

# Chapter 1

## Introduction

### 1.1 Schrödinger Equation for Molecules

we consider a molecule formed by  $N_{\text{nuc}}$  atoms which are counted by  $n = 1, 2, \dots$  with atomic numbers  $Z_1, Z_2, \dots$ ;

nuclear coordinates are denoted by  $\mathbf{R}_n$ , and the whole set of coordinates by  $R = \{\mathbf{R}_n\}$ ;

the total number of electrons is  $N_{\text{el}}$ ; if we consider a neutral molecule we get  $N_{\text{el}} = \sum_n Z_n$ ;

electron coordinates are  $\mathbf{r}_j$ , and the whole set of coordinates is abbreviated by  $r = \{\mathbf{r}_j\}$ ;

the molecule has  $3N_{\text{el}} + 3N_{\text{nuc}}$  spatial degrees of freedom; subtracted are the three degrees of freedom of translation and rotation of the total system;

$N_{\text{el}}$  spin degrees of freedom have to be added; single electron spin-quantum number is denoted as  $\sigma_j$ ;

nuclear spins need not to be considered as dynamical variables;

the used Hamiltonian should represent a non-relativistic approximation; spin-orbit coupling is neglected;

the Hamiltonian of a molecule contains the kinetic energy of the electrons  $T_{\text{el}}$ , the kinetic energy of the nuclei  $T_{\text{nuc}}$ , the repulsive interaction among all electrons  $V_{\text{el-el}}$  and among all nuclei  $V_{\text{nuc-nuc}}$  and, finally, the attractive interaction between electrons and nuclei  $V_{\text{el-nuc}}$ ;

$$H_{\text{mol}} = T_{\text{el}} + V_{\text{el-el}} + V_{\text{el-nuc}} + V_{\text{nuc-nuc}} + T_{\text{nuc}}$$

$$T_{\text{el}} = \sum_j \frac{\mathbf{p}_j^2}{2m_{\text{el}}}$$

$$V_{\text{el-el}} = \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_{\text{el-nuc}} = - \sum_{j,n} \frac{Z_n e^2}{|\mathbf{r}_j - \mathbf{R}_n|}$$

$$V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{m,n} \frac{Z_m Z_n e^2}{|\mathbf{R}_m - \mathbf{R}_n|}$$

$$T_{\text{nuc}} = \sum_n \frac{\mathbf{P}_n^2}{2M_n}$$

the sum formulas exclude divergent terms;  
stationary Schrödinger equation for the molecule reads:

$$H_{\text{mol}}\Psi_{\lambda}(\{\mathbf{r}_j, \sigma_j\}, \{\mathbf{R}_n\}) = \mathcal{E}_{\lambda}\Psi_{\lambda}(\{\mathbf{r}_j, \sigma_j\}, \{\mathbf{R}_n\})$$

since electrons are identical particles (with spin one half) the wave function has to be antisymmetric with respect to an interchange of the electron coordinates  $\mathbf{r}_j, \sigma_j$ ; this is not valid for the nuclei (except some very special cases)

solution of the stationary Schrödinger equation fixes the energy spectrum  $\mathcal{E}_{\lambda}$  and the eigenfunctions  $\Psi_{\lambda}$ ;

if  $\mathcal{E}_{\lambda} < 0$ , the molecule as a bound state of atoms is stable;

for future use we write  $\Psi(r, \sigma, R)$  instead of  $\Psi(\{\mathbf{r}_j, \sigma_j\}, \{\mathbf{R}_n\})$

stationary Schrödinger equation takes the form

$$H_{\text{mol}}\Psi_{\lambda}(r, \sigma, R) = \mathcal{E}_{\lambda}\Psi_{\lambda}(r, \sigma, R)$$

in the same manner we obtain the time-dependent Schrödinger equation as

$$i\hbar\frac{\partial}{\partial t}\Psi(r, \sigma, R; t) = H_{\text{mol}}\Psi(r, \sigma, R; t)$$

the formal solution reads

$$\Psi(r, \sigma, R; t) = e^{-iH_{\text{mol}}(t-t_0)/\hbar}\Psi(r, \sigma, R; t_0)$$

the wave function  $\Psi(r, \sigma, R; t_0)$  represents the initial value of the time-dependent wave function  $\Psi(r, \sigma, R; t)$ , and we introduced the time-evolution operator

$$e^{-iH_{\text{mol}}(t-t_0)/\hbar} = U_{\text{mol}}(t - t_0)$$

## The Electron Spin

while  $\Psi(r, \sigma, R)$  represents the molecular wave function for a particular spin configuration the correct wave function should be an eigenstate of the total electron spin operator and its  $z$ -component; a superposition of the  $\Psi(r, \sigma, R)$  for different spin configurations may become necessary

