Chapter 2

Solution of the Schrödinger equation for the nuclear motions: methods and techniques

The time evolution of a quantum mechanical system in the absence of dissipation (e.g. molecules or clusters in gas phase) is described by a Schrödinger equation in the Born-Oppenheimer approximation [1]

$$i\frac{\partial}{\partial t}\Psi(x_1, ..., x_n; t) = \hat{H}(x_1, ..., x_n; t)\Psi(x_1, ..., x_n, t). \qquad (2.1)$$

The wave function Ψ, as well as the Hamilton operator $\hat{H}$, are dependent on n nuclear coordinates $x_i; i = 1, n$ and time. The Hamilton operator can be separated into the molecular and interaction parts as follows

$$\hat{H}(x_1, ..., x_n; t) = \hat{H}_{mol}(x_1, ..., x_n) + \hat{H}_{int}(x_1, ..., x_n; t). \qquad (2.2)$$

The molecular Hamiltonian $\hat{H}_{mol}$ consists of the kinetic and potential energy operators:

$$\hat{H}_{mol}(x_1, ..., x_n) = \hat{T} + \hat{V}(x_1, ..., x_n). \qquad (2.3)$$

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[1]Throughout this chapter, the atomic units ($\hbar = 1$) will be used for the sake of simplicity.

The kinetic energy operator $\hat{T}$ in the simplest case, e.g. when x_i are Cartesian coordinates, is given by

$$\hat{T} = -\frac{1}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{1}{2m_2}\frac{\partial^2}{\partial x_2^2} - ... - \frac{1}{2m_n}\frac{\partial^2}{\partial x_n^2}, \tag{2.4}$$

and contains the mass-weighed sum of squares of quantum mechanical momenta conjugate to each of the nuclear coordinates. Corresponding masses are designated m_i. This form of the kinetic energy operator is not restricted to Cartesian coordinates; other coordinate systems such as normal coordinates (see Chapter 3) and Jacobi coordinates [41–43] also have the form of the kinetic energy operator given by equation (2.4). In many cases, however, the kinetic energy operator can have a much more complicated structure, for example, if so-called kinetic couplings – terms in the kinetic energy operator containing products of momenta operators corresponding to different coordinates – are present. Examples of such Hamiltonians will be presented in Chapters 4 and 5.

The potential energy operator $\hat{V}(x_1, ..., x_n)$ in equation (2.3) is usually obtained from *ab initio* quantum chemistry calculations, in the form of potential energy surface (PES), represented in the coordinates, in which the dynamics calculations are to be performed.

The interaction Hamiltonian $\hat{H}_{int}$ is treated in the semiclassical dipole interaction approximation, which is sufficient for the majority of systems of interest to the femtosecond chemistry. It is defined by the formula

$$\hat{H}_{int} = -\vec{\mu}(x_1, ..., x_n) \cdot \vec{\mathcal{E}}(t), \tag{2.5}$$

where $\vec{\mu}$ is the dipole moment function, defined either *ab initio* together with the potential energy surface, or approximated by a model function. Dipole moment is a vector quantity, and it is usually defined in a laboratory plane of reference perpendicular to the wave vector of the incident light.

So far no assumptions were made for the representation of the wave functions and operators in the Schrödinger equation (2.1). In this work the time dependent wave packet method of its solution will be utilized, which consists of the following steps:

I Representing the initial wave function and operators on a finite discrete spatial grid.

II Propagating the discretized wave function in time.

III Analyzing the wave function taken at certain characteristic times for quantities of interest.

Let us consider these steps, the first of which concerns the representation of the wave function and operators on a grid. The grid in question does not necessarily have to be equidistant, in fact, some methods (e.g. discrete variable representation (DVR) [44, 45]) operate with nonuniform grids, gaining advantages of better sampling of the wave function in the regions of interest. However, the majority of propagation methods operate on equidistant grids, with sampling criteria varying greatly from one method to the other. Such equidistant grids are defined as follows:

$$x_i^j = x_i^{\min} + (j - 1)\Delta x_i, \quad i = 1, ..., n; \quad j = 1, ..., N_i. \tag{2.6}$$

Here the index i refers to the nuclear coordinate, and index j to the grid point. The number of grid points in each coordinate is given by N_i, and the grid spacing Δx_i is given by

$$\Delta x_i = (x_i^{\max} - x_i^{\min})/(N_i - 1). \tag{2.7}$$

The values $x_i^{\max}$ and $x_i^{\min}$ define the coordinate values for the upper and lower grid boundaries, respectively, in each of the coordinates x_i.

