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Quantum recurrence from a semiclassical resummation

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Abstract

The semiclassical expression for the momentum autocorrelation function of a particle in a one-dimensional box is analyzed. The classical autocorrelation function is shown to be the first term of the semiclassical series. Systematical inclusion of all the terms restores quantum recurrence of the momentum autocorrelation function.

Keywords: Momentum autocorrelation function; Wigner–Weyl representation; Semiclassical dynamics; Quantum corrections

In an early paper, Deutch et al. [1] compared classical and quantum momentum autocorrelation functions of a particle in a one-dimensional box. They found that the classical autocorrelation function decays irreversibly whereas the quantum function displays recurrence, a signature of phase coherence. The classical autocorrelation function is the simple $\hbar \to 0$ limit of the quantum result, however, an analytic expansion of the quantum autocorrelation function in terms of $\hbar$ has not been obtained. The non-analytic nature of the quantum correlation function is related to the time-divergence in classical response theory [2–6]. Specifically, the reported divergence arises from the interchange of non-commuting limits of $\hbar \to 0$ and $t \to \infty$. A semiclassical analysis of microcanonical response functions leads to the phase-space quantization [3], which removes the classical divergence and results in a correspondence between quantum transitions and classical trajectories. In this paper, we derive a semiclassical $\hbar$ expansion of the canonical correlation function using the Weyl–Wigner symbol-calculus approach and resum the expansion to obtain non-perturbative expression which captures the quantum recurrence in canonical correlation functions.

Following [1] we adopt the symmetrized quantum mechanical correlation function

$$C(t) = \frac{1}{2}\mathrm{Tr}\left[\hat{\rho}_{\mathrm{eq}}(\hat{p}(t)\hat{p} + \hat{p}\hat{p}(t))\right], \tag{1}$$

where $\hat{\rho}_{\mathrm{eq}}$ is the Boltzmann operator. $C(t)$ is often used in literature because of its Fourier relation with the imaginary part $\chi''(\omega)$ of the response function, $C(\omega) = \hbar\coth(\beta\hbar\omega/2)\chi''(\omega)$. For a particle in one-dimensional box, the autocorrelation function (1) is given by [1]

$$\begin{aligned} C(t) = {} & \left(\frac{\hbar^2\sqrt{\pi}}{\zeta^3 L^2 Z}\right)\sum_{k=-\infty}^{+\infty}\sum_{n=-\infty}^{+\infty}\exp\left[-\left((2k+1)\frac{T}{2}-\frac{n\pi}{\zeta}\right)^2\right] \\ & \times\left\{\left[\frac{2}{(2k+1)^2}-\frac{4}{(2k+1)^2}\left((2k+1)\frac{T}{2}-\frac{n\pi}{\zeta}\right)^2\right]\right. \\ & \times\cos\left((2k+1)^2\frac{T\zeta}{2}\right)-\frac{4\zeta}{(2k+1)}\left((2k+1)\frac{T}{2}-\frac{n\pi}{\zeta}\right) \\ & \left.\times\sin\left((2k+1)^2\frac{T\zeta}{2}\right)\right\}, \end{aligned} \tag{2}$$

where $T = t\sqrt{2\pi^2/\mu\beta L^2}$, $\zeta = \hbar\sqrt{\beta\pi^2/2\mu L^2}$ and $Z = \sum_{n=1}^{\infty}\exp(-n^2\zeta^2)$ is the partition function. The quantum correlation functions (2) plotted on Fig. 1 for two different temperatures show the recurrence, a characteristic of the quantum autocorrelation function. However, as shown in [1], the simple classical limit of $C(t)$

