Theoretical description of the photodissociation process in a lithium dimer

P. Jasik and J. E. Sienkiewicz

Katedra Fizyki Teoretycznej i Informatyki Kwantowej, Wydział Fizyki Technicznej i Matematyki Stosowanej, Politechnika Gdańska, ul. Gabriela Narutowicza 11/12, 80-952 Gdańsk, Polska

Introduction

During the last 20 years, the physics of dilute gases has seen major advances in two fields: laser cooling of atomic and molecular samples and femtosecond chemistry. In both cases, a strong motivation is to use laser light in order to achieve a better control of the system by reducing the energy distribution of the various degrees of freedom. In this context, two fundamental processes, i.e., photoassociation and photodissociation, or in other words formation and breaking of the chemical bond, have motivated a lot of theoretical and experimental studies. Photodissociation of diatomic and small polyatomic molecules is an ideal field for investigating molecular dynamics at a high level of precision. In this poster we present the general theoretical description of the photodissociation process. In Figures from 1. to 5. we show the various types of photodissociation schemes using calculated by us adiabatic potential energy curves of the lithium dimer.

Transition probability

The time-dependent Schrödinger equation for the wavefunction describing the evolution of our molecular system, $\Phi(\mathbf{R}, \mathbf{r}, t)$ is given by expression

$$\left[i\hbar \frac{\partial}{\partial t} - \hat{H}(\mathbf{R}, \mathbf{r}) \right] \Phi(\mathbf{R}, \mathbf{r}, t) = 0 \tag{1}$$

where the molecular Hamiltonian $\hat{H}(\mathbf{R}, \mathbf{r})$ includes all nuclear R and all electronic r degrees of freedom. When the laser light is switched off, $\hat{H}$ is time-independent and therefore $\Phi(\mathbf{R}, \mathbf{r}, t)$ separates into a time-independent part and time-dependent phase factor,

$$\Phi_a(\mathbf{R}, \mathbf{r}, t) = e^{-iE_a t/\hbar} \phi_a(\mathbf{R}, \mathbf{r}). \tag{2}$$

The time-independent Schrödinger equation can be written as

$$[\hat{H}(\mathbf{R}, \mathbf{r}) - E_a] \phi_a(\mathbf{R}, \mathbf{r}) = 0 \tag{3}$$

where $\phi_a(\mathbf{R}, \mathbf{r})$ are the stationary wavefunctions and E_a are eigenenergies. When the light beam is switched on at time $t = 0$ the total Hamiltonian can be expressed as $\hat{H}_{tot}(t) = \hat{H} + \hat{h}(t)$, where the perturbation $\hat{h}(t)$ represents the time-dependent interaction of the electromagnetic field with the molecule. The molecular system is perturbed by $\hat{h}(t)$, which induces transition between eigenstates $|\phi_a\rangle$. In order to solve the equation (1), including the perturbation, the molecular wavefunction is expanded in terms of the $\phi_a(\mathbf{R}, \mathbf{r})$,

$$\Phi(\mathbf{R}, \mathbf{r}, t) = \sum_a a_a(t) \phi_a(\mathbf{R}, \mathbf{r}) e^{-iE_a t/\hbar} \tag{4}$$

with time-dependent coefficients $a_a(t)$. We obtain these coefficients inserting expansion (4) into (1) with total Hamiltonian $\hat{H}_{tot}(t)$. Multiplication with $\langle \phi_a |$ and using the orthogonal relation yields the following set of coupled equations,

$$i\hbar \frac{d}{dt} a_a(t) = \sum_{a'} h_{aa'}(t) a_{a'}(t) e^{i\omega_{aa'}t}, \tag{5}$$

where the time-dependent matrix elements of the perturbation operator,

$$h_{aa'}(t) = \langle \phi_a | \hat{h}(t) | \phi_{a'} \rangle = \int d\mathbf{R} \, d\mathbf{r} \, \phi_a^*(\mathbf{R}, \mathbf{r}) \, \hat{h}(t) \, \phi_{a'}(\mathbf{R}, \mathbf{r}), \tag{6}$$

