guide for the path ahead.

The text concentrates on ionic materials and on electrical and electrochemical properties in order to keep the contents within bounds. On the whole, we will refer to a “mixed conductor”, for which ion and electron transport are both important and with regard to which the pure electronic conductor and the pure ionic conductor represent special cases. We will specifically address material transport with regard to its significance for electrochemistry and reaction kinetics. Whenever necessary, indications of the generality of the concepts are interspersed. In order to make the treatment reasonably complete, references are given whenever a detailed consideration is beyond the scope of the book.

We start with an extensive introduction to the perfect solid, its bonding and its vibrational properties, knowledge of which is necessary for understanding the physical chemistry of the processes involved. In order not to lose sight of the purpose of the book these sections have been kept as simple as possible (but as precise as necessary). The same applies to the general thermodynamic and kinetic sections, which also serve to introduce the formal aspects. Nevertheless, in view of the heterogeneity of the potential readership, this detailed mode of presentation has been chosen deliberately in order to be able to assume a uniform degree of knowledge when discussing defect chemistry. Some material may be repeated later in the text and this is intended to ensure that some chapters can be omitted by the advanced readers without loss of internal consistency.

The text will have fulfilled its purpose in an ideal manner, if it not only conveys to the reader the elegance and power of the defect concept, when it not only puts him or her in the position of being able to recognize the common aspects of different properties and processes such as doping and neighbouring phase effects, ionic and electronic conductivity, passivation and corrosion of metals, diffusion and reaction processes, synthesis kinetics and sintering kinetics in solids, electrode reactions and

catalysis, sensor processes and battery processes; but also puts the reader in the position to optimize the solid state “strategically” at the “writing desk” in those situations in which the desired parameters are already known.

1.2 The defect concept: Point defects as the main actors

As already mentioned, phenomenological understanding of condensed phases with regard to the tunability of chemical and electrical properties implies knowledge of the defects as the relevant particles and their interactions, rather than (or at least in addition to) knowledge of the structure of the perfect state. This is known to be the key to phenomenological understanding of the aqueous phase and to control its chemical and electrical properties. In pure water these defects or “chemical excitations” are H_3O^+ and OH^- ions. Let us consider the first row in Fig. 1.2. As shown, it is advantageous, in a purely phenomenological sense, to subtract from

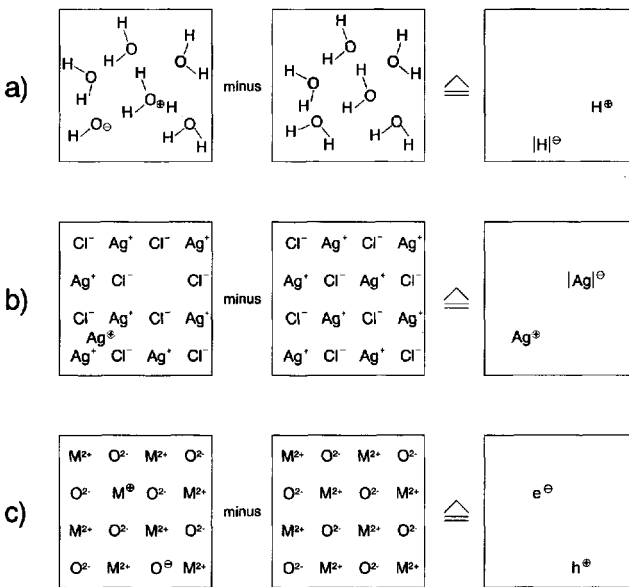
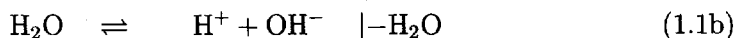
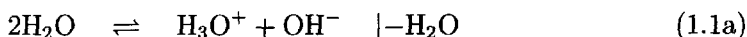


Fig. 1.2: a) If the basic compositionally unperturbed structure (chemical ground structure) is subtracted from the real structure, the point defects shown on the right remain. Naturally each is surrounded by a distorted region (effective radius of the point defect) which affects at least the immediate neighbourhood. In the case of fluid phases (see above) this procedure can only be regarded as an instantaneous picture. Owing to the absence of defined sites no distinction is made between various types of defect reactions as is done in the solid state. b) Frenkel disorder is sketched in the second row. c) The third row shows the case of purely electronic disorder whereby localized charge carriers are assumed for the sake of clarity [14].

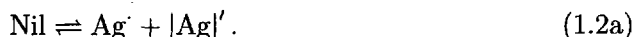
the real structure the instantaneous perfect water structure. We are left with an excess proton and a missing proton, i.e. a “proton vacancy”. This is also the result of subtracting the H_2O molecule completely (Eq. (1.1c)) from the autoprotolysis

reaction² according to

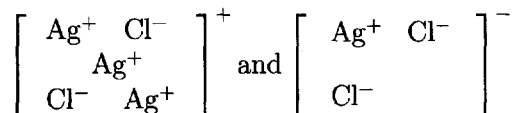


Here $|\text{H}|^-$ denotes a proton vacancy³.

Let us now consider disorder in a crystalline phase, to be specific, in solid AgCl. In this case some silver ions have left their regular sites⁴, and hence, left vacancies behind. As one can see (Fig. 1.2b), there is a very close analogy to Eq. (1.1). Even the nature of the driving force for the internal dissociation, namely the gain in entropy of configuration, is identical. The “subtraction” of the perfect structure as an invariant yields an excess cation (Ag') and a cation vacancy ($|\text{Ag}|'$) as the relevant particles. Just as in Eq. (1.1c) we can write



The old-fashioned charge designations (dot and dash) denote the relative charges: The crystal segments containing the defects such as



are positively or negatively charged in an absolute sense, but the local positive or negative charge at the proper defect-site — interstitial or vacant site — represents a charge relative to the perfect situation. This differentiation between absolute and relative charge was naturally not necessary for H_2O .

²It is naturally possible to formulate the whole of aqueous acid–base chemistry in water in this minimal notation. Eq. (1.1c) would also formally describe autoprotolysis in liquid ammonia. An analogous Cl^- disorder reaction would be suitable for describing the dissociation of SOCl_2 :



instead of



Conversely, these considerations emphasize that internal acid–base chemistry of solids involves point defects [15]. In Chapter 5 we will see that such acid–base reactions, together with redox-reactions, constitute defect chemistry.

³According to Eq. (1.1c) we could also refer to the OH^- ion (more precisely to the difference of OH^- and H_2O) as a proton hole or an anti excess-proton. The following joke may be instructive in this context: A mathematics teacher notices that 10 pupils left the class-room even though only 9 have been in. His comment: If one pupil enters the room, the occupation is zero and the world is in order again.

⁴Perfect AgCl is dissociated in the sense that it consists of ions; but it is not dissociated into free particles since Ag^+ and Cl^- are trapped in their deep Coulomb potentials. The latter, “superionic” dissociation is described by Eq. (1.2).

The disorder in the electron shells is to be comprehended in an analogous manner. Here the bonding electrons, more precisely the valence electrons, have left their “regular” positions and have been excited into the conduction band. This also creates excess particles and missing particles, which are conduction electrons (e') and electron holes (h'). Let us take a metal oxide with the (perfect) composition MO as our model compound and for the purpose of better visualization assume that, to a good approximation, the valence band is composed of the oxygen p-orbitals, while the conduction band is composed of the outer metal orbitals. Hence, the reaction can also be formulated as an internal redox reaction

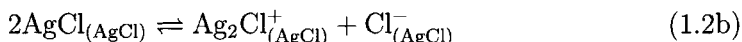


The minimal notation (subtraction of the perfect phase MO on both sides of the equation, see Fig. 1.2c) then becomes

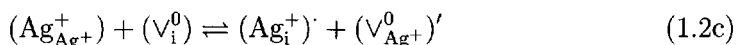


In silver chloride this corresponds to the charge transfer from Cl^- to Ag^+ . The advantage of the notation used in Eq. (1.3b) is that it is independent of such detailed bonding considerations. The building element formulation of Eqs. (1.2a), (1.3b) and also of Eq. (1.1c) is an adequate notation for the thermodynamic, i.e. phenomenological treatment and emphasizes the superposition of perfect and defect components in energetic questions.

