

Chapter 5

Simulation Methods

Because of the complexity of systems embedded in an environment and the large number of degrees of freedom arising from this fact, full quantum mechanical calculations are not feasible. On the other hand classical dynamics calculations will be suitable to describe the motion of the nuclei, but they do not include electronic state transitions, which have been observed by experiments [78]. One way to deal with this problem is to derive the potentials from methods like DIM and to perform some exact quantum mechanical calculations on them. These exact calculations will lack the influence of the other host atoms, which will play an important role in the course of the dynamics, but they will take into account the correct behaviour of the wavepacket, decoherence and state transitions. In this work classical dynamics were performed and the results will be compared to the quantum simulations performed by Dr. Mikhail Korolkov (Minsk, FU-Berlin), based on selected DIM potential surfaces. Also one- and two-dimensional calculations were performed and will be compared in section 6.8 for Cl₂ in argon and in section 7.7 for CIF.

The classical simulations of this work were performed by first calculating the energies and forces using the DIM method, and then the nuclei were propagated using the Gear algorithm, utilizing the di2pag package from the IMSL library with a timestep of 1 or 5 fs. At each timestep the energies and forces are recalculated, taking into account the now changed geometry.

$$H_{total}|\Phi_i(r(t))\rangle = V_i^a(r(t))|\Phi_i(r(t))\rangle \quad (5.1)$$

The time dependence will result from the instantaneous positions of the nuclei and gives the adiabatic potential surface $V^a(r(t))$. This method of calculating all of the essential values at each time step *on the fly*, leads to an adiabatic

potential surface, which includes the different form of the wavefunction and with this reorientation effects of the molecular orbital. The nuclear motions are here confined to a single adiabatic surface.

5.1 Classical Dynamics

Dynamical calculations of a system can be calculated by solving the equations of motion for a system in a particular potential. A classical system with k independent degrees of freedom or k independent coordinates can be described by $2k$ terms, for example by the generalized coordinates q_k and the generalized velocities \vec{v}_k :

$$\vec{r} = \{q_1, q_2, q_3, \dots, q_k\} \quad (5.2)$$

$$\vec{v} = \{\dot{q}_1, \dot{q}_2, \dot{q}_3, \dots, \dot{q}_k\} \quad (5.3)$$

The classical equations of motion can be expressed in the Lagrangian \mathcal{L} form:

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}_k} \right) - \left(\frac{\partial \mathcal{L}}{\partial q_k} \right) = 0 \quad (5.4)$$

with the Lagrangian function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})$ consisting of the kinetic and potential energies $\mathcal{L} = E_{kin} - E_{pot}$ and depending on the coordinates and the time derivatives by

$$E_{kin} = \sum_{i=1}^N \sum_{x,y,z} \frac{p_{i,x,y,z}^2}{2M_i} \quad (5.5)$$

$$E_{pot} = \sum_i \sum_{j>i} V(r_i, r_j) \quad (5.6)$$

The potential energy is here just given as pair potentials of the system, in this work we used the potential energy derived by the DIM method. Plugging these into the Lagrangian equations of motion results in

$$f_i = m_i \frac{\partial^2}{\partial r_i^2} \quad (5.7)$$

with m_i being the mass of atom i and the appropriate force working on this atom:

$$f_i = \nabla_{r_i} \mathcal{L} = -\nabla_{r_i} E_{pot} \quad (5.8)$$

For molecules the motion of the center of mass will be calculated, f in this case representing the total force on the molecule.

The connection between generalized momentum and coordinate is given as

$$p_k = \frac{\partial \mathcal{L}}{\partial \dot{q}_k} \quad (5.9)$$

Using the Hamiltonian function

$$H(p, q) = \sum_k \dot{q}_k p_k - \mathcal{L}(q, \dot{q}) \quad (5.10)$$

the Hamiltonian form of the equation of motion can be calculated by performing the total differential of the Lagrangian function, using the Hamiltonian function additionally to the Lagrangian equations.