The initial wave function $\Psi(x_1, ..., x_n; 0)$ is often defined analytically, e.g. in the models utilizing the well-known model potential functions like the Morse potential [46]. For problems involving reactive scattering [47, 48] or association [14, 49], it is customary to take a Gaussian wave packet

$$\Psi(x_1, ..., x_n; 0) = C \prod_{i=1}^{n} e^{-\beta_i(x_i - x_i^0)^2}, \tag{2.8}$$

as the initial wave function (here C is chosen such that the product wave functions is normalized, β_i and x_i^0 are the width parameters and positions of the maximum of the

distribution in each nuclear coordinate, respectively). When the initial wave function and/or operators are defined analytically, the discretization is trivial. However, for many processes, e.g. pump-probe spectroscopy [50], photodissociation [13], selective preparation of states and control [14], vibrational eigenstates have to be taken as initial wave functions. In this case one has to solve the time-independent eigenvalue problem, choosing the grid that will be later used for propagation, or to employ interpolation techniques to recast the eigenfunctions to different grids [51].

For the propagation step there exists a variety of different approaches. For a comprehensive survey of the methods and their efficiency, the reader is refered to the review of Balakrishnan et al. [47]. The main criterion for the evaluation of the methods is the scaling properties. However, the issues of accuracy, convergence, conservation of norm during the propagation also have to be taken into account.

Historically, the first methods for solution of the time-dependent Schrödinger equation (2.1) have been the finite difference methods [52], the most widely used variant being the second order difference (SOD) [53] method. The SOD propagator is the easiest one to implement in an actual program, however, it has several fundamental flaws: for the reasons of convergence the time steps of propagation have to be chosen very small, which severely limits the ability of this method to treat multidimensional long-time dynamics, and the fact that it fails in the presence of imaginary optical potentials, which are used to dampen the wave function at grid boundaries. Due to these reasons, the SOD schemes are rarely used nowadays for time dependent wave packet simulations.

The breakthrough in the solution of wave packet propagation problems was achieved, when the fast Fourier transformation (FFT) technique was applied by Feit and Fleck [54, 55] and Kosloff and Kosloff [56] for evaluation of the kinetic energy part of the Hamiltonian. The essence of the method is the fact that the quantum mechanical momentum operators, nonlocal in the coordinate representation, are local in the momentum representation, where their action can be evaluated by simple multiplication. For example, in our case the image of the wave function

in the momentum space is given by

$$\tilde{\Psi}(k_1, ..., k_n) = \left(\frac{1}{\sqrt{2\pi}}\right)^n \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \Psi(x_1, ..., x_n) e^{-i(k_1 x_1 + ... + k_n x_n)} dx_1 ... dx_n, \quad (2.9)$$

and the transformation back to the coordinate space is defined as follows:

$$\Psi(x_1, ..., x_n) = \left(\frac{1}{\sqrt{2\pi}}\right)^n \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \tilde{\Psi}(k_1, ..., k_n) e^{i(k_1 x_1 + ... + k_n x_n)} dk_1 ... dk_n. \quad (2.10)$$

Let us consider the action of the kinetic energy operator on the wave function given by equation (2.9):

$$\hat{T}\Psi(x_1, ..., x_n) = -\sum_{i=1}^{n} \frac{1}{2m_i} \frac{\partial^2 \Psi(x_1, ..., x_n)}{\partial x_i^2} =$$
$$= \left(\frac{1}{\sqrt{2\pi}}\right)^n \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \tilde{\Psi}(k_1, ..., k_n)(k_1^2 + ... + k_n^2) e^{-i(k_1 x_1 + ... + k_n x_n)} dx_1 ... dx_n.$$
$$(2.11)$$

As we can see, in the momentum space (or *k-space*) the action of the kinetic energy operator is reduced to multiplication with the sum of squares of wave numbers corresponding to each coordinate.