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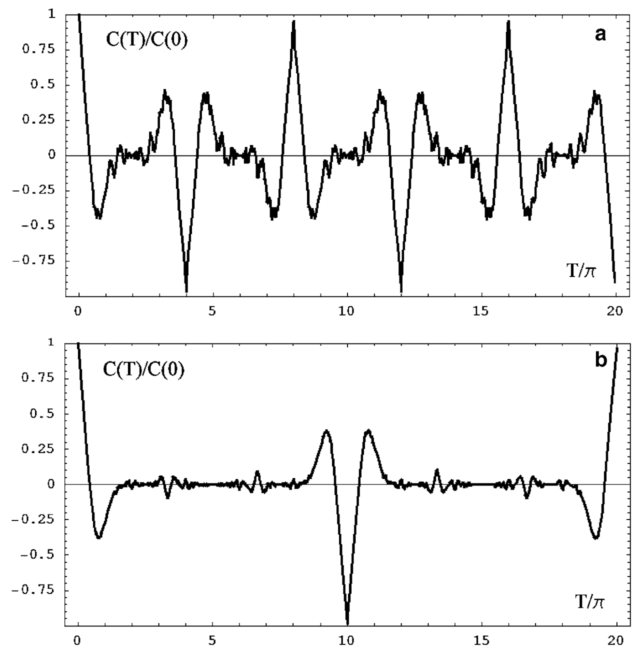

Fig. 1. Quantum momentum autocorrelation functions for (a) $\zeta = 0.5$ and (b) $\zeta = 0.2$.

$$C_{\mathrm{cl}}(t) = \langle p(t)p(0)\rangle = \int_0^L \mathrm{d}q \int_{-\infty}^{\infty} \mathrm{d}p\rho_{\mathrm{eq}}(p)pp(t) \tag{3}$$

has a monotonically decaying profile (Fig. 2).

To systematically examine the classical limit of Eq. (1) we use the Weyl–Wigner symbol-calculus approach [7–10], which allows an alternative representation of quantum mechanics in terms of scalar functions $a_\hbar(p,q)$

$$\mathrm{symb}(\widehat{A}) \equiv a_\hbar(p,q) = \int \mathrm{d}v\mathrm{e}^{(\mathrm{i}/\hbar)p\cdot v}\left\langle q-\frac{1}{2}v\middle|\widehat{A}\middle|q+\frac{1}{2}v\right\rangle, \tag{4}$$

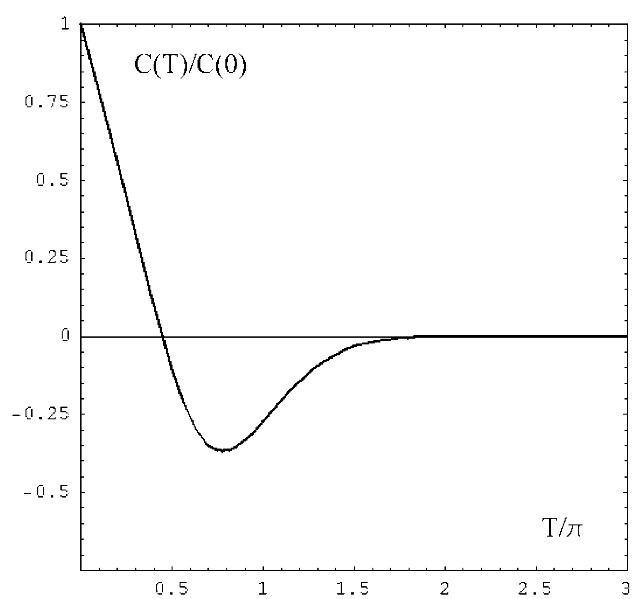

Fig. 2. Classical momentum autocorrelation function (which is independent of temperature in scaled time coordinates).

where 'symb' represents the Weyl–Wigner symbolic function. The product of two operators corresponds to a non-commutative Moyal product of Weyl symbols

$$\mathrm{symb}(\widehat{A}\widehat{B}) \equiv a_\hbar * b_\hbar = a_\hbar \exp\left(\frac{\mathrm{i}\hbar}{2}\left[\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right]\right) b_\hbar, \tag{5}$$

where the arrows indicate the direction of action of the derivatives. Using the property $\mathrm{Tr}(\hat{A}\hat{B}) = (2\pi\hbar)^{-N}\int \mathrm{d}p\, \mathrm{d}q a_\hbar(p,q) b_\hbar(p,q)$, the expression (1) takes the form

$$C(t) = \int \mathrm{d}p\,\mathrm{d}q\rho_\hbar(p,q) \times \left\{ p_\hbar(p,q,t)\cos\left[\frac{\hbar}{2}\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right)\right] p_\hbar(p,q)\right\}. \tag{6}$$