Unfortunately the formulation suffers from a lack of vividness precisely on account of the high degree of abstractness. From a descriptive point of view, structure element formulation is to be preferred. Nonetheless, descriptions utilizing very detailed structural elements, as in Eq. (1.1b) or Eq. (1.1a), are not employed in the case of ionic solids, although the disorder in AgCl (Eq. (1.2a)) could certainly be analogously formulated as the “dissociation reaction of the lattice molecule” according to



(the lower index refers to the perfect state), or even — by analogy to H_9O_4^+ — by inclusion of further regular neighbours (see Chapter 5). The author has resisted, for two reasons, the temptation to select such a “molecular” notation: Firstly, the field of the “internal chemistry” of solids is already conceptually overloaded, and secondly, such a chemical notation would be clumsy for complicated solids or in kinetic considerations. Instead the conventional Kröger–Vink notation [3] is used: It also considers structural elements, in that it refers to absolute structures, but “boiled down” to only the “atomic” particles actually reacting. That means in the case of our silver chloride example that the anion–sublattice is completely omitted from the description, while, on the other hand, vacancies (here in the cation–sublattice) are explicitly taken into account as structural elements using the symbol v . So instead of Eq. (1.2a) or (1.2b) we write



or abbreviated by the omission of all absolute charges



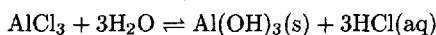
The superscript in Eq. (1.2d) again represents the relative charge, i.e. the difference between the charge in the real case and that in the perfect case ($\cdot \hat{=} -1$, $\cdot \hat{=} +1$). An effective charge of zero is not indicated or is sometimes indicated by means of a cross (“x”). The subscript denotes the crystallographic position in the perfect structure (i: interstitial site). Specifically Eq. (1.2d) indicates that a silver ion (Ag^+) has moved from a regular silver ion position (subscript Ag) to a vacant (V stands for vacancy) interstitial site (subscript i) where it becomes an interstitial silver ion Ag_i^{\cdot} and leaves a vacancy (V'_{Ag}) in the silver ion lattice. The regular components such as Ag_{Ag} , V_i or Cl_{Cl} do not carry an effective charge, while the interstitial silver ion bears the relative charge +1 ($= +1 - 0$) and the silver vacancy the relative charge -1 ($= 0 - (+1)$). Structure element notation is not used in the case of electronic defects, rather the building element notation of Eq. (1.3b). This has the advantage that, firstly, the formulation is independent of the nuances of the bonding and that, secondly, a possible double counting of electronic states⁵ is avoided. Since an ionic crystal is a rigid body with well-defined sites and the picture is only slightly complicated by vibrations (or rotations) about the equilibrium state, it is possible (and necessary) to distinguish in contrast to the fluid phase water, between several defect types, as will be discussed in Section 5.5.

In addition to defects intrinsically formed in pure substances by thermal disorder, defects are also generated by the incorporation of foreign substances. Hence, the (substitutional) incorporation of a D^{2+} cation in place of an M^+ cation leads to a point defect (D_{M}^{2+}) $\equiv \text{D}_{\text{M}}^{\cdot}$, while the (additive) interstitial incorporation of a cation of higher valence leads to a defect with a higher effective charge, namely D_i^{\cdot} . Although dissolved foreign substances are similarly important in liquids, it is necessary to point out another basic difference between liquid and solid phases: The simultaneous dissolution of cations and anions does not normally constitute a difficulty in the case of deformable fluids, and electroneutrality is automatically guaranteed. The normal case in the solid state is that either only the anion or the cation (here D^{2+}) is soluble. The dissolution of D^{2+} then takes place either by substitution of M^+ or by taking up an unoccupied interstitial position⁶. The change in charge must be compensated by creation of another defect. Thus, the introduction of D^{2+} (by substituting⁷ for an M^+ or by occupation of a free interstitial position) is associated with the formation of negatively charged ionic and electronic defects

⁵The electronic shell is included in the symbol for the element.

⁶As in organic chemistry, it is possible to distinguish between addition, substitution and elimination reactions (in and on the “giant molecule solid”). Rearrangement reactions also occur (cf. phase transitions).

⁷Such substitution reactions also play a role in aqueous solution: The precipitation reaction,



such as cation vacancies (V'_M) and conduction electrons. Such electronic (redox) and ionic (acid–base) effects are not independent of each other but appear simultaneously in a coupled way. Figure 1.3 shows cation vacancies created by substitution of a

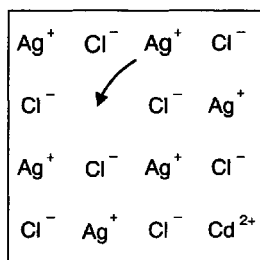


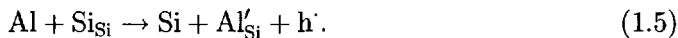
Fig. 1.3: Doping AgCl with CdCl₂ (only Cd²⁺ dissolves) leads to the formation of silver vacancies. The arrow indicates that silver conductivity is produced in this manner (migration of the vacancies in the opposite direction). This doping process generates electronic effects too, although to a small degree (see Section 5.6).

monovalent silver ion by a divalent cadmium ion. A further example is the creation of a high concentration of oxygen vacancies, and thus a high ionic conductivity in ZrO₂ by doping with CaO or Y₂O₃. This important ceramic material is used in automobile exhaust gas sensors and in high temperature fuel cells. The oxygen vacancies (V''_O) compensate for the charges of the Ca²⁺_{Zr} or Y³⁺_{Zr} defects. Electronic effects play a very minor role in this oxide. In defect notation the incorporation can be written as



A third example is the partial replacement of La³⁺ in La₂CuO₄ by Sr²⁺ (forming the defect Sr'_{La}). As in the previous example oxygen vacancies and electron holes are also produced here; but unlike in the previous case the electronic effects are significant. Hence, the substitution brings about marked oxydation of the crystal. The oxydation is necessary for the occurrence of “high temperature superconduction” in this oxide.

The procedure is similar for covalently bonded materials, such as silicon or organic polymers, although sites in the latter are not always sharply defined. If pentavalent phosphorus is introduced into silicon, this leads to the formation of some P_{Si} defects (that is P⁺ on Si), since the fifth valence electron in the sp³ hybridized basic silicon structure can be readily delocalized as a quasi-free electron. In the same manner trivalent aluminium takes electrons from silicon, that is from the valence band (Fig. 1.4). This defect (Al'_{Si}) bears the formal charge (−1) ((Al'_{Si0})). The electronic counterdefect is a delocalized electron hole (h[·]):



Ionic and electronic defects can also be created by an excess or deficit of a native component⁸ instead of by the introduction of foreign species. This takes place,

e.g., corresponds to the substitution of hydroxide groups by chloride in the aqueous substrate. This process too is associated with considerable changes in chemical (cf. acidity) and electrical (cf. proton conduction) properties.

⁸Native components are understood as components occurring in the pure material (i.e. M and X in MX). In binary compounds the phase width corresponds to the toleration of redox effects.

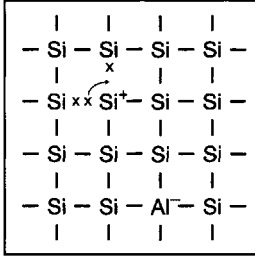


Fig. 1.4: Al doping of silicon effects the formation of a “vacancy” in the electronic shell (see arrow tip). The arrow indicates that this results in electronic (hole) conductivity. The electron hole migrates in the opposite direction.

for instance, in an oxide by interaction with the oxygen of the neighbouring phase (see Fig. 1.5). At sufficiently high temperatures, varying the oxygen content of the

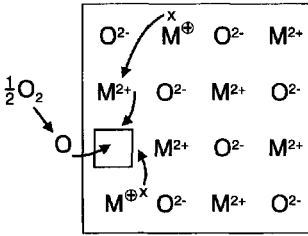


Fig. 1.5: Oxygen incorporation resulting from the jump of an adsorbed oxygen particle into a vacant oxygen site with the uptake of two electrons. In the example, the excess electron states correspond to monovalent metal ions. It is assumed, for the sake of the example, that the absorbed oxygen before passing into the vacancy, is in the neutral state, but this is generally not the case mechanistically.

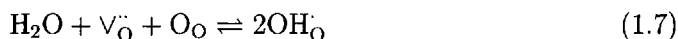
gas phase makes possible a continuous tuning of the precise position in the phase diagram. Such phase widths are often tiny and the changes obtained often negligible with respect to total mass or to the energy of the phase, but the change in defect density and all the properties specifically associated with it can be immense. Thus, in n-conducting SnO₂ an increase of the oxygen partial pressure of the surroundings leads to a drastic reduction in conductivity, according to:



In this case the oxygen introduced occupies oxygen vacancies in the lattice. It is incorporated in the form of O²⁻, and electrons are required for this; these are available in SnO₂ in the form of conduction electrons. In more chemically oriented terms we may state that reduced Sn states (Sn^{m+}, m<4) are oxydized and, thus, annihilated. If, as in La₂CuO₄, there are (almost) no excess electrons in the material, the incorporation of oxygen is associated with the consumption of bonding electrons. Holes are then created in the valence band and the p-type conductivity increases. Chemically⁹ speaking this corresponds to the oxydation of Cu²⁺ or O²⁻ to Cu³⁺ or O⁻. The hole density in La₂CuO₄ is increased in this manner and induces superconductivity at low temperatures.

⁹This simple chemical notation in terms of defined valence changes only provides a correct picture in those cases in which valence or conduction bands can be overwhelmingly assigned to the cation or anion (see Section 5.3). However, in general, there is a hybridization, as for the Cu and O orbitals in the case of cuprates.

For simplicity of presentation individual mechanisms have been emphasized until now. However, in practice, various different defect states occur simultaneously. Their distribution, i.e. their concentration, can be obtained from solution of the overall reaction scheme. This will be treated systematically in Chapter 5. Here we just mention that oxygen vacancies cannot only be destroyed by redox reactions but also by pure acid–base reactions. Thus, H_2O can be dissolved in many oxides with the formation of internal OH groups (OH^- on O^{2-} positions). According to



the “ OH^- part” of the water molecule occupies the vacancy, while the “ H^+ part” is added to a regular O^{2-} (i.e. O_{O}).