$$|\Psi_{S, S_z}(r, R)\rangle = \sum_{\sigma} \Psi(r, \sigma, R)|\sigma\rangle$$

the superposition is not necessary when the so-called **closed shell configuration** is present; this is valid if the number of all electrons is even and  $N_{\text{el}}/2$  electrons are in a spin-up state and the same number in the spin-down state; the singlet state (zero overall spin) may be written as

$$|\Psi_{S=0, S_z=0}(r, R)\rangle = \Psi(r, R) \sum_{\sigma} \zeta(\sigma)|\sigma\rangle$$

the spatial electronic and nuclear degrees of freedom enter a single molecular wave function  $\Psi(r, R)$  (the function  $\zeta(\sigma)$  realizes the overall singlet spin configuration); we will exclusively consider this case in the following;

### 1.1.1 The Born–Oppenheimer Ansatz: Expansion with Respect to Adiabatic Electronic States

when solving the molecular Schrödinger equation we may profit from the huge mass difference between electrons and nuclei; the mass ratio reads:  $m_{\text{el}}/M_n < 10^{-4}$ ; we may assume that the electronic motion is much faster than that of the nuclei (semi-classical argument since nuclear coordinates have a spatial uncertainty); nuclear motion induces an *adiabatic* change of the potential  $V_{\text{el-nuc}}$ ; general procedure: we, first, compute the electronic states (electron configuration) for a fixed nuclear configuration; the resulting wave functions  $\phi_a(r; R)$  and energies  $E_a(R)$  parametrically depend on the nuclear configuration  $R$ ; they should be a good starting point for a solution of the molecular Schrödinger equation  $\rightarrow$  *Born–Oppenheimer ansatz*;

$$\Psi(r, R) = \chi(R)\phi(r; R)$$

#### Electronic Schrödinger Equation

electronic Hamiltonian depends on the actual nuclear configuration  $R$ :

$$H_{\text{el}} = T_{\text{el}} + V_{\text{el-nuc}} + V_{\text{el-el}} = H_{\text{el}}(R)$$

related Schrödinger equation:

$$H_{\text{el}}(R)\phi_a(r; R) = E_a(R)\phi_a(r; R)$$

eigenvalues  $E_a(R)$  are known as *adiabatic electron terms* referring to *adiabatic electronic wave functions*  $\phi_a(r; R)$  ;

it is the subject of *Quantum Chemistry* to solve the electronic Schrödinger equation and to describe the energy spectrum and the wave functions in detail

the reference method is the Hartree–Fock approach, where the wave function is represented as an anti-symmetrized product of single electron wave functions; numerous improvements have been introduced over the years (configuration interaction methods, coupled cluster approach, Moller–Plesset perturbation theory); a very different approach is known as the *density functional method*;

adiabatic electronic wave functions form a complete set (for every nuclear configuration); therefore we may expand the molecular wave function with respect to the electronic wave functions

$$\Psi(r, R) = \sum_a \chi_a(R)\phi_a(r; R)$$

this reproduces the Born–Oppenheimer ansatz in a more involved version; the expansion coefficients  $\chi_a(R)$  depend on the nuclear configuration and obey the following normalization condition (note the abbreviation of the integrals with respect to electronic and nuclear coordinates):

$$\int dr dR |\Psi|^2 = \sum_a \int dR |\chi_a|^2 = 1$$

## Operator of Nonadiabatic Coupling

the expansion coefficients  $\chi_a(R)$  can be obtained by inserting the expansion of the molecular wave function into the molecular Schrödinger equation

$$\begin{aligned} H_{\text{mol}}\Psi &= (H_{\text{el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}}) \sum_a \chi_a \phi_a \\ &= \sum_a \left( E_a \chi_a \phi_a + (T_{\text{nuc}} + V_{\text{nuc-nuc}}) \chi_a \phi_a \right) = \mathcal{E} \sum_a \chi_a \phi_a \end{aligned}$$

we multiply with  $\phi_b^*$  from the left and carry out an integration with respect to all electronic coordinates; it follows an equation for the expansion coefficients  $\chi_a$

$$\begin{aligned} \langle \phi_b | H_{\text{mol}} | \Psi \rangle &= \int dr \phi_b^* H_{\text{mol}} \Psi \\ &= (E_b + V_{\text{nuc-nuc}}) \chi_b + \sum_a \langle \phi_b | T_{\text{nuc}} | \phi_a \rangle \chi_a = \mathcal{E} \chi_b \end{aligned}$$

the dependence of the electronic wave function  $\phi_a$  on the nuclear coordinates has to be properly taken into account:

$$\begin{aligned} \langle \phi_b | T_{\text{nuc}} | \phi_a \rangle \chi_a &= \sum_n \langle \phi_b | \frac{\mathbf{P}_n^2}{2M_n} | \phi_a \rangle \chi_a \\ &= \sum_n \frac{1}{2M_n} \langle \phi_b | \left( [\mathbf{P}_n^2 | \phi_a \rangle] \chi_a + 2[\mathbf{P}_n | \phi_a \rangle] \mathbf{P}_n \chi_a + | \phi_a \rangle \mathbf{P}_n^2 \chi_a \right) \end{aligned}$$

the first two terms of this expression will be abbreviated by

$$\hat{\Theta}_{ba} = \langle \phi_b | [T_{\text{nuc}} | \phi_a \rangle] + \sum_n \frac{1}{M_n} \langle \phi_b | [\mathbf{P}_n | \phi_a \rangle] \mathbf{P}_n$$

they form the *nonadiabaticity operator*, the *operator of nonadiabatic coupling*; the approach turned the total molecular Schrödinger equation into a Schrödinger equation which focuses on the nuclear motion (note the interchange of  $a$  and  $b$ )

$$\mathcal{E} \chi_a = (T_{\text{nuc}} + E_a + V_{\text{nuc-nuc}}) \chi_a + \sum_b \hat{\Theta}_{ab} \chi_b$$

supposition for a solution is the solution of the electronic Schrödinger equation (at all nuclear configurations); respective quantum numbers of nuclear motion are  $\lambda$ ; total electronic spectrum determines the solution for a particular  $\lambda$ ; coupling between different functions  $\chi_a$  realized by the operator  $\hat{\Theta}_{ab}$ ; molecular wave function takes the form:

$$\Psi_\lambda(r, R) = \sum_a \chi_{a\lambda}(R) \phi_a(r; R)$$

normalization

$$\langle \Psi_\lambda | \Psi_{\lambda'} \rangle = \sum_a \langle \chi_{a\lambda} | \chi_{a\lambda'} \rangle = \delta_{\lambda, \lambda'}$$

## Potential Energy Surfaces

repulsive potential between different nuclei plus the electronic eigenvalue with its parametric dependence on the nuclear coordinates forms an effective potential

$$U_a(R) = E_a(R) + V_{\text{nuc-nuc}}(R)$$

this potential determines the nuclear motion and is known as the *Potential Energy Surface (PES)*;

presence of  $E_a$  in the formula for  $U_a$ :

electron cloud around the nuclei of the molecule screens their mutual repulsive interaction; attraction becomes possible; formation of bound states;

if the electronic wave function is real the diagonal part of the  $\Theta$ -operator becomes a multiplication operator; it will be included into the definition of the PES

$$U_a = E_a + V_{\text{nuc-nuc}} + \Theta_{aa}$$

if the nonadiabatic coupling is of less importance we arrive at

$$(T_{\text{nuc}} + U_a)\chi_{a\nu}^{(\text{adia})} = \mathcal{E}_{a\nu}^{(\text{adia})}\chi_{a\nu}^{(\text{adia})}$$

the solutions refer to a single adiabatic energy level  $E_a$  and are named *adiabatic approximation* of the electron-vibrational states; the  $\nu$  are the quantum numbers of vibrational motion and the respective energy spectrum is given by  $\mathcal{E}_{a\nu}^{(\text{adia})}$ ; the  $\chi_{a\nu}^{(\text{adia})}$  can be considered as eigenstates of the vibrational Hamiltonian

$$H_a = T_{\text{nuc}} + U_a$$

the PES should have a minimum at  $R_0$ ; if  $\phi$  is used at  $R = R_0$  we arrive at the simple adiabatic approximation or the so-called *Born-Oppenheimer approximation* (Born and Oppenheimer, 1927);

detailed knowledge of the PES  $U_a(R)$  forms the basis for an understanding of vibrational dynamics, conformational changes, formation and breaking of chemical bond (dynamics of chemical reactions);

shape of the PES defines molecular structure, presence of tautomers, form of reaction pathways;

## Time-Dependent Nuclear Schrödinger Equation

we use the expansion of the molecular wave function with respect to adiabatic electronic states in the case of a time-dependent molecular wave function

$$\Psi(r, R; t) = \sum_a \chi_a(R, t)\phi_a(r; R)$$

the expansion coefficients  $\chi_a(R, t)$  become time dependent, thus they form time-dependent nuclear wave functions and obey the following Schrödinger equations

$$i\hbar \frac{\partial}{\partial t} \chi_a(R, t) = H_a \chi_a(R, t) + \sum_b \hat{\Theta}_{ab} \chi_b(R, t)$$

the motion of the wave function in the adiabatic electronic state  $\phi_a$  is determined by the vibrational Hamiltonian  $H_a$ ; the nonadiabatic coupling operators  $\hat{\Theta}_{ab}$  induce transitions to other electronic states;