couple state $|\phi_a\rangle$ with all other state $|\phi_{a'}\rangle$. The transition frequencies $\omega_{aa'}$ are defined by $\omega_{aa'} = (E_a - E_{a'})/\hbar$. The time-dependent coefficients $a_a(t)$ together with the stationary basis functions $\phi_a(\mathbf{R}, \mathbf{r})$ describe completely the state of the molecule at each instant t [1]. The perturbation $\hat{h}(t) = \hat{\mathbf{d}} \cdot \mathbf{E}_0 \cos \omega t$ within the electric dipole approximation, where $\hat{\mathbf{d}}$ is the electric dipole operator of the molecule and $\mathbf{E}_0$ is the electric field vector of the light beam [2]. Insertion of above expression into (6) yields

$$h_{aa'}(t) = d_{aa'} \cos \omega t, \qquad d_{aa'} = \langle \phi_a | \mathbf{E}_0 \cdot \hat{\mathbf{d}} | \phi_{a'} \rangle = E_0 \langle \phi_a | \mathbf{e} \cdot \hat{\mathbf{d}} | \phi_{a'} \rangle, \tag{7}$$

where $E_0 = |\mathbf{E}_0|$ and e being a unit vector in the direction of the electric field. Using equations (7) in (5) and replacing the coefficients $a_{a'}(t)$ on the right-hand side by their initial values at $t = 0$ ($a_i(0) = 1$ and $a_{a\neq i}(0) = 0$), the evolution of each final state ($f \neq i$) is given by the equation

$$i\hbar \frac{d}{dt} a_f(t) = d_{fi} \cos \omega t \, e^{i\omega_{fi}t}. \tag{8}$$

From above expression and the fact that the probabilities $|a_a|^2$ do not significantly change while the light beam is switched on ($a_i(t)|^2 \approx 1$ and $\sum_{f\neq i} |a_f(t)|^2 \ll 1$), we obtain the time-dependent probability for making a transition from initial state $|\phi_i\rangle$ to final state $|\phi_f\rangle$ under the influence of the photon beam with frequency ω

$$P_{fi}(t) = |a_f(t)|^2 = \left(\frac{d_{fi}}{\hbar}\right)^2 \frac{\sin^2[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)^2}. \tag{9}$$

Using the representation of well known for the Dirac delta-function [2] we can rewrite (9), in the limit as t goes to infinity, as

$$P_{fi}(t) = \frac{\pi}{2} \left(\frac{d_{fi}}{\hbar}\right)^2 t \, \delta(\omega_{fi}-\omega). \tag{10}$$

The probability rises linearly with time and therefore it leads to a constant transition rate $k_{fi} = \frac{d}{dt} P_{fi}$, transition probability per unit time interval [3].

The photodissociation cross section

In order to determine the absorption cross section $\sigma(\omega)$ we should consider a several assumptions. The light beam propagates along the z-axis through a cavity containing the molecular lithium gas. N is the total number of molecules in the volume of the cavity V. We also assume that the beam produces the monochromatic light with frequency $\omega = \omega_{fi}$. Let us consider a thin slice perpendicular to the z-axis with length dz and area A. The slice is sufficiently thin that the intensity I (energy crossing through a unit area per unit time) as well as the energy density W (energy per volume) are approximately constant within the slice [2]. If the energy in the slice is $S = A \, dz \, W$, the result of molecular transition from initial state $|\phi_i\rangle$ to final state $|\phi_f\rangle$ is decreasing it to expression

$$dS = -N \frac{A \, dz}{V} \hbar \omega_{fi} k_{fi} \, dt = A \, dz \, dW \tag{11}$$

within the time interval dt, where $N A dz/V$ is the number of molecules within the slice, $\hbar \omega_{fi}$ is the absorbed energy per molecule and k_{fi} is the transition rate. Using the above equation in which we insert (7) and transition rate expression we get the following term

$$dW = -\omega_{fi} \, \delta(\omega_{fi} - \omega) \, dt \frac{\pi N E_0^2}{2\hbar V} |\langle \phi_f | \mathbf{e} \cdot \hat{\mathbf{d}} | \phi_i \rangle|^2, \tag{12}$$

where E_0 is the amplitude of the electric field and e is a unit vector in the direction of $\mathbf{E}_0$. Inserting the relation $E_0^2 = 2W/\epsilon_0$ [2], where ϵ_0 is the electric permittivity, we obtain

$$\frac{dW}{dt} = -\omega_{fi} \, \delta(\omega_{fi} - \omega) \frac{\pi N W}{\hbar \epsilon_0 V} |\langle \phi_f | \mathbf{e} \cdot \hat{\mathbf{d}} | \phi_i \rangle|^2. \tag{13}$$