In this manner defects do not just constitute the “internal chemical life” but also the (chemical) “communication with the environment”. Naturally, the detailed kinetics must also be based on the defect concept. Every chemical or electrochemical process is made up of an interfacial reaction (more precisely a coupled scheme of individual elementary reactions at an interface) and the “transport reaction”, that is a site exchange process within the bulk of the solid. This is also valid for true solid state reactions involving the formation of a new phase. The necessary internal mobility is also made possible by the presence of defects, as shown in Figs. 1.3, 1.4 and also 1.5. The arrows indicate that an atomic vacancy or an electronic hole migrates by neighbouring atoms or electrons occupying the vacant sites. Hence, in this case defect transport and mass transport are in opposite directions. When excess ions or excess electrons migrate, the direction of defect transport and mass transport is identical. Diffusion processes, as described in this manner, frequently constitute the rate-determining step in solid state chemical kinetics. However, elementary reactions at interfaces, which are defect reactions, too, may also dominate the kinetics in many cases¹⁰.

Since the defects involved carry charges, they play a prominent role in the conversion of chemical signals to electrical signals (and vice versa). The example given in Fig. 1.6 can serve as leitmotif for this. As already explained, varying the oxygen content alters the internal chemistry (i.e. defect concentrations) of oxides, with immense effects on the electrical conductivity. The measurement of the electrical signal “conductivity” can be used for elegant and accurate detection or even for control of the oxygen content of the environment. Such a chemical sensor is only one of many highly interesting electrochemical applications.

This example also indicates the arrangement of this book. The thermodynamics of defects (Chapter 5) will enable us to specify the concentrations of the individual ionic and electronic defects and, thus, the ionic and electronic conductivities as a function of the relevant thermodynamic parameters (such as temperature and composition

¹⁰In the spirit of Chapter 5 the interface represents a (higher-dimensional) defect itself. Point defects within the interface are centres of enhanced reactivity (excitations within the higher-dimensional defect).

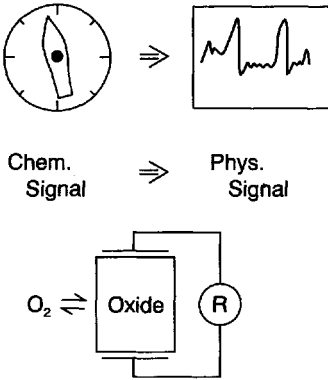


Fig. 1.6: The conversion of a chemical signal into a physical signal, using a conductivity sensor as an example. There the interaction with oxygen takes place in accordance with Fig. 1.5 and significantly influences the carrier concentrations. The implication arrow can usually be reversed and the physical signal can be applied to adjust the “chemistry”.

of neighbouring phase). In this way the (thermochemical¹¹) equilibrium state of the solid is precisely defined. In the defect chemical kinetics chapter (Chapter 6) we then consider mechanistically how and how rapidly changed state parameters bring about compositional changes. It is of particular importance for our example to elucidate how rapidly the defect concentrations and the conductivities change as the oxygen content changes. The charge of the defects makes electrochemistry a relevant subject *per se*. Since the thermodynamic and kinetic considerations already involve electrochemical equilibrium and nonequilibrium effects, the special electrochemical chapter (Chapter 7) at the end of the book is devoted to electrochemical systems that are of scientific importance — for the measurement, interpretation and control of interesting properties — or of technological importance for energy utilization or information conversion.

This main part of the book (Chapters 5, 6, 7) is obviously related to Materials Science; it is almost a trivium to conclude that, at least for ionic solids, now defect chemistry is fundamental to and, to a large extent, the substance of this interdisciplinary area¹². Materials research is synonymous with the strategic exploitation of structure–property relationships, with a view to the optimization of properties. If the question posed by material research is, say, the optimization of electrical properties via selection of materials and control parameters, then this question immediately refers back to the thermodynamics and kinetics of defect chemistry. As far as materials are concerned, we concentrate on ceramics and in particular on

¹¹The external shape, i.e. the surface, also belongs to the detailed description. Like the precise macrostructure (bulk plus surfaces) the “microstructure” (inclusion of internal interfaces, dislocations etc.) is almost without exception a nonequilibrium structure but highly relevant on account of its metastability (see Section 5.4).

¹²Materials research implies structure optimization on all relevant scales. The most important step is the selection of the solid ground state, i.e. synthesis of the chemical compound that is able to provide the optimizable “property world”. Within this framework tuning the defects allows fine-adjustment, but this is frequently accompanied by enormous variation in properties. The adjustment of the supra-atomic architecture in the form of nano-, micro- and macrostructure (external shape) completes the procedure. The appropriate combination of different materials then leads to the design of relevant systems (as treated in Chapter 7).

electroceramics. Although implicitly discussed, classical semiconductor materials as well as polymers are only touched on in order to emphasize the generality of the concepts.

The first four chapters dealing with the perfect state are more introductory. According to Fig. 1.2 we formally construct our real solids by superposition of the perfect solid ("chemical groundstate") and the defects ("chemical excitations"). Both ensembles are not independent of each other but strictly coupled in equilibrium. For this reason we start with a concise treatment of the chemically perfect solid. Firstly, there is a discussion (Chapter 2) of the chemical bonding and then of the formation of the solid state, followed by a discussion of lattice vibrations (Chapter 3).

The purpose of the chapter dealing with equilibrium thermodynamics of the perfect solid (Chapter 4) is to elaborate, on the one hand, simple expressions for the thermodynamic functions of the "chemical ground state" and, on the other hand, to make the reader familiar with questions of internal and external equilibria, not least with the intention to provide the equipment to deal with the thermodynamics of defect formation. (The major portion of the free enthalpy at absolute zero consists of bonding energy, while the temperature dependence is largely determined by the vibration properties.)

Evidently, the structure of this book refers to the classical areas of Physical Chemistry (bonding theory, thermodynamics, kinetics, electrochemistry) related, however, to the solid state. In this sense, the monograph may partly serve as a textbook of physical chemistry of solids. In order not to lose track of our subject we will confine ourselves to the simplest cases. Nonetheless the introductory chapters are rather comprehensive in order to take account of the heterogeneity of potential readers. This, however, should not distract from the actual topic of the book. Those, who are familiar with these aspects or who are only interested operatively in the application of the defect-chemical formalism can skip these introductory chapters with an acceptable loss of continuity or they can refer to them later if relevant problems arise in understanding.

2 Bonding aspects: From atoms to solid state

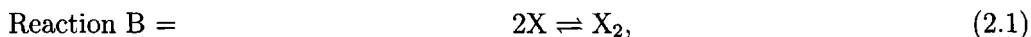
Strictly speaking, a knowledge of the state variables (these are temperature, pressure, etc. and the numbers of the different particles involved) is all that is required to calculate the equilibrium composition, structure and even the external equilibrium form (i.e. the shape of the solid body) using the Schrödinger equation (or more precisely its relativistic generalization, i.e. Dirac's equation). However, in view of the many-body problem such a statement is almost without exception purely academic. This is even more true in the case of nonequilibrium, and particularly for instationary systems. Calculations of this type are limited to the simplest of examples even if we separate the electronic from the nuclear motion and treat the systems in the time-independent single-electron approximation neglecting relativistic effects. Even then the uncertainties of the numerical solution are frequently of the order of magnitude of the differences of interest, when, for example, the stability of a given crystallographic structure is considered. For this reason the procedure generally employed is a combination of a priori chemical knowledge with respect to atomic and molecular properties and a posteriori knowledge with respect to the crystallographic structure.

Since a solid body represents a giant three-dimensional molecule ("3-D polymer") with possible anisotropy in the chemical bonding and with terminal groups constituting its surfaces, the description according to bonding theory is a many-body problem — in terms of both nucleons and electrons. It is appropriate to start out from the simplest type of chemical bond, namely the two-atom problem in the single-electron approximation. This is not only didactically appropriate, but also useful in so far as the energetics of the whole solid state are frequently largely represented by the short range interactions.

2.1 Chemical bonding in simple molecules

2.1.1 Ideal covalent bonding

Let us first consider an arrangement of two (a, b) atoms of the same nature (X_a, X_b) produced according to



in which it is only necessary to take account of one electron, a condition that is only strictly met in the H_2^+ molecule; hence, there are two relevant wave functions $|\widehat{ab}\rangle$ and $|\bar{a}\bar{b}\rangle$, which correspond to bonding and antibonding states and which are, to an approximation (according to the LCAO method), composed of the wave functions

of the single atom problems $|a\rangle$ and $|b\rangle$ as follows^{1,2}:

$$|\widehat{ab}\rangle \propto |a\rangle + |b\rangle \quad (2.2a)$$

$$|\widetilde{ab}\rangle \propto |a\rangle - |b\rangle. \quad (2.2b)$$

If the probability densities were merely summed, then, in a quasi-classical manner, the total probability density would be proportional to the sum of the squares (integrated and taking into account complex functions: $\langle ab|ab\rangle \propto \langle a|a\rangle + \langle b|b\rangle$). Since the wave functions interfere, there is, however, a higher electron density between the nuclei in the case of the bonding state ($\langle \widehat{ab}|\widehat{ab}\rangle \propto \langle a|a\rangle + \langle b|b\rangle + 2\langle a|b\rangle$) and a greatly reduced electron density in the case of an antibonding state ($\langle \widetilde{ab}|\widetilde{ab}\rangle \propto \langle a|a\rangle + \langle b|b\rangle - 2\langle a|b\rangle$). Nonetheless, it would be wrong to make the increased potential energy due to the increased electron density between the nuclei (cf. the term $2\langle a|b\rangle$) solely responsible for the bonding. The potential energy balance is not so favorable since the accumulation or removal of electrons from the centre takes place at the cost of the density at the atoms. Attention must therefore be paid to the conservation of charge and thus to the normalization (cf. proportionality factor in Eq. (2.2)). Moreover, the kinetic energy makes a significant proportion of the chemical bonding, as will be considered again below³. Overall, the situation in the two-atom problem now corresponds to the modified energy states $\widehat{\epsilon}$ and $\widetilde{\epsilon}$ which are approximately⁴ altered by $\pm\beta$ with respect to the initial energy $\epsilon_a = \epsilon_b$:

$$\widehat{\epsilon} = \epsilon_a - |\beta| \quad \text{and} \quad \widetilde{\epsilon} = \epsilon_a + |\beta|. \quad (2.3)$$

¹The procedure mentioned here is that of L. Pauling [16] and corresponds to a linear combination of atomic orbitals (LCAO) [17] which is extensively employed in the molecular orbital theory [18].