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \quad (5.11)$$

$$\dot{p}_k = -\frac{\partial H}{\partial q_k} \quad (5.12)$$

Note that \dot{q}_k is assumed to be a function of the momenta p . When the potential will be independent of velocities and time, as performed here by recalculating at each time step, these equations get to their very simple form:

$$\dot{r}_i = p_i / m_i \quad (5.13)$$

$$\dot{p}_i = -\nabla_{r_i} E_{pot} = f_i \quad (5.14)$$

By this way for computing some trajectories one has to solve a system of either second-order differential equations 5.7 or a set of first-order differential equations 5.13 and 5.14. The standard method for that would be a finite difference approach as invented by Verlet or Gear.

5.2 Finite Differences Method

In this work the Gear method was used for calculating the molecular dynamics of the system. This method uses the finite differences method and with it a predictor-corrector algorithm [67]. The principle behind this can be described as follows: Starting at time t , where the general information about the system like coordinates and momenta are known, trajectories are calculated for time-increments δt , which

should be sufficiently small. From this initial conditions the new coordinates, momenta, accelerations etc. at time $t + \delta t$ will be estimated by Taylor expansion at time t :

$$\vec{r}_i^p(t + \delta t) = \vec{r}_i(t) + \delta t \vec{v}_i(t) + \frac{1}{2} \delta t^2 \vec{a}_i(t) + \frac{1}{6} \delta t^3 \vec{b}_i(t) + \dots \quad (5.15)$$

$$\vec{v}_i^p(t + \delta t) = \vec{v}_i(t) + \delta t \vec{a}_i(t) + \frac{1}{2} \delta t^2 \vec{b}_i(t) + \dots \quad (5.16)$$

$$\vec{a}_i^p(t + \delta t) = \vec{a}_i(t) + \delta t \vec{b}_i(t) + \dots \quad (5.17)$$

$$\vec{b}_i^p(t + \delta t) = \vec{b}_i(t) + \dots \quad (5.18)$$

With the index p means predicted value, and abbreviations $\vec{a} = \partial^2 / \partial \vec{r}_i^2$ and $\vec{b}_i = \partial \vec{a}_i / \partial \vec{r}_i$. After performing this as a predictor step, the new coordinates $\vec{r}_i(t + \delta t)$ will give rise to a new set of forces working on the system. The accelerations resulting from these new forces are determined and compared to the predicted ones by

$$\Delta \vec{a}_i = \vec{a}_i^c(t + \delta t) - \vec{a}_i^p(t + \delta t) \quad (5.19)$$

with c denoting the correct values.

By this, corrections will be applied to all the values in the system:

$$\vec{r}_i^c(t + \delta t) = \vec{r}_i^p(t + \delta t) + c_0 \Delta \vec{a}_i(t + \delta t) \quad (5.20)$$

$$\vec{v}_i^c(t + \delta t) = \vec{v}_i^p + c_1 \Delta \vec{a}_i(t + \delta t) \quad (5.21)$$

$$\vec{a}_i^c(t + \delta t) = \vec{a}_i^p(t + \delta t) + c_2 \Delta \vec{a}_i(t + \delta t) \quad (5.22)$$

$$\vec{b}_i^c(t + \delta t) = \vec{b}_i^p(t + \delta t) + c_3 \Delta \vec{a}_i(t + \delta t) \quad (5.23)$$

The coefficients c_i have been tabulated and depend on the order of the differential equation.

These prediction-correction steps can be performed in several loops, in this work the di2pag package of the IMSL library was used with timesteps of either 0.001 or 0.005 fs.

5.3 Tabulation of the Potential

One way to reduce the complexity of evaluating the potential and force directly is to tabulate their values. By this way on each time step the values of $\mathbf{r} = r_{ij}^2$ will be calculated for each pair of atoms and the potential, the first and the

second derivative are interpolated from these tabulated values. In this work the Newton-Gregory forward difference method was used.