Using equations (13) and some simple expressions $dW/dt = dI/dz$, $W = I/c$, $dI/dz = -\rho \, \sigma(\omega) \, I$, where $\rho = N/V$ is the density of the lithium gas in the cavity [1, 2], we finally can define the absorption cross section as

$$\sigma(\omega) = \frac{\pi}{\hbar \epsilon_0 c} \omega_{fi} \, \delta(\omega_{fi} - \omega) \, |\langle \phi_f | \mathbf{e} \cdot \hat{\mathbf{d}} | \phi_i \rangle|^2. \tag{14}$$

Within the Born-Oppenheimer approximation [4, 5, 6] the time-independent molecular wavefunctions for the various electronic states can be written as

$$\phi_{kl}(\mathbf{R}, \mathbf{r}) = \Psi_{kl}^{nu}(\mathbf{R}) \, \psi_k^{el}(\mathbf{r}, \mathbf{R}), \tag{15}$$

where ψ_k^{el} is the k-th solution of the electronic Schrödinger equation and Ψ_{kl}^{nu} is a distinct solution of the nuclear Schrödinger equation for this particular electronic state with energy E_{kl}. The index l labels the particular solution of the nuclear Schrödinger equation. Inserting (15) into (14) yields the following expression for the absorption cross section for a transition from initial state $|\phi_{k_i l_i}\rangle$ to final state $|\phi_{k_f l_f}\rangle$,

$$\sigma(\omega) = \frac{\pi}{\hbar \epsilon_0 c} \omega_{k_f l_f, k_i l_i} \, \delta(\omega_{k_f l_f, k_i l_i} - \omega) \, |\langle \Psi_{k_f l_f}^{nu}(\mathbf{R}) | \mu_{k_f k_i}^s(\mathbf{R}) | \Psi_{k_i l_i}^{nu}(\mathbf{R}) \rangle|^2, \tag{16}$$

where $\mu_{k_f k_i}^s(\mathbf{R}) = \vec{e} \cdot \vec{\mu}_{k_f k_i}$ is defined as the transition dipole moment function,

$$\mu_{k_f k_i}^s(\mathbf{R}) = |\langle \psi_{k_f}^{el}(\mathbf{r}, \mathbf{R}) | \hat{\mathbf{d}} | \psi_{k_i}^{el}(\mathbf{r}, \mathbf{R}) \rangle|^2. \tag{17}$$

Below we present the necessary scheme of the calculation of absorbtion cross section in bound-bound transitions [1]:

- The adiabatic potential energy curves $V_{k_i}(\mathbf{R})$ and $V_{k_f}(\mathbf{R})$ for the electronic states between which the transition occurs.
- The transition dipole moment function $\vec{\mu}_{k_f k_i}(\mathbf{R})$.
- The nuclear wavefunctions $\Psi_{k_i l_i}^{nu}(\mathbf{R})$ and $\Psi_{k_f l_f}^{nu}(\mathbf{R})$.
- The overlap of the nuclear wavefunctions and transition dipole moment function, $\langle \Psi_{k_f l_f}^{nu} | \mu_{k_f k_i}^s | \Psi_{k_i l_i}^{nu} \rangle$.