²In agreement with literature the Dirac bra/ket notation is used here to represent functions as vectors that are formed from the infinite set of the function values (or in a more operational representation as vectors in Hilbertian space spanned by the countable infinite set of basis-functions in which the function under regard is developed): $\langle c|$ designates the complex conjugate of $|c\rangle$, the scalar product $\langle c|d\rangle$ is then the sum over the products of the individual function values that is the integral over the corresponding product of the functions. The scalar product $\langle c|c\rangle$ is a measure of the integrated electron density referring to c and may be normalized to unity. Linear combination is naturally an approximation. That linear combination, which corresponds to the lowest energy, is, hence, not necessarily identical to the "true function", but, nevertheless, the readily proved variation theorem shows that it is the nearest of all possible alternative linear combinations to this. A variation calculation leads, in the case of a linear combination, to a normal minimax problem in the coefficients and to the solutions given above, as described in all quantum chemical textbooks (e.g. [19–22]). There is a clear treatment of the physical basis in Ref. [23].

³With respect to the complex interaction between kinetic and potential energy as a function of the nuclear distance and the importance for chemical bonding, cf. Ref. [24].

⁴Strictly speaking the above model yields

$$\widehat{\epsilon} = \frac{H_{aa} + H_{ab}}{1 + S} = (H_{aa} + H_{ab})(1 - S_{ab} + S_{ab}^2 - S_{ab}^3 + \dots)$$

If we now adopt for the two-electron problem (one bonding electron per X) the energy levels from this single-electron model⁵ and compare with the initial states, the bonding energy of the two atoms X_a and X_b in the molecule X_2 formed, i.e. the reaction energy in Eq. (2.1), is obtained as $\Delta_B \epsilon = 2\bar{\epsilon} - 2\epsilon_a \cong -2|\beta|$. The (negative) quantity β here represents the reduced resonance integral⁴

$$\beta = \langle a|\mathcal{H}|b\rangle - \langle a|\mathcal{H}|a\rangle\langle a|b\rangle. \quad (2.4)$$

In these integrals \mathcal{H} represents the Hamiltonian operator, that is the energy operator in the Schrödinger equation

$$\mathcal{H}|ab\rangle = \epsilon|ab\rangle. \quad (2.5)$$

As is well known this is obtained from the operators for the potential energy and the kinetic energy⁶. The integrals $\langle a|\mathcal{H}|b\rangle$ (resonance integral $\equiv H_{ab} = H_{ba}^* = H_{ba}$) and $\langle a|b\rangle$ (overlap integral $\equiv S_{ab} = S_{ba}^* = S_{ba}$) are measures of the overlap of the atomic orbitals, for they only have contributions differing from zero at those positions, for which both $|a\rangle$ and $|b\rangle$ differ from zero. Conversely, for a given internuclear distance, the contribution of the Coulomb integral $\langle a|\mathcal{H}|a\rangle$ ($\equiv H_{aa} = H_{bb} \equiv \langle b|\mathcal{H}|b\rangle$, also known as α) is only appreciably different from zero in the region of the nucleus. However, there the interaction with the neighbouring nucleus may be neglected and \mathcal{H} be set as equal to the Hamiltonian operator of the single atom problem; in consequence α can be represented by $\epsilon_a (= \epsilon_b)$, as already used in Eq. (2.3). Nevertheless, the presentation of the energy states by

$$\bar{\epsilon}_{ab} = \alpha - |\beta| \quad \text{and} \quad \bar{\epsilon}_{ab} = \alpha + |\beta| \quad (2.6)$$

is more generally valid than Eq. (2.3). Figure 2.1 illustrates the matrix elements and energy functions discussed as functions of the internuclear distance of H_2^+ .

$$\bar{\epsilon} = \frac{H_{aa} - H_{ab}}{1 - S} = (H_{aa} - H_{ab})(1 + S_{ab} + S_{ab}^2 + S_{ab}^3 + \dots).$$

Obviously the distance of $\bar{\epsilon}$ to H_{aa} is less than that of H_{aa} to $\bar{\epsilon}$. If $S_{ab} \ll 1$, β in Eq. (2.3) and Eq. (2.6) might be identified with the resonance integral; this assumption is generally unjustified (see [20]), but is frequently employed. The better approximation (Eq. (2.3) and Eq. (2.4)) does not completely agree with the second approximation of this presentation, but is a favourable approximation for the present problem since the missing term ($S_{ab}H_{ab}$) and the second order terms partially compensate (see sign).

⁵We obviously ignore electron-electron interactions. Later on, some situations in which such interactions will be important, will be briefly considered (see in particular Mott-Hubbard criterion). In these cases the ratio of the interaction energy and β is decisive for the strength of the effect.

⁶While the first is derived from classical momentum (\mathbf{p}) considerations via the transformation $\mathbf{p} \rightarrow \frac{\hbar}{2\pi i} \nabla$, the classical expression is retained in the case of the potential energy that only depends on the local coordinate. \mathcal{H} is, thus, given in the end by the space functions and the second space derivatives (kinetic energy \propto (momentum)²). It can be shown that \mathcal{H} is a Hermitian operator, i.e. $\langle a|\mathcal{H}|b\rangle = \langle b|\mathcal{H}|a\rangle^*$. The star denotes the complex conjugate. Such Hermitian operators have, as they must, real eigenvalues: Because $\langle a|\mathcal{H}|a\rangle = \epsilon\langle a|a\rangle$ and $\langle a|\mathcal{H}|a\rangle^* = \epsilon^*\langle a|a\rangle^* = \epsilon^*\langle a|a\rangle$, it follows that $\epsilon = \epsilon^*$.

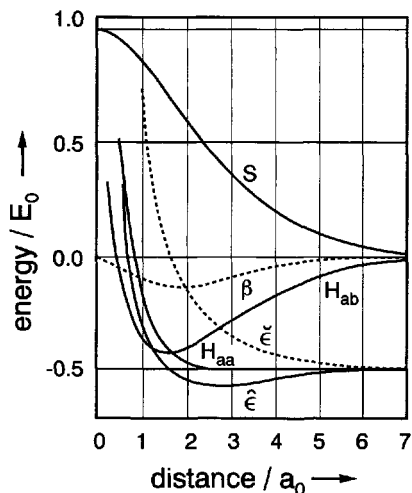
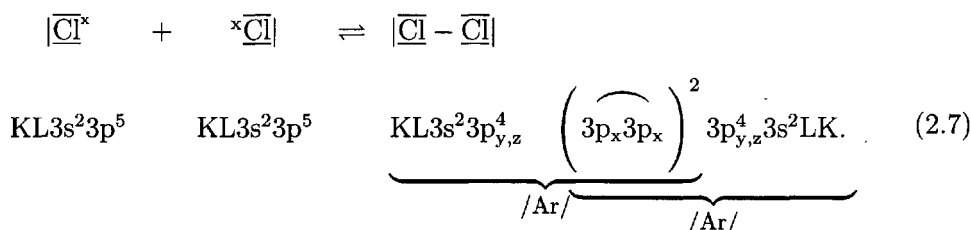


Fig. 2.1: The matrix elements $S_{ab} \equiv S, H_{ab}, H_{aa}$, the reduced resonance integral β and energy eigenvalues of H_2^+ as functions of nuclear distance. The equilibrium value corresponds to the minimum of $\hat{\epsilon}$ in the LCAO approximation used ($a_0 =$ Bohr unit of length $= 0.529 \text{ \AA}$; $E_0 =$ Hartree energy unit $= 27.21 \text{ eV}$). From Ref. [20].

