Section 12.2:Trajectory surface hopping with temporally localized forces*

Coker and Xiao [3] proposed a modified TSH algorithm that integrates the force (12.33). It employs a predictor-corrector method (see Section 15.2), breaking the time interval Δ up into $M = \frac{\Delta}{\delta}$ intermediate segments. A predictor step Hamiltonian matrix $H^p_{ij}(t' + m\delta)$ that linearly interpolates between $H^p_{ij}(t')$ and $H^p_{ij}(t' + \Delta)$:

$$H^p_{ij}(t' + m\delta) = E_i(t')\delta_{ij} + \frac{m\delta}{\Delta}\langle\psi_i(t')|\Delta V^p(t')|\psi_j(t')\rangle, \quad m \leq M, \tag{1}$$

comprising instantaneous adiabatic eigenstates ψ_i and ψ_j, is diagonalized at each instant $t' + m\delta$. The difference $\Delta V^p(t')$ involves the interaction between classical and quantal degrees of freedom at the time t' and the preceding time $t' - \Delta$:

$$\Delta V^p(t') = V^p(\mathbf{x}, \mathbf{X}[t']) - V^p(\mathbf{x}, \mathbf{X}[t' - \Delta]) \tag{2}$$

With these assignments, the propagation technique can be summarized as a sequence of three basic operations:

1. The interpolation (1) is used to advance the expansion coefficients c_i. More specifically, diagonalization of H^p_{ij} at each timestep $t' + m\delta$ yields new energy eigenvalues $E_n(t' + m\delta)$. These instantaneous eigenvalues, in turn, define a propagator matrix $\mathbf{T}(t'+(m+1)\delta, t'+m\delta)$ for the coefficients c_i. The short time approximation for $\mathbf{T}$ may be written in a *split operator form* (see Sect.15.2.2) as

$$\begin{aligned} T_{ij}(t' + m\delta, t + m\delta) = \exp[-\frac{i\delta}{2\hbar}(E_i(t' + (m+1)\delta) + E_j(t' + m\delta)] \\ \times \langle\psi_i(t' + (m+1)\delta)|\psi_j(t' + m\delta)\rangle \end{aligned} \tag{3}$$

   From

$$\mathbf{c}(t' + (\mathrm{m}+1)\delta) = \mathbf{T}(t' + (\mathrm{m}+1)\delta, t' + \mathrm{m}\delta)\mathbf{c}(t' + \mathrm{m}\delta) \tag{4}$$

   one deduces the hopping probabilities $g_{\alpha\beta}$ (11.15) at each time step and decides if a transition to another surface occurs or not, enforcing the constraint that the total instantaneous energy of a given trajectory must be greater than the adiabatic potential energy of the new state for a hop to take place.

2. If no hop occurs at any of the M steps into which the time interval is subdivided, the motion remains confined to the adiabatic potential energy

surface with index α. The nuclear motion results from the action of the Hellman-Feynman force

$$\mathbf{F}_{\alpha\alpha} = -\frac{\partial E_\alpha}{\partial \mathbf{X}} \tag{5}$$

If, on the other hand, a hop takes place to the level β , the instantaneous Pechukas force $\mathbf{F}_{\beta\alpha}$ (Eq. 12.33) is employed. The acceleration associated with $\mathbf{F}_{\beta\alpha}$ is used to define the velocity at the starting time of the interval Δ , namely:

$$\mathbf{v}(t') = \mathbf{v}(t' - \Delta) - \frac{(E_\beta - E_\alpha)}{\mathbf{A}^{\wedge}_{\beta\alpha}\mathbf{v}(t' - \Delta)} \frac{\mathbf{A}^{\wedge}_{\beta\alpha}}{M} \tag{6}$$

Simultaneously, all particle velocities are scaled to reconcile (6) with the energy conservation constraint (12.36). Lastly, nuclear dynamics in the interval Δ proceeds on the adiabatic energy surface β according to

$$\mathbf{X}(t' + \Delta) = \mathbf{X}(t') + \mathbf{v}(t')\Delta + \frac{\Delta^2}{2M}\mathbf{F}_{\beta\beta} \tag{7}$$