The Weyl symbol $p_\hbar(p,q)$ in coordinates $\{p,q\}$ is the phase space momentum p, which follows directly from the expression (4) written in $|p\rangle$ basis. However, $p_\hbar(p,q,t)$ does not have a simple classical correspondence [11]. For this reason we switch to action-angle variables $\{J,\varphi\}$ and express the Weyl transform (4) in $|\varphi\rangle$ basis using the semiclassical wave function

$$\langle \varphi \mid n\rangle = (2\pi)^{-1/2}\mathrm{e}^{\mathrm{i}n\varphi} \tag{7}$$

corresponding to eigenvalue $E_{\mathbf{n}} = H(J_n = n\hbar)$. We thus have

$$\begin{aligned} a_\hbar(J_n,\varphi,t) &= \int_{-\pi}^{\pi}\mathrm{d}\xi\mathrm{e}^{\mathrm{i}n\cdot\xi}\left\langle \varphi-\frac{1}{2}\xi\middle|\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}\widehat{A}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}\middle|\varphi+\frac{1}{2}\xi\right\rangle \\ &= \sum_{m,k}\langle k \mid \hat{A} \mid m\rangle \mathrm{e}^{\mathrm{i}(k-m)\varphi}\mathrm{e}^{\frac{\mathrm{i}t}{\hbar}(E_k-E_m)}\delta_{n,\frac{k+m}{2}}. \end{aligned} \tag{8}$$

The above semiclassical analysis assumes that $|k-m| \ll k$ [9,12], therefore the matrix element $\langle k \mid \hat{A} \mid m\rangle$ that satisfies the Hermitian property is given by [9]

$$\langle k \mid \hat{A} \mid m\rangle = \frac{1}{2\pi}\int_{-\pi}^{\pi} a\left(\frac{J_m+J_k}{2},\varphi\right)\mathrm{e}^{\mathrm{i}(m-k)\varphi}\,\mathrm{d}\varphi \tag{9}$$

and

$$\begin{aligned} E_k - E_m = E_{n+\frac{k-m}{2}} - E_{n-\frac{k-m}{2}} &= \left.\frac{\partial E}{\partial J}\right|_{J_n}(k-m)\hbar \\ &= \omega(J_n)(k-m)\hbar, \end{aligned} \tag{10}$$

where $\omega = \partial E/\partial J = \mathrm{d}\varphi/\mathrm{d}t$ is the rotational frequency of the angle variable. Substituting (9), (10) and the Fourier decomposition of the classical function $a(J,\varphi)$, i.e. $a(J,\varphi) = \sum_j a_j(J)\mathrm{e}^{\mathrm{i}j\varphi}$, into the expression (8), we get

$$a_\hbar(J_n,\varphi,t) = \sum_k a_k(J_n)\mathrm{e}^{\mathrm{i}k(\omega t+\varphi)}, \tag{11}$$

which is just the Fourier expansion of the *classical* function $a(t)$. The Weyl symbols $p_\hbar(J,\varphi,t)$ and $\rho_\hbar(J,\varphi)$ are thus classical functions:

$$p_\hbar(J_n,\varphi,t) = p[J_n,\varphi(t)] = \sum_k p_k(J_n)\mathrm{e}^{\mathrm{i}k(\omega t+\varphi_0)} \tag{12}$$

$$\rho_\hbar(J_n,\varphi) = \rho(J_n,\varphi) = \frac{1}{2\pi Z}\sum_m \mathrm{e}^{-\beta E(J_m)}\delta_{n,m}, \tag{13}$$

where Z is the partition function. Substituting (12) and (13) into (6) we get the semiclassical expression

$$''C(t) = \sum_n \int \mathrm{d}\varphi_0 \left(\frac{1}{2\pi Z}\sum_m \mathrm{e}^{-\beta E(J_m)}\delta_{n,m}\right) \times \left\{ p(J,\varphi(t)) \cos\left[\frac{\hbar}{2}\left(\frac{\overleftarrow{\partial}}{\partial\varphi_0}\frac{\overrightarrow{\partial}}{\partial J} - \frac{\overleftarrow{\partial}}{\partial J}\frac{\overrightarrow{\partial}}{\partial\varphi_0}\right)\right] p(J,\varphi(0))\right\}$$
$$= \langle p(t)p(0)\rangle_Q - \frac{\hbar^2}{8}\left\langle p(t)\hat{\mathrm{D}}^2 p(0)\right\rangle_Q + \frac{\hbar^4}{384}\left\langle p(t)\hat{\mathrm{D}}^4 p(0)\right\rangle_Q + \cdots, \tag{14}$$