The FFT method has many valuable advantages. In this technique, the operators are applied in the representations, in which they are local, making their evaluation very accurate. It can also be proven [56], that for a comparable accuracy, the FFT method does not require so fine a mesh of points as the finite differencing methods. Also, especially for multidimensional problems, the scaling properties of the Fourier method (where the computational effort scales as $N \log N$ with respect to the number of grid points N) give it an enormous advantage over other methods, allowing the treatment of larger systems.

The DVR methods are also a powerful and promising tool for time-dependent wave packet propagation, despite of the fact that the DVR technique was originally designed for time-independent problems. The application of these methods to dynamics is beyond the scope of this work. However, the DVR method was utilized in Chapter 4 for the solution of an eigenvalue problem. The technique used is described in Appendix B.

A very efficient and accurate propagation scheme for the Scrödinger equation (2.1) was introduced by Feit and Fleck [54, 55]. This technique, called the *split-operator method*, has been used throughout this work. It was originally intended for determining the modes of optical wave guides, where the wave equations are similar to the Schrödinger equation [57]. This method was then successfully applied to the quantum dynamics problems. The underlying logic behind this method shall be outlined below.

Assuming that the Hamilton operator in equation (2.1) is explicitly time-independent (which is true for the molecular Hamiltonian $\hat{H}_{mol}$), its formal solution can be written in the following form (for now, we assume $\hat{H}_{int} = 0$):

$$\Psi(t) = e^{-i\hat{H}t}\Psi(0) = e^{-i(\hat{T}+\hat{V})t}\Psi(0). \tag{2.12}$$

If we consider the evolution of the wave function during one time step, the equation (2.12) then becomes

$$\Psi(t + \Delta t) = e^{-i(\hat{T}+\hat{V})\Delta t}\Psi(t) \tag{2.13}$$

Since the potential and kinetic energy operators do not commute, we cannot rewrite the exponential of the sum of operators in (2.13) as a product of exponentials of each. Were such factorization to be performed, the error of the order of Δt^2 would be introduced in the energy. However, a certain arrangement of terms in the Hamilton operator allows to achieve higher accuracy. Let us consider the Baker-Campbell-Hausdorf theorem, applied to three operators $\hat{A}, \hat{B}, \hat{C}$.

$$\exp\left(\hat{A}\right)\exp\left(\hat{B}\right)\exp\left(\hat{C}\right) = \exp\left(\hat{A} + \hat{B} + \hat{C} + \frac{1}{2}[\hat{A},\hat{B}] + \frac{1}{2}[\hat{A},\hat{C}] + \frac{1}{2}[\hat{B},\hat{C}]\right.$$
$$\left. + \frac{1}{12}[[\hat{A},\hat{B}],\hat{A} + \hat{B} + \hat{C}] + ...\right)$$
$$\tag{2.14}$$

Let us define the operators $\hat{A}, \hat{B}$ and $\hat{C}$ as follows:

$$\hat{A} = \hat{C} = -i\frac{\hat{T}}{2}\Delta t \quad \hat{B} = -i\hat{V}\Delta t. \tag{2.15}$$

Substituting these into the equation (2.14) yields

$$e^{-i\frac{\hat{T}}{2}\Delta t}e^{-i\hat{V}\Delta t}e^{-i\frac{\hat{T}}{2}\Delta t} = e^{-i(\frac{\hat{T}}{2}+\hat{V}+\frac{\hat{T}}{2})\Delta t + O(\Delta t^3)} \approx e^{-i\hat{H}\Delta t}. \tag{2.16}$$

Combining the equations (2.13) and (2.16), we obtain the split-operator propagator in the final form:

$$\Psi(t + \Delta t) = \mathrm{e}^{-\mathrm{i}\frac{\hat{T}}{2}\Delta t}\mathrm{e}^{-\mathrm{i}\hat{V}\Delta t}\mathrm{e}^{-\mathrm{i}\frac{\hat{T}}{2}\Delta t}\Psi(t). \tag{2.17}$$

Obviously, the procedure of dividing the kinetic energy operator in two equal parts, as defined by equations (2.15), could be performed instead on the potential energy operator without affecting the accuracy. One can choose either form of the split-operator, depending on the implementation of the programs of wave packet propagation. The split-operator method is accurate to the second term in the Δt, and the error is proportional to $\Delta t^3[[\hat{T}, \hat{V}], \hat{H}]$ as can be seen from the equation (2.14).