The centring or symmetrical “sharing” of two bonding electrons can be generalized to cover the bonding of homonuclear atoms and, in the concrete case of the bonding of say a Cl_2 molecule, corresponds formally to the creation of two noble gas configurations (Ar-configuration $\equiv /Ar/$):



This is naturally a very approximate description in which not even all the outer electrons are included in bond formation. A more precise procedure creates 8 orbitals from the outer s and p electrons (which are referred to as σ and π orbitals depending on symmetry: $\sigma(s), \sigma^*(s), \sigma(p), \sigma^*(p)$ and two $\pi(p)$ and $\pi^*(p)$ orbitals⁷). The number of “real bonds” in the case of the example given above, e.g. in the case of the Cl_2 molecule is 1, since the corresponding antibonding orbitals are also filled for all orbitals apart from $\sigma(p)$ (14 outer electrons) and, thus, energetically nullify the effect of filling the respective bonding states approximately (Eq. (2.3)) (cf. “bond order” [21]). Figure 2.2 applies to the atomic dimers of the first octet in the periodic table. The energetic order of the levels shown comes from the fact that the s orbitals are energetically lower than the p orbitals and that the degree of overlap of the π orbitals is less than that of the σ orbitals and so, to an approximation, the corresponding

⁷The overlap of s-orbitals and of p-orbitals lying in the direction of the bonding axis (p_x see above) leads to σ orbitals, which are rotationally symmetrical about their bonding axis, while the p_y, p_z orbitals perpendicular to the axis form π bonds. For every MO orbital type there is a bonding ($\bar{\sigma}, \bar{\pi}$ or simply σ, π) and an antibonding ($\bar{\sigma}, \bar{\pi}$ or σ^*, π^*) level.

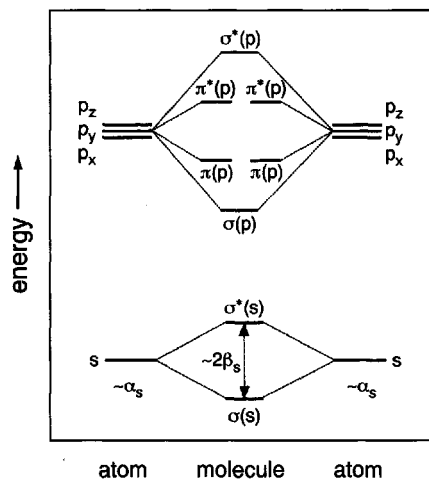


Fig. 2.2: The approximate position of the energy levels of the molecular orbitals in the homonuclear molecule X_2 formed from the atomic levels in X . Consider N_2 as an example. Since every nitrogen contributes 5 outer shell electrons, the lowest 5 MOs are doubly occupied. It is the occupation of the $\sigma(p)$ and of the two $\pi(p)$ orbitals, that contribute to bonding, the s interaction is nonbonding: $[N \equiv N]$. In the same manner a double bond is formed for O_2 from the p orbitals. However, here the $\pi^*(p)$ orbitals are singly occupied and the ground state is a triplet state. This explains the paramagnetism of the O_2 molecule.

$|\beta|$ values are smaller and the size of the splitting too. When orbital interactions are taken into account, these energy levels are altered; the changes are perceptible, at least for the light dimers of the first octet. The approximate Eq. (2.6) and Fig. 2.2 do not take into account that, strictly speaking, the splitting of the levels is asymmetrical⁴. The distance of the nonbonding states to the antibonding levels is greater than to the bonding levels. Already this explains why Ne_2 is unstable, while Fig. 2.2 merely predicts a nonbonding situation. In such cases the electron correlation, which has also been neglected, is of additional importance.

A slightly more complex example is the methane molecule CH_4 which exhibits four single bonds. Since each C–H two-centre interaction generates a bonding and an antibonding orbital and the four bonds are identical for reasons of symmetry, it is advantageous to consider these as having been formed from hybrid sp^3 atomic orbitals. These hybrids are linear combinations of the atomic orbitals, the molecular orbitals approximately linear combinations of the hybrid orbitals and, hence, as before, linear combinations of atomic orbitals. When, in hydrocarbons, there are three bonding neighbours it is advantageous to refer to sp^2 hybridized bonds, and in the case of two neighbours to sp hybridized bonds. The remaining p orbitals can form π bonds. The extensive literature on chemical bonding should be consulted for further discussion and in particular, if d and f orbitals are involved (e.g. [19–25]).

2.1.2 Polar covalent bonding

For reasons of symmetry the X_2 molecule already treated does not exhibit any permanent dipole moment. Permanent dipole moments are always the result of the charge being distributed asymmetrically in the bonded state, and thus occur in diatomic molecules formed from different atoms. According to

$$|\hat{a}\hat{b}\rangle \propto |a\rangle + \lambda |b\rangle \quad (2.8)$$

a different weighting of the atomic wave functions⁸ ($\lambda \neq 1$) is necessary. The degree of the effect (in molecule XY) is reflected by the difference in the electronegativity. According to Pauling this is obtained from the square root of the difference in the bonding energies of the virtually unpolarized molecule and of the actual molecule containing the ionic contributions. The first contribution is estimated from the arithmetic or geometric mean of the bonding energies of X_2 and Y_2 . If the electronegativities of the bonding partners are very different, the charge transfer is almost complete ($\lambda \rightarrow 0$ or $\lambda \rightarrow \infty$). In these cases the orbital relevant for bonding approximates to a pure atomic orbital ($|a\rangle$ or $|b\rangle$) and the corresponding resonance integral β is almost zero in such cases. This corresponds to the limiting case of ion formation described below. The α values for the two atoms naturally differ considerably and are also no longer identifiable with the energy of the single-atom problem.

If we take into account the difference in the α values by $\alpha_a = \bar{\alpha} + \Delta\alpha$ and $\alpha_b = \bar{\alpha} - \Delta\alpha$, then a Hückel calculation, which is only justifiable for weakly polar bonds (see Ref. [20]), yields instead of Eq. (2.6)

$$\bar{\epsilon}_{ab} = \bar{\alpha} - \Delta\alpha/\gamma \quad \text{and} \quad \bar{\epsilon}_{ab} = \bar{\alpha} + \Delta\alpha/\gamma, \quad (2.9)$$

where $\gamma = \Delta\alpha/\sqrt{(\Delta\alpha)^2 + \beta^2}$ represents the charge displacement or polarity⁹. $\Delta\alpha = (\alpha_a - \alpha_b)/2$ is sometimes also referred to as the polar energy.

Let us consider once again the H_2 molecule as the extreme case of the ideal covalent bond ($\Delta\alpha \rightarrow 0$, $\Delta\alpha/\gamma \rightarrow |\beta|$). Since two electrons occupy the lowest energy state twice in the case of the H_2 molecule and since we neglect electronic correlations, the bonding energy of two hydrogen atoms, is $2\beta = -2|\beta|$. Naturally there is no dipole moment in this case. According to Eq. (2.9) a weakly asymmetrical bond results in an approximate bonding energy¹⁰ of $2\beta(1 + (1/2)(\Delta\alpha/\beta)^2)$. Obviously there is only a second order correction on account of $|\Delta\alpha/\beta| \ll 1$, while the effect on the charge displacement is of first order and identical to $|\Delta\alpha/\beta|$ (see above).

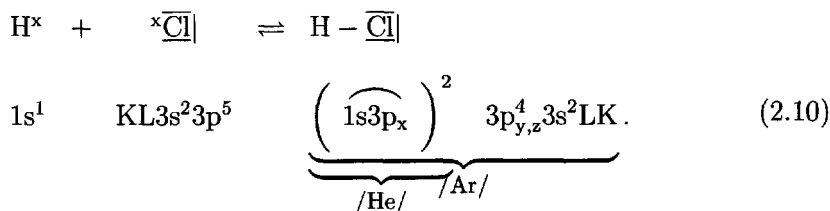
A polar atomic bond occurs, for instance, when a hydrogen atom comes into contact

⁸A dipole moment may also occur if the charges attributed to X and Y in a molecule XY are identical. This "homopolar dipole contribution" is caused by an asymmetry of the electron density centred between the two nuclei (overlap of "orbitals of differing sizes").

⁹The analogously defined parameter $\frac{|\beta|}{(\beta^2 + (\Delta\alpha)^2)^{1/2}}$ can be considered as the covalency of the bond [26].

¹⁰ $2\bar{\epsilon} - \epsilon_a - \epsilon_b = 2(\bar{\epsilon} - \bar{\alpha}) = -2\sqrt{(\Delta\alpha)^2 + \beta^2}$. Note, it follows for small x that $\sqrt{1+x} \simeq 1 + x/2$ since $(\sqrt{1+x} - \sqrt{1})/(1+x-1) \simeq d\sqrt{1+x}/dx|_{x=0} = \frac{1}{2}$. If we define the bond order as half the change in bonding energy with β [27], the result coincides with the covalency defined in footnote 9.

with a chlorine atom



In the language of the molecular orbital theory the orbital, that is relevant for bonding, is an energetically low, fully occupied $\sigma(1s, 3p_x)$ orbital, while the corresponding antibonding orbital remains unoccupied.

In principle, as for the X_2 molecule (see Fig. 2.2), the participation of other orbitals (e.g. $3p_{y,z}(\text{Cl})$ or $2s(\text{H})$) must be considered. However, in the case of HCl these differ so much energetically that Eq. (2.10) represents a good approximation¹¹.

On account of the finite charge transfer within the bond corresponding to an admixture of ionic, mesomeric structures, the stable configuration is best represented by $\text{H} \leftarrow \text{Cl}$ or $\text{H}^{\delta+} - \text{Cl}^{\delta-}$.