where $\hat{\mathrm{D}} = \left(\frac{\overleftarrow{\partial}}{\partial\varphi_0}\frac{\overrightarrow{\partial}}{\partial J} - \frac{\overleftarrow{\partial}}{\partial J}\frac{\overrightarrow{\partial}}{\partial\varphi_0}\right)$ and the average $\langle\cdots\rangle_Q$ is taken over the phase density (13) with *quantized* actions. The phase space averaging $\langle\cdots\rangle_Q$ is related to the averaging $\langle\cdots\rangle$ over continuous phase space. Indeed, the summation over the discrete variable can be converted to an integration over the continuous variable using delta-functions [1]

$$\sum_{n=1}^{\infty} = \int \mathrm{d}J \sum_{n=1}^{\infty}\delta(J-n\hbar). \tag{15}$$

We know that for $J>0$

$$\sum_{n=1}^{\infty}\delta(J-n\hbar) = \sum_{n=-\infty}^{\infty}\delta(J-n\hbar) = \frac{1}{\hbar} + \frac{2}{\hbar}\sum_{m=1}^{\infty}\cos(2\pi mJ/\hbar). \tag{16}$$

Combining (15) with (16) we have

$$\langle f\rangle_Q = \frac{A}{Z\hbar}\langle f\rangle + \frac{2A}{Z\hbar}\left\langle \sum_{m=1}^{\infty} f\cos(2\pi mJ/\hbar)\right\rangle, \tag{17}$$

where $A = \int_0^\infty \mathrm{e}^{-\beta E(J)}\,\mathrm{d}J$. The WKB approximation [8,13,14] (7) assumes that motion occurs mainly in the region of $J \gg \hbar$ implying that the temperature is sufficiently high $1/\beta \gg \hbar^2\pi^2/2\mu L^2$. Thus $A/Z\hbar \simeq 1$ as shown in [1] and we may skip the overall factor $(A/Z\hbar)$ from further considerations.

The momentum autocorrelation function (6) thus reads

$$C(t) = \langle p(t)p(0)\rangle + 2\sum_{m=1}^{\infty}\left\langle p(t)p(0)\cos\left(\frac{2\pi mJ}{\hbar}\right)\right\rangle - \frac{\hbar^2}{8}\left\langle p(t)\hat{\mathrm{D}}^2 p(0)\right\rangle - \frac{\hbar^2}{4} \times \sum_{m=1}^{\infty}\left\langle \left(p(t)\hat{\mathrm{D}}^2 p(0)\right)\cos\left(\frac{2\pi mJ}{\hbar}\right)\right\rangle + \cdots \tag{18}$$

The first term in the expression (18) is the classical correlation function $C_{\mathrm{cl}}(t)$ and the remaining terms are quantum corrections expressed as phase space averages of classical functions. We note that in the usual classical limit, the $\hbar^{2n}$-terms in Eqs. (18) or (14) are omitted. However, every $\hbar^{2n}$-term in (14) has time-divergent derivatives (stability matrix) $\partial p(t)/\partial J$, which grows linearly in time for integrable systems and exponentially for chaotic systems. The small value of the factor $\hbar^{2n}$ can be always compensated by the large value of t. Thus the omission of these terms is not justified and leads to the well-known problem of time-divergence of the classical response functions [4–6].

The above argument can be supported by calculating $C(t)$ with $\hbar^{2n}$-terms omitted. The results from the evaluation of the first two terms in Eq. (18): $C_{\mathrm{cl}}(t)$ and its correction for phase space quantization, are plotted in Fig. 3. Comparing Figs. 1 and 3 one can see that phase space quantization alone is not sufficient to restore quantum beatings and higher-order terms in $\hbar$ are needed.