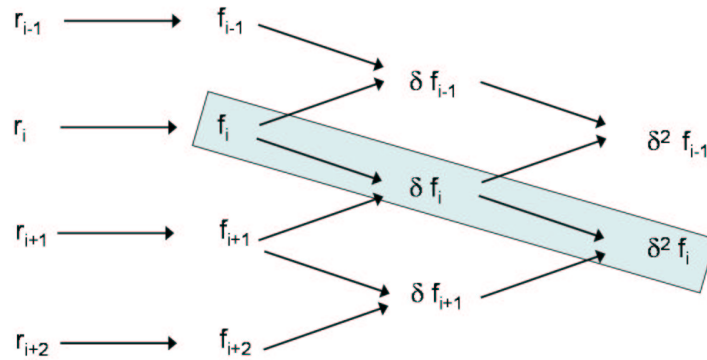


Figure 5.1: Newton-Gregory forward difference method, [67]

Suppose a tabulated function $g(\mathbf{r})$ with function values $g_1 = f(\mathbf{r}_1)$, $g_2 = g(\mathbf{r}_2)$, $g_3 = g(\mathbf{r}_3)$, etc. at regular intervals $\delta \mathbf{r}$. Now the *forward differences* will be defined as:

$$\delta g_i = g_{i+1} - g_i \quad \text{first forward difference} \quad (5.24)$$

$$\delta^2 g_i = \delta g_{i+1} - \delta g_i \quad \text{second forward difference} \quad (5.25)$$

$$\delta^n g_i = \delta^{n-1} g_{i+1} - \delta^{n-1} g_i \quad (5.26)$$

Equally the *backward differences* are defined:

$$\delta g_i = g_i - g_{i-1} \quad (5.27)$$

$$\delta^2 g_i = \delta g_i - \delta g_{i-1} \quad (5.28)$$

$$\delta^n g_i = \delta^{n-1} g_i - \delta^{n-1} g_{i-1} \quad (5.29)$$

With

$$\xi = \frac{\mathbf{r} - \mathbf{r}_0}{\delta \mathbf{r}} \quad (5.30)$$

we get the Newton-Gregory forward polynomial:

$$g(\mathbf{r}) = g_0 + \xi \Delta f_0 + \frac{\xi(\xi-1)}{2!} \Delta^2 g_0 + \dots + \frac{\xi(\xi-1)\dots(\xi-n+1)}{n!} \Delta^n g_0 \quad (5.31)$$

which is usually truncated after the quadratic term in Δ . By this way all the values lying between g_i and g_{i+1} can be interpolated from the values of g_i , δg_i and $\delta^2 g_i$.

For calculations of the forces f one uses the relation:

$$f_{ij} = -\nabla_{r_{ij}} v(r_{ij}) \quad \text{with} \quad (5.32)$$

$$r_{ij} = r_i - r_j \quad (5.33)$$

$$f_{ij} = -\frac{1}{r_{ij}} \left(\frac{dv(r_{ij})}{dr_{ij}} \right) r_{ij} \quad (5.34)$$

$$= -\frac{\mathcal{W}(r_{ij})}{r_{ij}^2} r_{ij} \quad (5.35)$$

Which is valid for pairwise potentials [67] and includes the virial function \mathcal{W} . Either one can tabulate these values separately or obtain them from differentiation of equation 5.31:

$$\frac{\mathcal{W}(r_{ij})}{r_{ij}^2} = \frac{\mathcal{W}(\mathbf{r})}{\mathbf{r}} = \frac{2df}{d\mathbf{r}} \quad (5.36)$$

5.4 Periodic Boundary Conditions

Simulating the dynamics of matrix-embedded molecules has, as simulations of large systems in general, the problem of surface effects. The lattice atoms on the surface of the constructed cube will experience different forces than the enclosed ones. This effect is quite dramatic, because for a cube consisting of 1000 atoms nearly 50 % will lie on the surface. This effect is overcome by using periodic boundary conditions. The box is repeated in space and by this a virtually infinite lattice is formed. Calculations of interactions of an atom i at $\vec{r}_i(x, y, z)$ then means interaction of all the images of atom i in the duplicated boxes. Only the coordinates of the central box will be calculated and then applied to the images in the other boxes. Each particle will interact with particles in the same and in the neighbouring boxes. The atoms in the central box will be enclosed and no surface effects are appearing, but the computational costs will be cut down.