## Adiabatic Electronic State Representation of the Molecular Hamiltonian

the  $\phi_a(r; R)$  form a complete basis (for every nuclear configuration  $R$ ); the single function can be considered as the coordinate representation of a state vector  $|\phi_a(R)\rangle$ :

$$\phi_a(r; R) = \langle r | \phi_a(R) \rangle$$

notation of the completeness relation independent on the actual representation

$$\sum_a |\phi_a(R)\rangle \langle \phi_a(R)| = 1$$

the adiabatic state representation of the molecular Hamiltonian is obtained as

$$\begin{aligned} H_{\text{mol}} &= \sum_{a,b} \langle \phi_a | H_{\text{el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}} | \phi_b \rangle | \phi_a \rangle \langle \phi_b | \\ &= \sum_a H_a | \phi_a \rangle \langle \phi_a | + \sum_{a,b} \hat{\Theta}_{ab} | \phi_a \rangle \langle \phi_b | \end{aligned}$$

the Hamiltonian does not depend on electronic coordinates; the coordinate representation is replaced by the *electronic state representation*; however, the description of nuclear coordinates stays in the *nuclear coordinate representation*; in this way an easy restriction to that part of the electronic spectrum becomes possible which is of interest to understand a particular process (experiment);

## Adiabatic Electron Vibrational State Representation of the Molecular Hamiltonian

to arrive at the respective expansion we change to the *adiabatic electron–vibrational state representation* and introduce the following replacement

$$\Psi_{av}^{(\text{adia})}(r, R) = \phi_a \chi_{av} \rightarrow |\Psi_{av}\rangle$$

the expansion of  $H_{\text{mol}}$  results in the following matrix elements

$$\begin{aligned} \langle \Psi_{av} | H_{\text{el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}} | \Psi_{b\mu} \rangle &= \int dr dR \phi_a^* \chi_{av}^* (H_{\text{el}} + T_{\text{nuc}} + V_{\text{nuc-nuc}}) \phi_b \chi_{b\mu} \\ &= \int dR \left( \delta_{a,b} \chi_{av}^* (T_{\text{nuc}} + U_a) \chi_{a\mu} + \chi_{av}^* \hat{\Theta}_{ab} \chi_{b\mu} \right) = \delta_{av,b\mu} \mathcal{E}_{av}^{(\text{adia})} + \Theta_{av,b\mu} \end{aligned}$$

accordingly, the molecular Hamiltonian takes the form

$$H_{\text{mol}} = \sum_{a\mu} \mathcal{E}_{av}^{(\text{adia})} |\Psi_{av}\rangle \langle \Psi_{av}| + \sum_{av,b\mu} \Theta_{av,b\mu} |\Psi_{av}\rangle \langle \Psi_{b\mu}|$$

the operator of the nonadiabatic coupling turned to the electron vibrational matrix elements  $\Theta_{av,b\mu}$ ; they couple the different vibrational multilevel systems which refer to the various adiabatic electronic states;

## 1.1.2 Expansion with Respect to Diabatic Electronic States

we assume a separation of  $H_{\text{el}}$  into a part  $H_0$  (zero-order part) and a remaining part  $V$  (perturbation);

the solution of the Schrödinger-equation which refers to  $H_0$  should be known (quantum numbers are denoted by  $m, n, \dots$ )

$$H_0\varphi_m = E_m\varphi_m$$

solution of the total molecular Schrödinger-equation is expanded with respect to the  $\varphi_m$

$$\Psi(r; R) = \sum_m \chi_m(R)\varphi_m(r; R)$$

the resulting representation is known as the *diabatic representation*; since the separation of  $H_{\text{el}}$  into  $H_0$  and  $V$  is not unique this definition of a diabatic representation is also not unique;

the equations for the nuclear wave functions take the form

$$\mathcal{E}\chi_m = (T_{\text{nuc}} + E_m + V_{\text{nuc-nuc}})\chi_m + \sum_n (\hat{\Theta}_{mn} + V_{mn})\chi_n ;$$

we introduced the matrix elements

$$V_{mn} = \langle \varphi_m | V | \varphi_n \rangle ; \quad (1.1)$$

those are named *static coupling*; these couplings are added to the nonadiabatic couplings;

since the nonadiabatic coupling follows from the matrix elements of the nuclear kinetic energy operators it is also known as the *dynamic coupling*;

general observation when using a diabatic representation: the static coupling dominates the dynamic coupling (the latter can be neglected); introduction of a diabatic representation can be made unique if the definition requires a vanishing of the dynamic coupling;

PES in the diabatic representation

$$U_m(R) = E_m(R) + V_{\text{nuc-nuc}}(R) + \Theta_{mm}(R) + V_{mm}$$