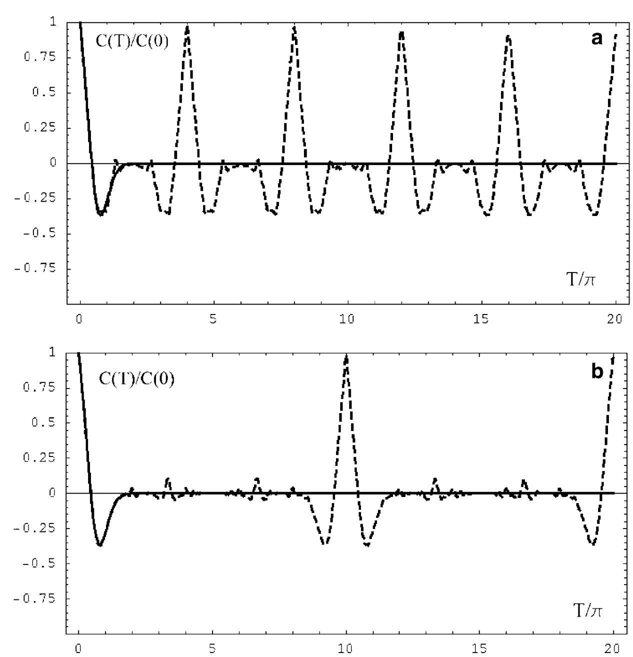

Fig. 3. Classical momentum autocorrelation functions with averaging over continuous (solid line) and quantized (dashed line) phase space for (a) $\zeta = 0.5$ and (b) $\zeta = 0.2$.

The convergence of series (18) can be shown analytically for the system under consideration. Substituting (12), (13) and (16), we have

$$C(t) = \int \mathrm{d}J\,\mathrm{d}\varphi_0 \left(1 + 2\sum_{m=1}^{\infty} \cos(2\pi mJ/\hbar)\right) \frac{1}{\hbar Z} \mathrm{e}^{-\beta E(J)} \times \left\{ \sum_k p_k(J) \mathrm{e}^{\mathrm{i}k(\omega t+\varphi_0)} \cos\left[\frac{\hbar}{2}\left(\mathrm{i}k\frac{\overrightarrow{\partial}}{\partial J} - \frac{\overleftarrow{\partial}}{\partial J}\mathrm{i}n\right)\right] \times \sum_n p_n(J) \mathrm{e}^{\mathrm{i}n\varphi_0} \right\}. \tag{19}$$

Since $\exp\left(\Delta J \frac{\partial}{\partial J}\right) f(J) = f(J + \Delta J)$, then

$$C(t) = \frac{1}{\hbar Z} \int \mathrm{d}J \left(1 + 2\sum_{m=1}^{\infty} \cos(2\pi mJ/\hbar)\right) \mathrm{e}^{-\beta E(J)} \times \sum_{n=-\infty}^{\infty} \left(|\, p_n|^2 \cos(n\omega t) \right)\Big|_{J-n\hbar/2}. \tag{20}$$

For a particle in one-dimensional box $p_{2k+1}(J) = 2J/(2k+1)L$, $\omega = \partial E/\partial J = \pi^2 J/\mu L^2$ and

$$C(t) = \frac{1}{\hbar Z} \int \mathrm{d}J \left(1 + 2\sum_{m=1}^{\infty} \cos(2\pi mJ/\hbar)\right) \mathrm{e}^{-\beta\frac{\pi^2 J^2}{2\mu L^2}} \times \sum_{k=-\infty}^{\infty} \frac{4}{(2k+1)^2 L^2} \left(J - \frac{\hbar(2k+1)}{2}\right)^2 \times \cos\left\{\frac{n\pi^2 t}{\mu L^2}\left(J - \frac{\hbar(2k+1)}{2}\right)\right\}. \tag{21}$$

The straightforward integration of the expression (21) gives the semiclassical expression

$$C(t) = \left(\frac{\hbar^2\sqrt{\pi}}{\zeta^3 L^2 Z}\right) \sum_{k=-\infty}^{+\infty} \sum_{m=-\infty}^{+\infty} \exp\left[-\left((2k+1)\frac{T}{2} - \frac{m\pi}{\zeta}\right)^2\right] \times \left\{ \left[\frac{2}{(2k+1)^2} - \frac{4}{(2k+1)^2}\left((2k+1)\frac{T}{2} - \frac{m\pi}{\zeta}\right)^2 + \zeta^2\right] \times \cos\left((2k+1)^2\frac{T\zeta}{2}\right) - \frac{4\zeta}{(2k+1)}\left((2k+1)\frac{T}{2} - \frac{m\pi}{\zeta}\right) \times \sin\left((2k+1)^2\frac{T\zeta}{2}\right) \right\}. \tag{22}$$

The semiclassical result (22) reproduces the quantum expression (2) almost exactly except for a constant term $\zeta^2 = \beta\hbar^2\pi^2/2L^2\mu$, which is negligible in the high temperature regime required for the semiclassical analysis leading to Eq. (22).