Once the electron distribution has been derived quantum-mechanically, it is possible to use classical considerations to calculate the forces occurring in the molecule, and thus also dipole forces; this is an expression of the Hellmann-Feynman theorem [28,29]. Such dipole-dipole interactions are naturally important when considering intermolecular interactions. The energy of dipole-dipole interactions decays with the third power of the distance of separation, the energies of dipole-multipole interactions fall off with a correspondingly higher power. The energy of dispersion interaction, which is still an interaction of comparatively long range and which is decisive for the interaction between neutral particles without permanent dipole, quadrupole or octupole moments, falls off more rapidly ($\propto R^{-6}$ for large R). This is responsible for the very weak form of bonding, which occurs, for instance, amongst noble gas atoms. It emerges from a higher order solution of the Schrödinger equation and can be regarded as resulting from interactions between mutually induced dipoles. This dipole moment disappears in the time average, but the interaction does not.

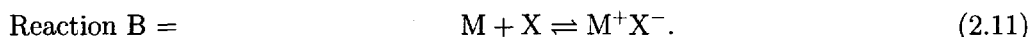
The hydrogen bond is a special sort of such an interaction. The bonding energies are generally considerably greater (typically 10...100 kJ/mol) and the bonding distances correspondingly smaller. One reason is the nature of the dipole moments that occur; in addition the electronegative partners can approach each other so closely that the hydrogen bonds take on the character of three-centre bonds with an electron excess. Exchange processes involving the protons (naked elementary particles) are expected to be important in many cases. The moderate values of the bonding energies and activation energies for formation and separation, which are less than

¹¹In the case of LiH it is not merely the two s orbitals but also $1s(\text{H})$ and $2p(\text{Li})$ that interact. However, these do not contribute appreciably to bonding.

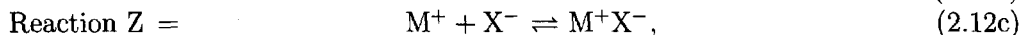
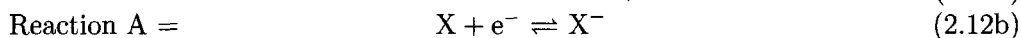
for ionic or covalent bonds but perceptible, predestine them for a fundamental role in biochemistry.

2.1.3 The ionic bonding

In the limiting case of ionic bonding ($\beta \rightarrow 0$) the bonding state corresponds to the double occupation of the relevant atomic orbital of the electronegative partner:



According to the treatment given in the previous section, a charge transfer of 1 (since $\Delta\alpha/\sqrt{(\Delta\alpha)^2 + \beta^2} \rightarrow 1$ for $\beta \rightarrow 0$) is correctly predicted. The predicted value for the energy of bonding, i.e. the energy of reaction B (2.11), $\Delta_B\epsilon = -2\Delta\alpha$, does emphasize the importance of the differing α values of the reactants, but is quantitatively incorrect, since the marked polarity of the bond exceeds the range of validity of Eq. (2.9). In order to avoid a more exact consideration, which would fall outside the terms of this sketch, we shall agree to use the following semiempirical approach. For the purpose of discussing the bonding energy of our “salt molecule” (such as occurs e.g. in the gas phase), we break up Eq. (2.11) into the partial steps



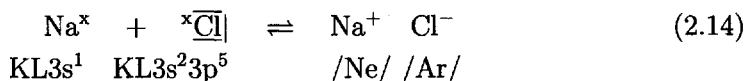
i.e. we first ionize atom M to yield the cation ($\Delta_I\epsilon = I_M =$ ionization potential of the metal) and transfer the released electron to X with the formation of the anion ($-\Delta_A\epsilon = A_X =$ electron affinity of X). Evidently, the third contribution then corresponds — assuming the nuclear distance (R) is sufficiently large — to the energy of the Coulomb interaction ($\Delta_Z\epsilon \propto (+1)(-1)/R$). Thus, the formation energy from the elements ($\Delta_B\epsilon$) only differs from the formation energy from the ions ($\Delta_Z\epsilon$) by the difference between the ionization potential of the electropositive partner and the electron affinity of the electronegative one:

$$\Delta_B\epsilon = (I_M - A_X) + \Delta_Z\epsilon = (I_M - A_X) - \text{const}/R. \quad (2.13)$$

Electron transfer does not occur solely as the result of the difference $I_M - A_X$ even in the case of caesium fluoride¹². The Coulomb energy between M^+ and X^- is essential. The third term in Eq. (2.13) is the only contribution that is directly dependent on both partners; however, it would be misleading to consider this contribution as the true bonding term, because the decision concerning whether complete charge transfer occurs, is dependent on the combination M/X and, hence, on $I_M - A_X$. The

¹²In the case of AgCl the formation of separate, gaseous ions of Ag^+ and Cl^- from the neutral gaseous components Ag and Cl (referred to 300K) requires ca. 3.8 eV ($I_{\text{Ag}} \simeq 7.55\text{eV}$, $A_{\text{Cl}} = 3.76\text{eV}$). It is bringing these together in the form of a gaseous “salt molecule” (gain of $|\Delta_Z\epsilon| = 6.9\text{eV}$) that finally leads to the release of energy (3.1 eV).

combination of an alkali metal element (e.g. Na) as a strongly electropositive component with a halogen (e.g. Cl) as a strongly electronegative component according to



is a prototype example of a primarily ionic bond. The transfer of the outer electron from sodium to chlorine means that both entities achieve a noble gas configuration: Na^+Cl^- is isoelectronic with NeAr , but exhibits a different charge distribution, reflecting the different character and strength of bonding.

Considering the last paragraphs it is not surprising that the important criterion for the formation of various types of bonds, that is the electronegativity, is also given by the arithmetical mean of the ionization and electron affinity: Thus, whether a molecule takes the form M^+X^- or the form M^-X^+ depends, according to Eq. (2.13), upon the difference $(I_M - A_X) - (I_X - A_M)$, so, in fact, upon $(I_M + A_M) - (I_X + A_X)$. The contribution described by Eq. (2.12c) does not enter the consideration because it is the same in each case. The equivalence of this concept by Mulliken with that of Pauling (see above) can be demonstrated by means of a simple Hückel calculation (see, for example, Ref. [20]).

The following ought to be mentioned concerning transition metal ions before we turn to the metallic bonding: Because of the differing spatial forms of the d orbitals (which are incompletely occupied in all relevant cases) an important correction is due to the splitting of the energy levels depending on the configuration of the nearest neighbours. If the ligands are octahedrally positioned the energy levels of the d_{xy^-} , d_{xz^-} and d_{yz^-} orbitals lie below that of the $d_{x^2-y^2}$ and the d_{z^2} orbitals. This is reversed if the ligand environment is tetrahedral; the degree of splitting is however lower in this case. These effects are of particular relevance in the discussion of the stability of complex ions and elementary ions in the crystal lattice, optical transition, magnetic effects and with regard to the correction of the lattice energy in crystals (cf. Section 2.2.2 and Ref. [30]).

2.1.4 Metallic bonding

Very electropositive atoms, such as the alkali metal elements, can only achieve the noble gas configuration by joint release of electrons



However, the complete expulsion of an electron is very unfavourable energetically; let us recall that the energy of reaction for this process is the highly positive ionization potential (5.2eV for Na). Stabilization in the form of bond formation only occurs in a many-body system ($N \gg 1$):



This will be discussed in more detail in Sections 2.2.1 and 2.2.5. In the molecular orbital picture many more nearest neighbours are bonded (Na: 8), than valence atom orbitals (4) and, in particular, many more than there are valence electrons (1) available. The bond formation in the metal is determined by ionization potential and the energy contributions ($\Delta\epsilon'$) required to condense¹³ the isolated charged particles to a solid and to delocalize the electrons (in the form of a quasi electron gas) in this structure:

$$\Delta_B\epsilon = I_M + \Delta\epsilon'. \quad (2.17)$$

The latter effect, which is of particular importance for the solid state electronic properties, can be explained in terms of the behaviour of electrons in extended systems. This will be discussed in Section 2.2.

A bonding mesomerism similar to that in metal crystals (see Section 2.2.1) can also occur under certain conditions within molecular subunits. If the ratio of metal to nonmetal element is unusually large with respect to the normal valence, metal clusters can occur as complex cations within which metal bonding is dominant. Such bonding peculiarities are discussed later (Section 2.2.6). The well-known situation in conjugated hydrocarbons is similar in a certain sense. In conjugated, unsaturated hydrocarbons the neighbouring carbons are joined by sp^2 bonds. As far as the remaining p-electrons are concerned, alternative limiting structures can be formulated, whose superposition is equivalent to partial delocalization.

2.1.5 Further intermediate forms of chemical bonding

Just as the polar atomic bonding already treated, is an intermediate form between ionic and covalent bonding (compare the series NaCl, MgCl₂, AlCl₃, SiCl₄, PCl₃, SCl₂, ClCl, in which the electronegativity of the more electropositive M element bonded to the constant X element is varied), there are also, according to the measuring rod of electronegativity, intermediate forms from covalent bonds and from ionic bonds in the direction of metallic bonds. While strongly electropositive elements, such as Na, form purely metallic bonds in a many-particle environment, that is the electrons play the role of (delocalized) anions, in the semimetals bonds occur that are intermediate between metallic and covalent bonding¹⁴. Examples include

¹³Cf. Eq. (2.12c) with $X^- \equiv e^-$.