The size of the boundary box has to be determined very carefully. Of course it should be large enough, so that the particles in the central box will not be influenced by the symmetry of the artificial lattice. For example, the halogen molecule in the central box should not be able to sense its own image in the surrounding boxes. Usually the size of the cell should be larger than $2 R_{cutoff}$, the *cut-off distance*. This distance results from the range of the interactions and the pair potential $v(r)$ is set to zero for all distances larger than R_{cutoff} . Usually the cutoff distance is

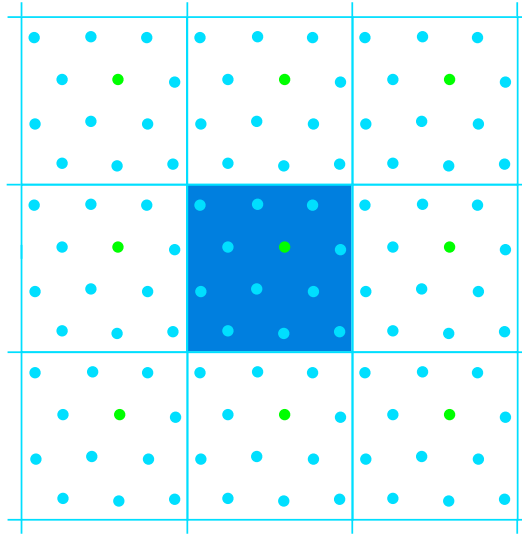


Figure 5.2: *Periodic boundary conditions*

taken at least 2.5 times larger than the minimum distance (2.5 for Lennard-Jones potentials) to include interactions of these length scale, but at this distance the potential should already be near to zero.

The *minimum image criterion* has to be applied, which means that the atom i will only interact with *one* image of atom j in the adjacent cell and not with its own image.

The second criterion for the box-size depends on the investigated subject. The box should be sufficiently large to include the characteristic size of the important features of the system or the length-scale of substantial effects. For investigations of phonon modes, the cell length should be in principle larger than the mean free path of the phonon, so that low-frequency phonon modes with large wavelengths are difficult to implement within periodic boundary conditions. Investigations of these kind of phonons in silicon showed that in this respect the results were better without periodic boundary conditions. There are other methods, like dynamical boundary conditions, which could circumvent this problem, but will not further discussed here. If investigations of phonon modes need to be performed, one should start with local modes, as a first step with the oscillations of the matrix atoms directly involved in the dynamics.

There is another problem which was already mentioned: atoms with sufficient kinetic energy to leave the box will reappear on the other side of it and proceed

their way, but now in the reverse direction. As we will see in chapter 6.6.1.1, in this case the dynamics of the whole system will be disturbed. So the box has also to be of an appropriate length to cover long-time dynamics. This is also the case, where long-time effects of the system will be important, like long-living phonon modes observed in systems like I_2 or Br_2 in rare gas matrices. For reduction of the periodic boundary box to a different, non-cubic size, like for calculating only a slab with expansion mostly in the important direction, while reducing the other ones, all these effects have to be considered carefully.

Summarising the task is to balance the high computational costs, which will rise with the number of interactions and can be reduced by introducing periodic boundary conditions, and the minimal number of atoms which have to be included to reflect the characteristic features of the system.

5.5 State Transitions

In this work we have focussed solely on the classical molecular dynamics and single adiabatic electronic states. The information about the coupling between different adiabatic states is contained in the coupling elements \mathbf{d}_{kj} between the states k, j . Here we follow the procedure used in the simulations of F_2 in Ar [22] and described in [25, 28, 27], which leads to the surface hopping algorithm. The surface hopping method allows to include some quantum effects, like state transitions, to the classical MD simulations of systems. The time dependent electronic Schrödinger equation is solved along the classical propagation of the system and calculation of the coupling elements allows the decision whether a 'hop' from one adiabatic surface to another may occur. The probability for a state transition at a two-state avoided crossing can be dependent on the atomic velocity and the non-adiabatic coupling vector. A transition can be expected when the so-called Massey parameter ζ is in order of unity:

$$\zeta = \left| \frac{\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{12}}{V_1 - V_2} \right| \geq 1 \quad (5.37)$$

and thus is dependent on the separation between the potential surfaces of the system. Now let us assign \mathbf{r} to the electronic and \mathbf{R} to the atomic coordinates, with the latter described classically along any trajectory $\mathbf{R}(t)$. The total Hamiltonian