In this article we have studied the classical limit of the quantum autocorrelation function. The semiclassical expression for the momentum autocorrelation function of a particle in a one-dimensional box is obtained. The Weyl–Wigner symbol-calculus approach allows to find the explicit expressions for the semiclassical corrections to the classical momentum correlation function. Resummation of the derived semiclassical series results in an almost exact quantum formula. Because of the semiclassical nature of the analysis, the agreement between quantum and semiclassical results improves at higher temperatures (compare Fig. 4 with Fig. 1).

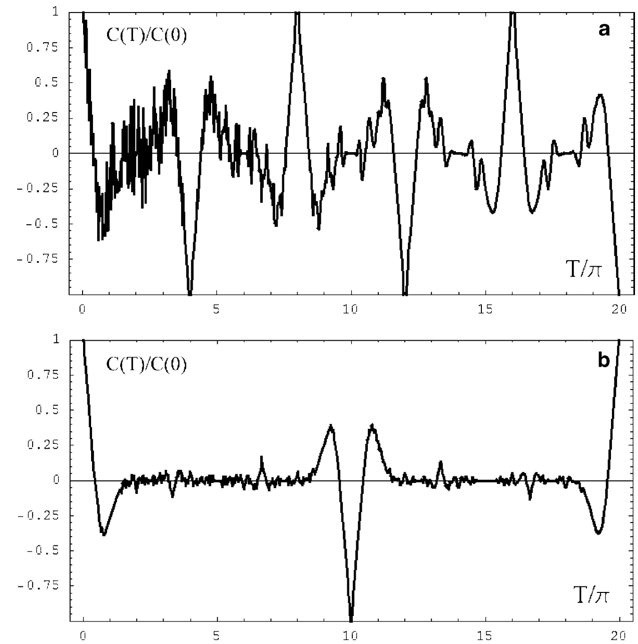

Fig. 4. Semiclassical momentum autocorrelation functions calculated from Eq. (22) for (a) $\zeta = 0.5$ and (b) $\zeta = 0.2$.

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References

[1] J.M. Deutch, J.L. Kinsey, R. Silbey, J. Chem. Phys. 53 (1970) 1047.
[2] J. Wu, J. Cao, J. Chem. Phys. 115 (2001) 5381.
[3] M. Kryvohuz, J. Cao, J. Chem. Phys. 122 (2004) 024109.
[4] M. Kryvohuz, J. Cao, Phys. Rev. Lett. (submitted).
[5] S. Mukamel, V. Khidekel, V. Chernyak, Phys. Rev. E 53 (1996) R1.
[6] W.G. Noid, G.S. Ezra, R.F. Loring, J. Phys. Chem. B 108 (2004) 6536.
[7] M.V. Berry, Phil. Trans. R. Soc. London 287 (1977) 237.
[8] C. Jaffe, S. Kanfer, P. Brumer, Phys. Rev. Lett. 54 (1985) 8.
[9] M.L. Koszykowski, D.W. Noid, R.A. Marcus, J. Phys. Chem 86 (1982) 2113.
[10] C.W. Eaker, G.C. Schatz, N.D. Leon, E.J. Heller, J. Phys. Chem 83 (1985) 2990.

[11] S.R. de Groot, L.G. Suttorp, Foundations of Electrodynamics, Noord-Hollandsche U.M., Amsterdam, 1972.
[12] L.D. Landau, E.M. Lifschitz, Quantum Mechanics Non-Relativistic Theory, Pergamon Press, Oxford, England, 1977.
[13] P. Pechukas, J. Chem. Phys. 57 (1972) 5577.
[14] W.H. Miller, A.W. Raczkowski, Faraday Discuss. Chem. Soc. 55 (1973) 45.