3. The final nuclear position vector $\mathbf{X}(t' + \Delta)$, obtained in the predictor cycle, is used to define a new interpolating Hamiltonian matrix for the subsequent corrector cycle. In analogy to Eq.(1), we write:

$$H^c_{ij}(t' + m\delta) = E_i(t')\delta_{ij} + \frac{m\delta}{\Delta}\langle\psi_i(t')|\Delta V^c(t')|\psi_j(t')\rangle, \quad m \leq M \tag{8}$$

and

$$\Delta V^c(t') = V^c(\mathbf{x}, \mathbf{X}(t' + \Delta]) - V^c(\mathbf{x}, \mathbf{X}(t')) \tag{9}$$

The steps (1) and (2) are now repeated adopting the corrected Hamiltonian (8).

Realizing this scheme allows for comparison with exactly solvable model problems and thus to assess the effect of the lack of unitarity that mars the semiclassical propagator approach, as pointed out in the preceding section, . Treating the cases of the *Tully canon* (see 11.2.1) by the numerical procedure outlined above, Coker and Xiao [3] arrive at results that typically deviate by ten percent from the quantum mechanical standard.

Bibliography

[1] P.Pechukas, Phys.Rev. 181,166 (1969).

[2] P.Pechukas, Phys.Rev. 181,174 (1969).

[3] Coker, Xiao, Jour.Chem.Phys. 102, 496 (1995).

[4] F.Webster et al., Jour.Chem.Phys. 100, 4835 (1994).

[5] J.C.Tully, Jour.Chem.Phys. 93, 1061 (1990).

[6] W.H. Miller, Jour.Chem.Phys. 53, 3578 (1970).

[7] R. Marcus, Jour.Chem.Phys. 56, 3548 (1972).

[8] H. Kreek, R.Marcus, Jour.Chem.Phys. 61, 3308 (1974).

[9] W.H.Miller, Jour.Phys.Chem.A 105, 2942 (2001).

[10] M.F.Herman, E. Kluk, Chem.Phys. 91, 27 (1984).

[11] X.Sun, W.H.Miller, Jour.Chem.Phys. 106, 6346 (1997).

[12] G.Stock, M.Thoss Phys.Rev.Lett. 78, 578 (1997).

[13] M.Thoss, G.Stock Phys.Rev.A 59, 64 (1999).

[14] J.Schwinger, in: *Quantum Theory of Angular Momentum*, edited by L.C.Biedenharn and H.Van Dam, Academic Press, New York 1965.

[15] T.Holstein, H. Primakoff, Phys.Rev 58, 1098 (1940).

[16] P.Garbaczewski, Phys.Rep. 36, 65 (1978).

[17] W.H.Miller Jour.Phys.Chem.A 113, 1409 (2009).

[18] M.Thoss, G.Stock, Adv.Chem.Phys.131, 243 (2005).

[19] M.Thoss, W.H.Miller, G.Stock, Jour.Chem.Phys. 112, 10282 (2000).

[20] K.K. Innes, I.G.Ross, W.R.Moomaw, J.Mol.Spectrosc. 132, 492 (1988).

[21] C. Woywod, W. Domcke, A. L. Sobolewski, and H.-J. Werner, Jour.Chem.Phys. 100, 1400 (1994).

[22] I. Yamazaki, T.Murao, T.Yamanaka, K. Yoshihara, Faraday Discuss. 75, 395 (1983).

[23] G.A.Worth, H.D.Meyer, L.Cederbaum, Jour.Chem.Phys. 109, 3518 (1998).

[24] E.Heller, Jour.Chem.Phys. 68, 2066 (1978).

[25] *Molecular Spectra and Molecular Structure III, Electronic Spectra of Polyatomic Molecules*, Van Nostrand, Princeton 1966.