¹⁴The term "localization" is not unambiguous (chemical localization vs. positional localization, electron localization vs. bond localization). Cf. Refs. [20,31,32] with regard to the difficulty and the demarcation of the terms "localized" and "delocalized", and with regard to the correspondence of local bonds and overall molecular orbitals in giant molecules. There it is shown that the local bond model can offer an appropriate description also in the many-particle system, namely for the limiting case of the covalent crystal with filled bands and significant gap ("equivalent orbitals"). A similar statement is true for the ionic crystal. However, in this case the local picture is to be preferred, as anion and cation states hardly overlap. Yet, it naturally fails in the case of the metallic bonding and for the intermediate forms discussed in Section 2.1.5.

graphite or bismuth^{15,16}. The transition from predominantly metallic behaviour to an exclusively covalent bonding is made clear by the following variation within a given row of the periodic system: NaNa, MgMg, AlAl, SiSi, PP, SS, ClCl.

A variation of the more electronegative partner X bonded to a constant electropositive atom M also transforms metals into nonmetals: Na, Na_xMg, Na_xAl, Na_xSi, Na₃P, Na₂S, NaCl. Here, in contrast to the previous case, the electron density is more and more shifted towards the (electronegative) partner¹⁴, eventually leading to ionic compounds: The intermediates in this row are the intermetallic compounds (cf. e.g. Na_xAl in the above row, or MgBi which may be compared with a Mg-metal on one side and with a Mg-halide on the other). These examples demonstrate that a deeper understanding requires the treatment of many-particle systems which are dealt with in Section 2.2.

2.1.6 Two-body potential functions

Although the various types of bonds may differ very greatly from each other they are very similar in one respect. The bond reacts to an increase in distance with a moderate restoring force, while the repulsive forces, that come into effect when the distance is reduced and which act over a small distance, react very sensitively to reduction of the equilibrium position. Hence, the potential function¹⁷ is of the form shown for the "bonding energy eigenvalue" in Fig. 2.1, and can be approximated, for example, by a superimposition of an r^{-m} and an r^{-n} term with $n > m$ (Mie potential [33]).

In the case of an ionic bond the first term is rather precise with $m=1$. Concerning the second term an $\exp(-\text{const. } r)$ law has a more fundamental basis as repulsion term (see Fig. 2.3). However, since the exponential term is also not strictly valid and the various models become equivalent for small displacements (cf. Morse potential [34], see also Lennard-Jones potential [35] and Born-Mayer potential [36] below), we will restrict ourselves to the Mie potential

$$\epsilon = Ar^{-n} - Br^{-m} = Ar^{-n} \left(1 - \frac{B}{A} r^{n-m} \right) = -Br^{-m} \left(1 - \frac{A}{B} r^{m-n} \right). \quad (2.18)$$

The condition for the equilibrium distance (\bar{r}), viz. $d\epsilon/dr = 0$, yields as a correlation between the bonding parameters A and B

$$\left(\frac{nA}{mB} \right)^{\frac{1}{n-m}} = \bar{r} \quad (2.19a)$$

¹⁵One band is almost full, the overlapped higher one almost empty (see Section 2.2).

¹⁶The fact that copper (a typical metal) has an electronegativity similar to bismuth (a semimetal) shows that electronegativity is not the decisive factor here.

¹⁷Since the motion of the electron is very rapid and therefore electronic equilibrium is usually established, with respect to r , it is possible to decouple electronic and nuclear problems. In the effective Schrödinger equation responsible for nuclear motion, the electronic energy plays the role of a potential energy. For this reason it is justifiable to call $\epsilon(r)$ the "potential function".

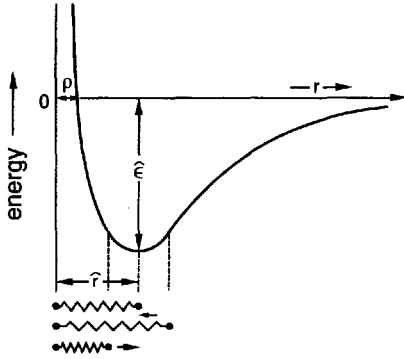


Fig. 2.3: Typical potential curve of a bond. The harmonic region of the displacement is indicated.

and hence for the equilibrium energy

$$\hat{\epsilon} = A\hat{r}^{-n} \left(1 - \frac{n}{m}\right) = -B\hat{r}^{-m} \left(1 - \frac{m}{n}\right). \quad (2.19b)$$

This makes it possible to express the potential in terms of the equilibrium parameters:

$$\frac{\epsilon}{\hat{\epsilon}} = \frac{1}{m-n} \left[m \left(\frac{\hat{r}}{r}\right)^n - n \left(\frac{\hat{r}}{r}\right)^m \right]. \quad (2.20a)$$

In the following text we will denote an equilibrium value by using an arc over the relevant species. Please note the different meaning of $\hat{\epsilon}$ compared with the previous paragraphs. There the same symbol denoted the energy of the bonding level at a given nuclear distance, while here it indicates the special value at the equilibrium distance. The Taylor expansion of the expression of Eq. (2.20a) yields a harmonic behaviour (Hooke's law) for small displacements ($r \simeq \hat{r}$) (see Fig. 2.3):

$$\frac{\epsilon - \hat{\epsilon}}{\hat{\epsilon}} = -\frac{1}{2}mn \left(\frac{r - \hat{r}}{\hat{r}}\right)^2. \quad (2.21)$$

A different representation refers r to $\rho \equiv r(\epsilon=0)$, that is to the value of r at the zero-point of the potential curve before ϵ rises rapidly (see Fig. 2.3). The parameter ρ is therefore a measure of effective particle size. Since for $r \equiv \rho$ the square brackets in Eq. (2.20a) equal zero, \hat{r} can be substituted by ρ via $\hat{r} = \rho(n/m)^{\frac{1}{n-m}}$, yielding

$$\frac{\epsilon}{\hat{\epsilon}} = \frac{1}{m-n} \left(\frac{n^n}{m^m}\right)^{\frac{1}{n-m}} \left[\left(\frac{\rho}{r}\right)^n - \left(\frac{\rho}{r}\right)^m \right]. \quad (2.20b)$$

For $n = 2m = 12$ this is the usual representation of the Lennard-Jones potential. The prefactor is then -4 .

These considerations are of particular importance when treating lattice energy and lattice vibrations. In the case of ionic bonding a Mie potential, supplemented with a term proportional to r^{-6} , is used usually for the mathematical simulation of the static and also the dynamic¹⁸ behaviour of atomic aggregates. Polarizability and covalency

¹⁸Molecular dynamics simulation or MD simulation for short.

effects are frequently accounted for by means of charge correction or by implementing a so-called shell model. In simple cases the conceptual difficulties with respect to the validity of the potential functions employed for such “computer experiments”¹⁹ can be avoided or diminished by carrying out a numerical *ab initio* calculation for the whole problem or by combining quantum-mechanical and empirical calculations [36–38].

2.2 Many atoms in contact: The solid state as a giant molecule

The formation of solids relies on the fact that bonding forces are not saturated in individual molecules. At sufficiently low temperatures the thermal energy is not high enough to “destroy” the intermolecular forces and a many-particle ensemble spontaneously forms a three-dimensional “polymer”²⁰, i.e. the solid. If the bonding forces in individual molecules are far from being saturated, the many-particle ensemble forms a solid body with a relatively large energy of formation (Fig. 2.4) from the molecules of which it is constituted. If they are approximately saturated then

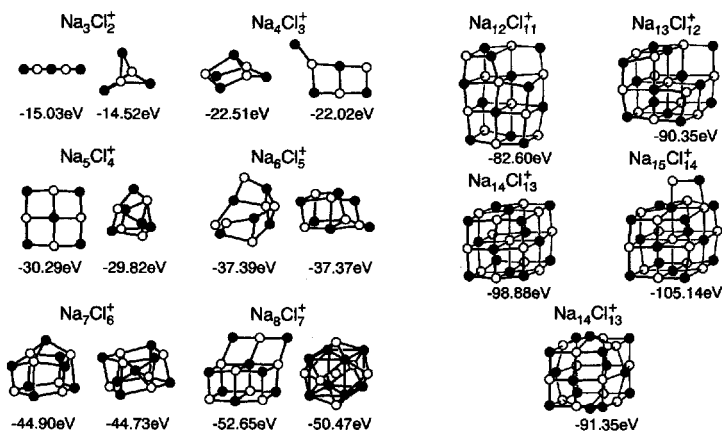


Fig. 2.4: Local stable (ionized) NaCl structures as a function of particle number (as detected in the mass spectrum) $((\text{NaCl})_N\text{Na}^+)$. The cubic rock salt structure is already established when $N > 10$. The formation energies (cf. numbers) refer to the reaction of the isolated ions. From Ref. [39].

the solid formed has a relatively low energy of formation and a low melting point. In this case there are large differences between intra- and intermolecular bonding forces.

Figure 2.4 shows the structural development from dimeric Na^+Cl^- to a very strongly bonded solid via (locally) stable, NaCl clusters (as a function of the particle number

¹⁹The expression “computer experiment” should not be taken too literally. It involves numerical mathematics with artificial input and not an experiment as such, in which, after all, “questions are put to nature”. However, it is possible to study the response to varying “external” conditions just as — or sometimes easier than — in a real experiment, and just as there the response needs to be interpreted.

