Appendix A

Kinetic energy evaluation

A.1 DVR and FFT methods

In this work two main methods were used to evaluate the kinetic energy operator for density matrices propagations, namely the Fast Fourier Transform (FFT) algorithm proposed by Berman and Kosloff [71], or alternatively the sinc–function Discrete Variable Representation (DVR) method of Colbert and Miller [150]. Here we restrict to a one dimensional problem, with the kinetic energy operator

$$\hat{T} = -\frac{1}{2\mu_z}\frac{\partial^2}{\partial z^2} \quad .$$

In the FFT algorithm, the commutator element $\left[\hat{T},\ \hat{\rho}\right]_{rs}$ required in the discretized Liouville–von Neumann equation(2.9) ($r,\ s$ are indices of the coordinate grid, $Z_r = Z_0 + r\Delta Z$) is evaluated by

(i) fast Fourier transforming the density matrix $\hat{\rho}$ to get $\hat{\rho}_k$, the density matrix represented in the reciprocal (momentum) space,

(ii) multiplying the (r, s) element of $\hat{\rho}_k$ by $\frac{1}{2\mu_Z}(k^2_{Z,r} - k^2_{Z,s})$ (the kinetic energy operator is local in momentum space [1]) and

(iii) backtransforming the resulting matrix to coordinate space.

In the Coupled Channel Density Matrix (CCDM) approach with one bound coordinate (x, say), treated in an eigenstate representation and only the other one (Z) treated with FFT, these steps have to be repeated separately for each density matrix block $\hat{\rho}_{kl}$ (with k, l being eigenstate indices).

In the sinc–function DVR method, the individual free kinetic matrix elements are evaluated directly according to [150]

$$T^{rt} = \frac{(-1)^{r-t}}{2\mu_Z \Delta Z'^2} \begin{cases} \frac{\pi^2}{3} - \frac{1}{2r^2} & ; r = t \\ \frac{2}{(r-t)^2} - \frac{2}{(r+t)^2} & ; r \neq t \quad . \end{cases} \tag{A.1}$$

In the latter Eqn., $\Delta Z'$ is the spacing between (equidistant) points on the sinc–function DVR grid, which in general may be different from the grid spacing ΔZ of the Fourier grid. The application of the operator on $\hat{\rho}$ corresponds simply to a matrix multiplication.

A.2 DVR versus FFT for CCDM calculations

To address the advantages and disadvantages of FFT or DVR methods to represent the free coordinate, we performed a series of calculations for D_2 (vibrational ground state), $\overline{E}_k(0) = 0.2$ eV, $K = 8$ (asymptotic basis), propagation time $t_\infty = 250\ fs$, timestep $\Delta t = 25\ fs$, Newton polynomial order $n = 300$, and varying grid sizes along Z. The potential parameters are the same as in subsections 5.1-5.4, listed in Table 5.1.

Let N be the number of Fourier and N' be the number of DVR grid points. Then, for an identical grid consisting of $N = N' = 64$ points, both methods gave identical results with regard to the first excited state population $P_1(t_\infty)$ to within 0.5%. ($P_1(t_\infty)$ is less than 10^{-4} at this low impact energy). The calculations took 13 and 7 hours on a HP9000/735 workstation for the DVR and the Fourier

basis, respectively. For $N = N' = 128$ points, the computation times increase to 156 (DVR) and 38 (FFT) hours, respectively, confirming the theoretically expected scaling laws of $N^2 logN$ for the FFT algorithm [71], and N^3 for DVR.

Hence, the FFT algorithm is clearly to be preferred for the present applications. The DVR algorithm, however, offers high flexibility in shaping the grid to desired low energy potential regions [150], and in choosing the number of grid points. (In the case of FFT, N has to be a product of prime number to the power of integers). Therefore, in certain cases (if $N' \ll N$), the DVR may become advantageous. For the FFT, a Fourier mapping method could be used to optimally design the grid for this cases [182].