Photodissociation schemes
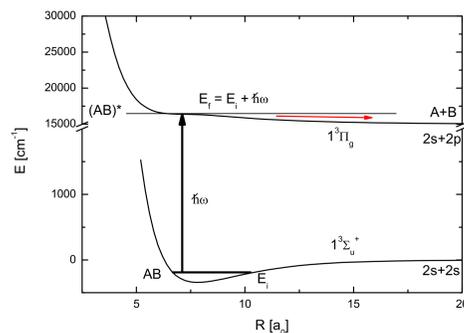
Fig. 1. The single UV photon direct photodissociation scheme. The photon creates a single quantum state in the upper electronic state.
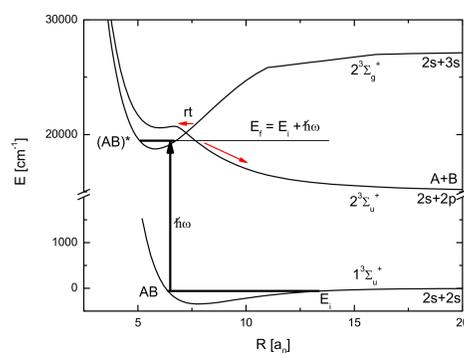
Fig. 2. The electronic predissociation scheme (Herzberg's type I predissociation). The photon excites first a binding electronic state. The molecule undergoes a radiationless transition (rt) from the binding to the repulsive state and subsequently decays.
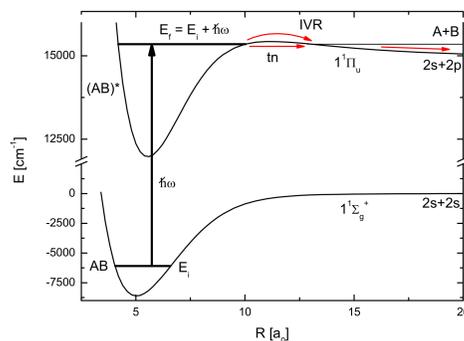
Fig. 3. The vibrational predissociation scheme (Herzberg's type II predissociation). The photon creates a quasi-bond state in the potential well which decays either by tunneling (tn) through the barrier or by internal vibrational energy redistribution (IVR).
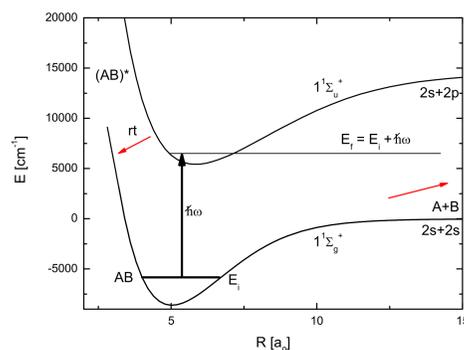
Fig. 4. Scheme of unimolecular decay induced by electronic excitation. The photon creates a bound level in the upper electronic state which subsequently decays as a result of radiationless transition (rt) to the highly excited vibrational-rotational quantum level above the dissociation threshold of the electronic ground state.
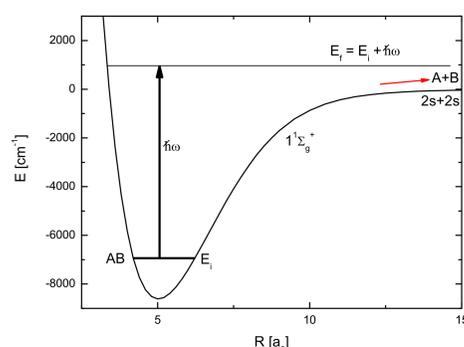
Fig. 5. Scheme of unimolecular decay induced by electronic excitation. The highly excited quantum state above the dissociation threshold is created directly by pumping a large amount of energy into the molecule by single-photon excitation of overtone vibrations.

The photodissociation cross section

Let us consider the situation that the photon excites states with energies above the dissociation threshold. In the continuum part of the molecular Hamiltonian, the absorption spectrum becomes a continuous function of the energy $E_f = E_i + \hbar \omega$. It rises that the nuclear wavefunctions are continuum wavefunctions which asymptotically behave like free waves and for each final energy E_f there are several possible dissociation channels represented by degenerate solutions of the nuclear Schrödinger equation. In order to expand the time-dependent molecular wavefunction $\Phi(\mathbf{R}, \mathbf{r}, t)$ for bound-free transition in terms of orthogonal and complete stationary wavefunctions $\phi_n(\mathbf{R}, \mathbf{r})$ we proceed in the same way as for the bound-bound transition. We should remember that the expansion functions for the nuclear part of the total wavefunction are now continuum wavefunctions [7, 8]. After equation (4), the total time-dependent molecular wavefunction $\Phi(\mathbf{R}, \mathbf{r}, t)$ is expanded within the Born-Oppenheimer approximation as

$$\Phi(\mathbf{R}, \mathbf{r}, t) = a_i(t) \, \psi_i(\mathbf{r}, \mathbf{R}) \, \Psi_i(\mathbf{R}, E_i) \, e^{-iE_i t/\hbar} + \int dE_f \sum_{n=0}^{n_{max}} a_f(t, E_f, n) \, \psi_f(\mathbf{r}, \mathbf{R}) \, \Psi_f(\mathbf{R}, E_f, n) \, e^{-iE_f t/\hbar}. \tag{18}$$