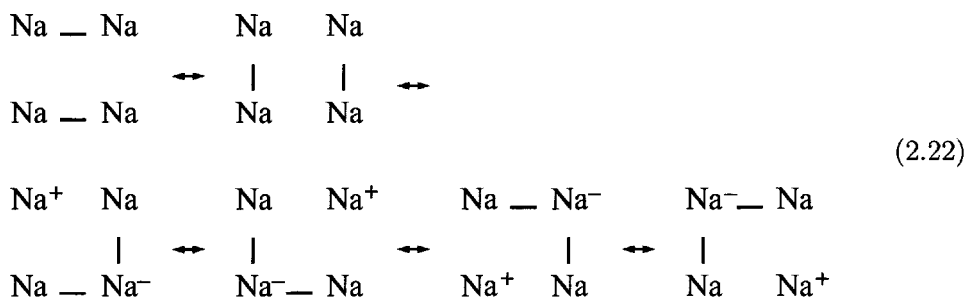
²⁰The bonding conditions as a function of the number of particles have been the subject of intensive investigation. This is particularly of interest for oligomeric clusters.

N). In this case the rock salt structure is realized very early on ($N > 10$)²¹. Molecular units can only be compositionally defined but not structurally or energetically identified. The interior of the “giant molecule”, the bulk, is structurally “screened” by the surfaces from the ambient. The surface region is, as it were, constituted by the terminal groups of the giant molecule, and is of fundamental importance in particular for the kinetics (see Section 5.4). Phase transformations correspond to rearrangement reactions of the total giant molecule. But let us now address the behaviour of electrons in the solid.

2.2.1 The band model

2.2.1.1 An electron in a potential-free box

As already mentioned the possibility of delocalization of electrons within a macroscopic aggregate is a characteristic of the crystalline solid state. The outer electrons of metals, in particular, behave as a “confined” electron gas. This is readily recognized by considering an arrangement of 4 Na atoms²². Such an ensemble represents a markedly electron-deficient state (one valence electron per Na); the energetically relevant mesomeric structures are²³



all of which contribute to the overall state with the result that the 3s electrons can be regarded as being distributed through the system without any perceptible localization effect and thus as being almost freely mobile.

For a further description, we use the single-electron approximation and confine a single electron for simplicity in a one-dimensional box of length L . We set the potential energy within the box to zero, while it is infinite at the walls of the box.

²¹If $a(N)$ is the mean energy of particles at the surface, $b(N)$ the corresponding mean energy of particles in the interior, then it follows approximately for the total energy of a cube that $E = 6aN^{2/3} + b(N - 6N^{2/3})$ or $E/N \simeq 6(a - b)N^{-1/3} + b$. (However, the cluster must however be so large that it is possible to neglect edge and corner effects.) According to Ref. [40] this relationship (a, b constant) is already fulfilled for surprisingly small NaCl-clusters ($N \geq 10$).

²²In the real Na crystal the deficit situation is more marked on account of the higher coordination number (8).

²³See also Ref. [25] here. Reference has already been made to the similarity of the situation in conjugated hydrocarbons (see Section 2.1.4) with respect to the p electrons remaining after sp^2 hybridization, even though there is not an electron deficit situation in the strict sense.

As a result of this the Hamiltonian operator reduces to the operator for the kinetic energy that is $-\hbar^2(\partial/\partial x)^2/(8\pi^2m)$.

The Schrödinger equation for the wave function $|k\rangle$ leads to a linear homogeneous differential equation of the form $(\partial/\partial x)^2|k\rangle \propto -|k\rangle$ for which sine and cosine functions are relevant solutions. At the two ends of our box $\langle k|k\rangle = 0$ and, hence, $|k\rangle = 0$ must hold²⁴. The disappearance of the function at $x = 0$ only permits the sine function:

$$|k\rangle \propto \sin kx = \sin \frac{2\pi}{\lambda}x. \quad (2.23)$$

The parameter k designates the wave vector which is reduced here to a component in the x direction; λ is the associated wavelength ($\lambda = 2\pi/k$)²⁴. The relationship between k (and hence also λ) and the energy eigenvalues ϵ is obtained by substitution in the Schrödinger equation $(-\hbar^2/8\pi^2m)(\partial/\partial x)^2|k\rangle = \epsilon|k\rangle$ as

$$k = \pi\sqrt{8m\epsilon/\hbar^2}, \quad (2.24)$$

and is, thus, a square root function.

However, only those wavelengths and, hence, values of k and energy eigenvalues, of which the corresponding wave functions are also zero at the other wall, that is at $x=L$, are permitted. This is obviously the case if $k\cdot L$ is an integral multiple of π or, in less abstract terms, if the length of the box is an integral multiple of the half wavelength. In other words (Eq. (2.24)) the following simple relationship between the energy eigenvalues and the box length must be obeyed:

$$\epsilon = \frac{\hbar^2 n^2}{8mL^2} \quad \text{with } n = 1, 2, 3, \dots \quad (2.25)$$

As can be seen from Eq. (2.25) and Fig. 2.5 the energy increases quadratically as a function of the quantum number n and falls quadratically with the length of the box. The energies of the highest occupied and the lowest unoccupied states at $T=0K$, ϵ_{HO} and ϵ_{LU} , which also vary with L^{-2} are of particular interest (see below).

Fig. 2.5 then shows us how, at given n in a one-dimensional arrangement, the energy levels decrease with the number of constituent nuclei and thus with the number of electrons introduced. Doubling the size of the one-dimensional atomic box results in a decrease of the energy term by a factor of four (in this model solely as a result of "kinetic energy"). This is — as already indicated above — of great importance in chemical bonding²⁵. But back to our problem: The two-centre bond showed us that two identical energy levels become two new levels displaced upwards or downwards by approximately β . In a similar manner 4 Na atoms yield four energetically different levels and N Na atoms N different levels (inset in Fig. 2.5). From this it does not

²⁴This interpretation of k follows from the periodicity: $\sin kx = \sin(kx+2\pi) = \sin[k(x+2\pi/k)] = \sin[k(x+\lambda)]$.

²⁵However, this must not be taken as evidence of the dominance of kinetic energy in molecule formation, since in the approximate picture the partitioning of the total energy into E_{kin} and E_{pot} is not the correct one.

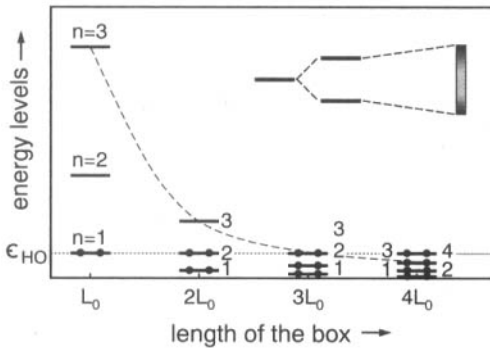


Fig. 2.5: The dependence of the energy level of an electron in a box on the quantum number and the length of the box. If we assume that a box of size L_0 contains just two particles, that of size $2L_0$ four particles etc., the dotted line shows the constancy of the width of the occupied zone (more generally: see Fermi level, Section 5.3). The broken line emphasizes for $n=3$ the reduction in energy with increasing box length for a given quantum number. The inset shows the splitting of a one-electron state at the start to a continuous band in the MO-LCAO model (cf. Fig. 2.2) for a chain of many atoms. Please note the difference in the density of states.

yet follow that individual sharp energy levels become bands; this is a consequence of the fact that according to Eq. (2.25), the energy difference between two levels decrease strongly (quadratically) as L increases:

$$\epsilon_{n+1} - \epsilon_n = \frac{2n+1}{L^2} \frac{h^2}{8m^2}. \quad (2.26)$$

The $\epsilon(k)$ curve then becomes virtually continuous. Equation (2.26) predicts a density of states which decays with increasing energy. Since the s-band of a sodium metal crystal (to remain with the example above) contains a limited number of states, Eq. (2.25) derived for the free electrons, cannot offer a sufficient description. The alternative treatment, which starts from atomic orbitals and yields the molecular orbitals of a one-dimensional chain via linear combination (cf. Section 2.1), leads to the nonmonotonic density of states shown in the inset of Fig. 2.5. (It follows from the fact that $\epsilon(k)$ depends on k via a cos-function (see following section, Eq. (2.32)); the density of states is great where the graph of $\epsilon(k)$ is flat.) One expects from Fig. 2.2 (and it will become obvious from Eq. (2.32) on page 43) that the width of the band will be of the same order of magnitude, namely $\sim \beta$. Accordingly the splitting of neighbouring levels is of the order of β/N . If there is 1 mol particles and $\beta = 6\text{eV}$ then β/N is $\sim 10^{-23}\text{eV}$ corresponding to 10^{-18}J/mol . This may be compared with the thermal molar energy RT which is still of the order of 10J/mol even at 1K .

In addition the density of states changes with dimensionality. This is already so in the case of the quasi-free electron approximation. A three-dimensional box with dimensions $L_x \times L_y \times L_z$, in which the energy eigenfunction has, on account of the factorizability of the wave function, the general form

$$\epsilon = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right); \quad (2.27)$$

there are already so many degeneracies at higher quantum numbers for each value of ϵ that, in fact, the density of the states increases with the energy ϵ . Let us consider