results as:

$$H = T_R + H_0(\mathbf{r}, \mathbf{R}) \quad (5.38)$$

with the electronic Hamiltonian $H_0(\mathbf{r}, \mathbf{R})$ for fixed atomic positions and T_R is the kinetic energy operator of the atomic motion. The matrix elements of H_0 can be described as

$$V_{ij}(\mathbf{R}) = \langle \phi_i(\mathbf{r}; \mathbf{R}) | H_0(\mathbf{r}, \mathbf{R}) | \phi_j(\mathbf{r}; \mathbf{R}) \rangle \quad (5.39)$$

which were derived here using the DIM method, see chapter 4, see equations 4.15, 4.85. The nonadiabatic coupling vector is defined as:

$$\mathbf{d}_{ij}(\mathbf{R}) = \langle \phi_i(\mathbf{r}; \mathbf{R}) | \nabla_R \phi_j(\mathbf{r}; \mathbf{R}) \rangle \quad (5.40)$$

The wavefunction, that describes the electronic state at time t is expanded in the set of electronic basis functions

$$\Psi(\mathbf{r}, t) = \sum_j c_j(t) \phi_j(\mathbf{r}, \mathbf{R}(t)) \quad (5.41)$$

The coefficients are obtained from the differential equation

$$i\hbar \dot{c}_k(t) = c_k(t) W_k(\mathbf{R}) - i\hbar \sum_j c_j(t) \dot{\mathbf{R}}(t) \mathbf{d}_{jk}(\mathbf{R}) \quad (5.42)$$

and after using the chain rule, we get :

$$\left\langle \phi_k \left| \frac{\partial \phi_j}{\partial t} \right. \right\rangle = \dot{\mathbf{R}}(t) \langle \phi_k(r, \mathbf{R}) | \nabla_R \phi_j(r, \mathbf{R}) \rangle \quad (5.43)$$

$$= \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}(\mathbf{R}) \quad (5.44)$$

The term \mathbf{d}_{kj} is derived, using the Hellman-Feynman theorem:

$$\mathbf{d}_{kj} = \frac{\langle \phi(\mathbf{r}, \mathbf{R}) | \nabla_R H_{el}(\mathbf{r}, \mathbf{R}) | \phi_j(\mathbf{r}, \mathbf{R}) \rangle_r}{W_j(\mathbf{R}) - W_k(\mathbf{R})} \quad (5.45)$$

Transitions between any of the electronic states are promoted now by two factors: First, the off-diagonal elements of V_{jk} , which are in the method used here the spin-orbit coupling terms and the coupling induced by interaction with the rare gas atoms. Second, the nonadiabatic coupling term, which includes the velocity

vector of the nuclei, $\dot{\mathbf{R}} \cdot \mathbf{d}_{kj}$.

The simulation is carried out as follows: The nuclei are propagated classically along the adiabatic surface W_k . At each point of the trajectory, the potential surfaces are constructed and the nonadiabatic couplings $\dot{\mathbf{R}} \cdot \mathbf{d}_{kj}$ are obtained. This procedure is performed for an ensemble of trajectories, which can be described by distribution in the ground state.

The probability for a 'hop' from state j to state k depends on the populations of the electronic states, $a_{jj} = c_j \cdot c_j^*$ and the change in population, which can be expressed in general as:

$$\dot{a}_{kk} = \sum_{l \neq k} b_{kl} \quad (5.46)$$

with b_{kl} being the change in population from state k to state l

$$b_{kl} = -2 \operatorname{Re}(a_{kl}^* \dot{\mathbf{R}} \cdot \mathbf{d}_{kl}) \quad (5.47)$$

So for example, in two level system, a switch from state 1 to 2 is assumed to take place if

$$\frac{\Delta t b_{21}}{a_{11}} > \zeta, \quad (5.48)$$

with ζ being a uniform random number $0 \leq \zeta \leq 1$, compare to eq. 5.37. In this work surface hopping was not applied beyond the determination of the nonadiabatic coupling elements from eq. 5.45. Still this allows the prediction of a state transition, based on the probabilities connected to the value of \mathbf{d}_{kj} .