The first part of above expression describes the initial state with energy E_i before the light beam is switched on and the second term represents the total wavefunction in the upper electronic state. The initial conditions for the corresponding time-dependent coefficients are $a_i(0) = 1$ and $a_f(0, E_f, n) = 0$ for all energies E_f and all vibrational channels n. The sum over a in (4) is replaced in (18) by an integral over E_f and a sum over n. The integral over E_f reflects the fact that the spectrum in the upper electronic state is continuous and the summation over all open vibrational channels n accounts for the degeneracy of the continuum wavefunctions [1]. Because of the phase factor $e^{-iE_f t/\hbar}$ governs the time dependence of all degenerate final states, the laser light excites resonantly all states having the same total energy E_f but different outgoing vibrational channels n. This is taken into account in the final expression for the total photodissociation cross section

$$\sigma_{tot}(\omega) = \sum_n \sigma(\omega, n) \tag{19}$$

with the partial photodissociation cross section given by

$$\sigma(\omega, n) = \frac{\rho \pi}{\hbar \epsilon_0 c} \omega_{fi} \, \delta(\omega_{fi} - \omega) \, |\langle \Psi_f(E_f, n) | \mu_{fi}^s | \Psi_i(E_i) \rangle|^2, \tag{20}$$

where the factor $\rho = (2\pi\hbar)^{-1}$ and the rest terms of above equation have the same meaning as in (16). Integrating (20) over an energy interval dE_f we finally obtain

$$\sigma(\omega, n) = \mathcal{C} \, E_{photon} \, |t(E_f, n)|^2, \tag{21}$$

where $\mathcal{C} = \rho \pi / \hbar \epsilon_0 c$ is a constant, and

$$t(E_f, n) = \langle \Psi_f(R, E_f, n) | \mu_{fi}^s(R, r) | \Psi_i(R, E_i) \rangle \tag{22}$$

is the partial photodissociation amplitude [3]. In the end we can define final vibrational state distributions for fixed frequency ω, $P(\omega, n) = \sigma(\omega, n)/\sigma_{tot}(\omega)$.

The time-dependent wavepacket

We consider the time-dependent nuclear Schrödinger equation in the form

$$\left[i\hbar \frac{\partial}{\partial t} - \hat{H}(\mathbf{R}) \right] \Theta(\mathbf{R}, t) = 0 \tag{23}$$

where Θ is a time-dependent wavepacket evolving on the adiabatic potential energy curve of the excited electronic state. We can define the wavepacket as a coherent superposition of stationary states, each being multiplied by the time-evolution factor $e^{-iEt/\hbar}$ [3, 9]. The construction of the time-dependent wavepacket can be given as

$$\Theta_f(R, r, t) = \int dE_f \sum_{n=0}^{n_{max}} c(E_f, n) \, \Psi_f(R, r, E_f, n) \, e^{-iE_f t/\hbar}, \tag{24}$$

Above equation is the formal analogue of equation (4) and $\Theta_f(R, r, t)$ is a solution of (23) because each stationary wavefunction $\Psi_f(R, r, E_f, n)$ is an eigenfunction of $\hat{H}$ with the energy E_f. In the next step we determine the initial condition in order to calculate coefficients $c(E_f, n)$,

$$\Theta_f(R, r, t = 0) = \mu_{fi}^s \, \Psi_i(R, r, E_i). \tag{25}$$

The initial condition informs us that the wavepacket at its start in the upper electronic state equals the wavefunction of the parent molecule, $\Psi_i(R, r, E_i)$, multiplied by the transition dipole function $\mu_{fi}^s(R, r)$. Using the equation (24) and the initial condition (25) we obtain the relation

$$c(E_f, n) = \rho \langle \Psi_f(E_f, n) | \mu_{fi}^s | \Psi_i(E_i) \rangle = \rho \, t(E_f, n), \tag{26}$$

where the amplitudes $t(E_f, n)$ are defined in (22). Multiplying (24) from the left by $\Theta_f(0)$ and integrating over all nuclear coordinates gives