Practical implementation of the split operator propagation requires the use of the FFT method, so that the actions of the operators will be evaluated in their respective local representations. Since the kinetic and potential energy operators in (2.17) are arguments of exponential functions, this procedure works only when the kinetic energy operator is diagonal in momentum space, for example, if it is given in Cartesian coordinates. However, certain modifications of the technique allow to use the split operator technique even for operators which do not satisfy this requirement [58].

In order to derive the expression for the split-operator propagator an assumption was made, that the Hamilton operator is not explicitly time-dependent. If the Hamilton operator contains the interaction part given by equation (2.5), this assumption does not hold. However, Kouri and coworkers [59,60] have shown, that it is possible to write an expression for the split-operator, which accomodates the explicitly time-dependent Hamiltonians correctly, retaining the accuracy of the method. In this case the potential-type splitting has to be used, and the final expression for the propagator reads

$$\Psi(t + \Delta t) = \mathrm{e}^{-\mathrm{i}\frac{\hat{V}(t+\Delta t)}{2}\Delta t}\mathrm{e}^{-\mathrm{i}\hat{T}\Delta t}\mathrm{e}^{-\mathrm{i}\frac{\hat{V}(t)}{2}\Delta t}\Psi(t). \tag{2.18}$$

Other methods of time dependent wave packet propagation, e.g. the Chebyshev polynomial expansion method [61, 62], or (t, t') method of Moiseyev et. al [63, 64]

shall not be considered here.

In the course of the propagation, a quantum wave packet may approach the end of the grid, on which it is defined, whether by design, as in the dissociation problems, or by accident. In this case the FFT method will give rise to the reflection of the wave packet from the grid boundary, since the FFT method requires the wave functions to be either band-limited or periodic. To prevent the unphysical behavior of the wave packet, one has to dampen the wave function near the grid boundaries. A way to achieve this is to multiply the propagated wave function at each time step by a function, which is equal to one in the grid regions where the dynamics takes place, and rapidly goes to zero in the certain predefined region in the immediate vicinity of the boundary. This approach was suggested by Bisseling et al. [65], and termed an absorbing boundary condition approach.

Alternatively, one can implement an absorbing boundary condition by adding to the Hamiltonian an artificial purely imaginary potential-type term. Drawing parallels from optics, such a term is often called imaginary optical potential. With exponential-type propagators, like split-operator, these terms lead to efficient damping of the wave function in the regions, where this imaginary optical potential is defined. In contrast with the previous approach, this term has to be added to the potential only once before the propagation, which leads to considerable speedup in computation. There exist many varieties of the imaginary optical potentials, differing by the damping function used. Given below is one of the most widely used imaginary optical potentials, the linear ramp of Neuhauser and Baer [66](in 1-D case for the sake of simplicity):

$$
U_{\text{opt}} = \begin{cases} -iU_0 \frac{x-x_{\text{opt}}}{\Delta x_{\text{opt}}} & x_{\text{opt}} < x \leq x_{\text{opt}} + \Delta x_{\text{opt}} \\ 0 & x \leq x_{\text{opt}} \end{cases} \tag{2.19}
$$

Here U_0 is the magnitude of the absorbing potential, x_{opt} is the position of the beginning of the absorbing boundary, and Δx_{opt} is its width. The width and magnitude of the imaginary optical potentials have to be chosen by careful experimentation, so that the damping is not too weak to allow a portion of the wave packet penetrate it, and not too strong to cause reflections of the wave packet from the beginning of

the absorbing boundaries. Reasonable initial guesses for these values can be estimated, if the energetics of the system is known [66], but some fine tuning is almost always required. Another variant of the imaginary optical potential with exponential damping will be shown in Chapter 4. The imaginary optical potentials are also called *gobbler functions*.

The third step of the time dependent wave packet method is the analysis of the evolving wave functions, and extraction of the information relevant to the physics of the process. There exist several standard approaches to the analysis of the wave functions, which are applied. The dynamics of the system is elucidated by means of the snapshots of the density of the wave function (the plots of its squared absolute value as a function of coordinate). Autocorrelation functions help to establish the recurring patterns in the evolution of the wave packets. Time-dependent populations of different vibrational and rotational states can be evaluated by projection of the wave function on the respective eigenstates. A brief outline of these and other techniques follows.