[26] Walton, Manolopoulos, Mol.Phys.87, 961 (1996).

[27] S. Krempl, M.Winterstetter, H.Plöhn, W.Domcke, Jour.Chem.Phys. 100, 926 (1994).

[28] S. Krempl, M.Winterstetter, W.Domcke, Jour.Chem.Phys. 102, 6499 (1995).

[29] X.Sun, W.H.Miller, Jour.Chem.Phys. 110, 6635 (1999).

[30] K.G.Kay, Jour.Chem.Phys. 101 2250 (1994).

[31] W.Schweizer, *Numerical Quantum Dynamics*, Kluwer Academic Publisher 2001.

[32] M.Herman, Chem.Phys.Lett. 275, 445 (1997).

[33] J.D.Doll, T.L.Beck, D.L.Freeman, Jour.Chem.Phys. 89,5753 (1988).

[34] V.S.Filinov, Nucl.Phys.B 271, 717 (1986).

[35] H.Wang, D.E.Manolopoulos, W.H.Miller, Jour.Chem.Phys. 115, 6317 (2001).

[36] H.Wang, X. Sun, W.H.Miller, Jour.Chem.Phys. 108, 9726 (1998).

[37] X.Sun, H.Wang, W.H.Miller, Jour.Chem.Phys. 109, 7064 (1998).

[38] X.Sun, H.Wang, W.H.Miller, Jour.Chem.Phys. 109, 4190 (1998).

[39] N.Makri, K.Thompson, Chem.Phys.Lett. 291, 101 (1998).

[40] W.H.Miller,Faraday Discuss. 110, 1 (1998).

[41] R.Gelabert, X.Gimenez,M.Thoss, H.B.Wang,W.H.Miller, Jour.Phys.Chem. 114, 2572 (2001).

[42] V.S.Batista,M.T.Zanni, B.J.Greenblatt, D.M. Neumark, W.H.Miller, Jour.Chem.Phys. 110 3736 (1999).

[43] V.Guallar, V.S.Batista, W.H.Miller, Jour.Chem.Phys. 113, 9510 (2000).

[44] D.E.Skinner, W.H.Miller, Jour.Chem.Phys. 111, 10787 (1999).

[45] M.V.Ovchinnikov, A.Apkarian, G.A.Voth, Jour.Chem.Phys. 114, 7130 (2001).

[46] E.Heller, Jour.Chem.Phys. 62, 1544 (1975).

[47] D.Huber, E.J.Heller, Jour.Chem.Phys. 89, 4753 (1988).

[48] E.J.Heller, Jour.Chem.Phys. 94, 2723 (1991).

[49] R. Schneider, W. Domcke, and H. Köppel, J. Chem. Phys. 92, 1045 (1990).

[50] G.Stock, R.Schneider, and W. Domcke, Jour.Chem.Phys. 90, 7184 (1989).

[51] G.Stock and W.Domcke, Jour. Chem. Phys. 93, 5496 (1990).

[52] L.Seidner, G.Stock, A.L.Sobolewski, and W. Domcke, Jour.Chem.Phys.96, 5298 (1992).

[53] A.L.Sobolewski, C. Woywod, and W. Domcke, Jour.Chem.Phys. 98, 5627 (1993).

[54] G.Stock, C.Woywod, W. Domcke, T. Swinney, and B. S. Hudson, Jour.Chem.Phys. 103, 6851 (1995).

[55] G.Stock, Jour.Chem.Phys. 103, 2888 (1995).

[56] G. Stock and W. H. Miller, Chem.Phys Lett. 197, 396 (1992).

[57] U. Müller and G. Stock, Jour.Chem.Phys. 107, 6230 (1997).

[58] U. Müller and G. Stock, Jour.Chem.Phys. 111, 77 (1999).

[59] N.Ananth, C. Venkataraman, W.H.Miller, Jour.Chem.Phys. 127, 084114 (2007).