$$S(t) \equiv \langle \Theta_f(0) | \Theta_f(t) \rangle = \rho \int dE_f \sum_{n=0}^{n_{max}} t(E_f, n) \langle \Theta_f(0) | \Psi_f(E_f, n) \rangle \, e^{-iE_f t/\hbar}, \tag{27}$$

$$S(t) \equiv \langle \Theta_f(0) | \Theta_f(t) \rangle = \rho \int dE_f \sum_{n=0}^{n_{max}} |t(E_f, n)|^2 \, e^{-iE_f t/\hbar}, \tag{28}$$

where $S(t)$ is the autocorrelation function. Using some simple manipulations and following the equation (21) yields the final expression for the total photodissociation cross section,

$$\sigma_{tot}(E_f) = \mathcal{C} E_{photon} \int_{-\infty}^{+\infty} dt \, e^{-iE_f t/\hbar} \, S(t). \tag{29}$$

Below we present the necessary scheme of the time-dependent calculation of the photodissociation cross section: i) Propagation of the wavepacket $\Theta_f(t)$ in the upper electronic state with initial condition $\Theta_f(0) = \mu_{fi}^s \Psi_i(E_i)$; ii) Calculation and Fourier transformation of the autocorrelation function $S(t)$ in order to yield the total dissociation cross section; iii) Propagation of the wavepacket until it has completely left the interaction zone and calculation of the partial cross sections $\sigma(E_f, n)$ [1].

Let us consider the photodissociation of the lithium dimer. Since the nuclear Hamiltonian is time-independent the wavepacket at time $(t + dt)$ follows from the wavepacket at time t according to

$$\Theta(t + dt) = e^{-i\hat{H} dt/\hbar} \, \Theta(t) \tag{30}$$

Following Kosloff [10] the time evolution-operator is expanded in terms of Chebychev polynomials φ_k,

$$e^{\hat{X}} \approx \sum_{k=0}^{K} a_k \varphi_k(\hat{X}), \tag{31}$$

where $\hat{X} = -i\hat{H} dt/(\hbar s)$, s is a scaling factor and the expansion coefficients a_k are special complex numbers. The Chebychev polynomials satisfy the recursion relation $\varphi_k(\hat{X}) = 2\hat{X} \varphi_{k-1}(\hat{X}) + \varphi_{k-2}(\hat{X})$, starting with $\varphi_0(\hat{X}) = 1$ and $\varphi_1(\hat{X}) = \hat{X}$. Inserting (31) into (30) we obtain the wavepacket at $(t + dt)$

$$\Theta(t + dt) \approx \sum_{k=0}^{K} a_k \Theta^{(k)}(t + dt) \tag{32}$$

where we have defined $\Theta^{(k)}(t + dt) = \varphi_k(\hat{X}) \Theta(t)$. The $\Theta^{(k)}$ fulfil the same recursion relation as the Chebychev polynomials, namely

$$\Theta^{(k)}(t + dt) = 2\hat{X} \Theta^{(k-1)}(t + dt) + \Theta^{(k-2)}(t + dt) \tag{33}$$

with $\Theta^{(0)}(t + dt) = \Theta(t)$ and $\Theta^{(1)}(t + dt) = \hat{X} \Theta(t)$. Above equations provide a very convenient iteration scheme for the wavepacket at each coordinate point.

References

References

[1] R. Schinke, Photodissociation dynamics, Cambridge University Press, Cambridge, 1993.

[2] R. Loudon, The quantum theory of light, Oxford University Press, Oxford, 1983.

[3] C. Cohen-Tannoudji, B. Diu and F. Laloë, Quantum mechanics, Vols. I and II, Wiley, New York, 1977.

[4] M. Weissbluth, Atoms and molecules, Academic Press, New York, 1978.

[5] R. Daudel, G. Leroy, D. Peeters and M. Sana, Quantum chemistry, Wiley, Chichester, 1983.

[6] H. Lefebvre-Brion and R.W. Field, Perturbations in the spectra of diatomic molecules, Academic Press, Orlando, 1986.

[7] T.Y. Wu and T. Ohmura, Quantum theory of scattering, Englewood Cliffs, Prentice-Hall, 1962.

[8] J.R. Taylor, Scattering theory: The quantum theory on nonrelativistic collisions, Wiley, New York, 1972.

[9] M.S. Child, Semiclassical mechanics with molecular applications, Clarendon Press, Oxford, 1991.

[10] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. 81, 3967, 1984.