Analysis of the snapshots of the wave function is a very illustrative approach. It allows to construct a "movie" of the wave packet evolution, and to gain insight on the fundamental microscopic dynamics of a system. The snapshots are easy to generate and understand, when the number of degrees of freedom is less or equal to two. If we study the systems with greater dimensionality, this approach encounters problems. For example, a 3-D wave function can be represented as a 3-D equidensity contour plot, and if there are more than two or free contours, they are not anymore distinguishable. For problems of higher dimensionality, the contour plots are no longer an option.

The difficulties of visualization of multidimensional wave functions are resolved by projecting the n-dimensional picture on a subspace with lower dimensionality by integrating over several degrees of freedom, which are not of interest for the particular visualization. For example, a two-dimensional projection of the n-dimensional

wave function on the (x_k, x_l) coordinate plane is defined as (assuming $k < l < n$):

$$\psi(x_k, x_l; t) = \int ... \int \int ... \int \int ... \int |\Psi(x_1, ..., x_n)|^2 \times$$
$$\times \, dx_1...dx_{k-1}dx_{k+1}...dx_{l-1}dx_{l+1}...dx_n. \tag{2.20}$$

This approach was used to generate the 2-D snapshots of 3-D wave functions in Chapter 3, by integrating over one of the coordinates.

Some valuable information can be gained from the analysis of the autocorrelation functions of wave packet propagations, which are defined as overlap integrals between the wave function at a given moment of time and the initial wavefunction:

$$I(t) = \langle \Psi(0)|\Psi(t)\rangle = \int_{x_1^{\min}}^{x_1^{\max}} ... \int_{x_n^{\min}}^{x_n^{\max}} \Psi^*(0)\Psi(t)dx_1...dx_n. \tag{2.21}$$

The more different the wave function is from itself at $t = 0$, the less the absolute value of the correlation function. Thus one can establish the recurring patterns in the dynamics of the wave function, and obtain the information on the timescales of the processes occuring during the time evolution. The Fourier transformation of autocorrelation function allows us to obtain the linear absorption [67] and Raman spectra [68].

If one is interested in the *state-selectivity* of the process, that is, how different vibrational (or vibrational-rotational) states of a molecule are being prepared and evolve, the time-dependent populations of the respective eigenstates have to be considered. For an eigenstate with the quantum number v, the population is defined as follows:

$$P_v(t) = |\langle \psi_v|\Psi(t)\rangle|^2 = \int_{x_1^{\min}}^{x_1^{\max}} ... \int_{x_n^{\min}}^{x_n^{\max}} |\psi_v^*\Psi(t)|^2 dx_1...dx_n, \tag{2.22}$$

where ψ_v is the eigenfunction corresponding to the state v. The wave functions ψ_v and Ψ have to be normalized to unity. In that case, the maximum value of the P_v is one, in case when the wave function Ψ becomes the v-th eigenstate. Norm of the wave function is calculated as follows

$$\mathcal{N}(t) = \int_{x_1^{\min}}^{x_1^{\max}} ... \int_{x_n^{\min}}^{x_n^{\max}} |\Psi(t)|^2 dx_1...dx_n, \tag{2.23}$$

and it is also a useful benchmark for the stability of the propagator.

So far no limitation was placed on the number of degrees of freedom of the system. However, even with the extremely favorable scaling properties of the FFT method, simulations of the time-dependent wave packet dynamics of three-dimensional systems are a very demanding task, both with respect to the storage space required and to the computation time. For example, the 3-D grid used for the studies of silver trimers in Chapter 3 has more than 8,000,000 elements, which means that *every* storage array containing the wave function has the size of 150 MByte. The extremely large size of the propagation grids for Ag_3 is due to the importance of large amplitude motions for this system. If large amplitude motions do not occur in the system under investigation, the grid sizes, and hence the computational effort can be significantly reduced, allowing easier and/or more rigorous treatment of three-dimensional [69–71] problems, and also making quantum dynamical simulations with higher dimensionality possible, as manifested by the reports on four- [27, 28], five- [29], six- [30] and even 24-dimensional [31] simulations. Nevertheless, for most of the calculations in more than three dimensions certain approximations have to be introduced, in order to make the problems tractable.

A possible way to overcome the difficulties caused by the insufficient computer resources is to take advantage of the possibilities provided by the new computer architectures. In this work the 3-D calculations have been performed on a massively parallel supercomputer Cray T3E, which enabled to overcome the storage and speed constraints of a typical workstation. However, performing the calculation on a massively parallel machine requires extensive adaptation of the simulation programs. The outline of the issues involved can be found in Appendix A.

So far, the solution of the time-dependent Schrödinger equation (2.1) has been discussed, since it is the heart of the wave packet propagation methods. However, it is also essential to be able to solve the corresponding time-independent problem

$$\hat{H}_{mol}(x_1, ..., x_n)\Psi(x_1, ..., x_n) = E\Psi(x_1, ..., x_n), \qquad (2.24)$$

that is, to find the eigenfunctions and eigenvalues of the molecular Hamilton operator, defining the energetics of the systems by finding the energies of the stationary

states $\{E_i\}$, and obtaining the corresponding stationary state wave functions $\{\psi_i\}$, to serve as initial states for propagation and to be used in the analysis of the time-dependent wave packets.

A powerful technique for the solution of the time-independent Schrödinger equation is the Fourier grid Hamiltonian (FGH) technique of Marston and Balint-Kurti [72], which can also be extended for multidimensional problems [73]. The limitation of the FGH method is the fact that in its original form it is applicable only to the Cartesian-like kinetic energy operators, where the kinetic couplings and first order coordinate derivatives are absent.

Another set of methods for the solution of the eigenvalue problem of the Schrödinger equation are the DVR methods, which do not impose limitations on the form of the Hamilton operator. In fact, the FGH method is a special case of discrete variable representation. The description of the DVR technique can be found in the Appendix B.

For the problems of high dimensionality, especially when only a few of the eigenfunctions are needed, a good alternative method for solution of the time-independent problem was presented by Tal-Ezer and Kosloff [74]. This technique, called direct relaxation method, or propagation in imaginary time, is easy to implement, and can be used in conjunction with the existing propagation programs.

The direct relaxation method is implemented as follows. The time is redefined as imaginary ($\tau = \mathrm{i}t$). The formal solution of the Schrödinger equation (2.12) then takes the form:

$$\Psi(\tau) = \mathrm{e}^{-\hat{\mathrm{H}}\tau}\Psi(0). \tag{2.25}$$

The initial wave function $\Psi(0)$ can be expanded in the basis of the eigenstates of the Hamilton operator $\hat{\mathrm{H}}$:

$$\Psi(0) = \sum C_k|\psi_k\rangle, \quad \text{where} \quad \hat{\mathrm{H}}|\psi_k\rangle = E_k|\psi_k\rangle. \tag{2.26}$$

Substituting this expansion into the propagator (2.25), one obtains:

$$\Psi(\tau) = \mathrm{e}^{-\hat{\mathrm{H}}\tau}\sum C_k|\psi_k\rangle = \sum C_k\mathrm{e}^{-E_k\tau}|\psi_k\rangle. \tag{2.27}$$

With the increase in (imaginary) time τ, the contributions of the eigenstates with higher energy decrease exponentially with respect to the ones with lower energy, and the sum converges to the eigenstate with the lowest energy (the ground state ψ_0). To implement the propagation, the split-operator method is suitable. However, since the norm of the wave function decreases exponentially, the wave function has to be renormalized after each few timesteps.

To obtain the eigenstates other than the ground vibrational state, one can remove the state with the lowest energy from the Hilbert space by projection after each time step:

$$\psi_k^{(j+1)} = \left(\hat{I} - \sum_{l=0}^{k-1} \langle \psi_l | \psi_k^{(j)} \rangle \right) \psi_k^{(j)}, \tag{2.28}$$

where $\hat{I}$ is the identity operator, and the index j denotes the time step.

As an initial state for the propagation in imaginary time any arbitrary wave function can be taken, but the fastest convergence is achieved by taking a reasonable initial guess, for example, a Gaussian wave packet defined by equation (2.8).

This method is easy to implement and, due to the excellent scaling properties for the lowest lying eigenstates, has few alternatives for three-dimensional problems. However, the projection operation is costly, and the error in the wave functions is accumulated, since the calculation of each of the higher lying eigenfunction relies on the previously computed lower ones. For the detailed discussion of the ways to overcome these difficulties, see [75]. Still, the method gives very reasonable results for three-dimensional problems, and was used for the calculation of eigenfunctions in Chapter 3.