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Explicit approximate semigroup property of the semiclassical canonical density matrix

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Abstract. For a system of N identical particles it is shown explicitly by asymptotic analysis that the canonical density matrix in semiclassical approximation of orders $\hbar^0$ and $\hbar^2$ has semigroup property approximately to orders $\hbar^0$ and $\hbar^2$, respectively. Similar approximations appearing in applications of the Trotter formula have that property to order $\hbar^0$ only for diagonal elements.

1. Introduction

The exact canonical density matrix or thermodynamic Green function $C(\boldsymbol{x}, \boldsymbol{x}', \beta) = \langle \boldsymbol{x}|\exp(-\beta\hat{H})|\boldsymbol{x}'\rangle$ of a system of N identical particles with Hamiltonian $\hat{H}$ and $\beta = (k_B T)^{-1}$ forms a semigroup in the sense of equations (5) and (6) below. In general, this property is lost, however, if approximations to C are made.

One of the basic approximations to C is the well known semiclassical or high temperature approach first given by Wigner (1932) and by Kirkwood (1933) for the diagonal elements of C. A corresponding expansion including off-diagonal elements has been derived by ter Haar (1954) to calculate quantum corrections to the second virial coefficient. In this work the density matrix is given as a product of the free-particle expression which is not analytical with respect to $\hbar$, and of an exponential of a power series of β. The latter exponential can be expanded again and re-ordered to yield a power series of $\hbar$.

Another high temperature expression appears as an initial approximation in the work of some authors (Storer 1968a, b, Grimm and Storer 1969, Handler and Wang 1972, Handler 1973) who calculate the density matrix for low temperatures by means of the Trotter formula (Golden 1957, Nelson 1964). In this approach C is approximated for large β by a multiple product of matrices belonging to small β, and it is assumed implicitly that the high temperature factors of the product representation are good approximations and hence satisfy the semigroup condition quite well.

It is the aim of the present work to investigate quantitatively to what extent the semigroup property is violated when C is replaced by the high temperature approximations mentioned.

In § 2 some basic relations satisfied by the exact density matrix and its semiclassical approximation up to second order of $\hbar$ are recapitulated for Boltzmann statistics. In § 3 the C matrix product appearing in equation (6) is evaluated by an asymptotic expansion. Clearly, the product cannot be calculated by expanding in powers of $\hbar$ and equating coefficients because C has an essential singularity at $\hbar=0$. The resulting expression is manipulated further in § 4. For the sake of completeness, quantum statistics is taken into account in § 5. In § 6 the semigroup property is analysed for the high temperature matrix that appears in the Trotter formula. Results are summarised and discussed in the last section.

2. The canonical density matrix and its semiclassical approximation for Boltzmann particles

Let us consider a system of N identical particles obeying classical statistics with Hamiltonian

$$\hat{H}(\boldsymbol{x})=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_{\boldsymbol{x}_i}^2+V(\boldsymbol{x})\equiv-\frac{\hbar^2}{2m}\nabla_{\boldsymbol{x}}^2+V(\boldsymbol{x}) \tag{1}$$

where $\boldsymbol{x}=(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)$ and $\boldsymbol{x}_i$ is the position vector of the ith particle. From the complete set $\{\Psi_j(\boldsymbol{x})\}$ of eigenfunctions satisfying

$$\hat{H}(\boldsymbol{x})\Psi_j(\boldsymbol{x})=E_j\Psi_j(\boldsymbol{x}) \tag{2}$$

the canonical density matrix is defined by

$$C(\boldsymbol{x},\boldsymbol{x}',\beta)\equiv\sum_{j=1}^{\infty}\Psi_j^*(\boldsymbol{x}')\Psi_j(\boldsymbol{x})\exp(-\beta E_j)=\langle\boldsymbol{x}|\exp(-\beta\hat{H})|\boldsymbol{x}'\rangle. \tag{3}$$

C satisfies the Bloch equation

$$\hat{H}(\boldsymbol{x})C(\boldsymbol{x},\boldsymbol{x}',\beta)=-\frac{\partial C(\boldsymbol{x},\boldsymbol{x}',\beta)}{\partial\beta}. \tag{4}$$

Since the particles obey classical statistics and due to the completeness of the set of eigenfunctions, the initial condition for C is given by

$$C(\boldsymbol{x},\boldsymbol{x}',0)=\delta(\boldsymbol{x}-\boldsymbol{x}')\equiv\prod_{i=1}^{N}\delta(\boldsymbol{x}_i-\boldsymbol{x}_i'). \tag{5}$$

From orthonormality of the $\Psi_j(\boldsymbol{x})$ it is readily seen that

$$\int \mathrm{d}^{3N}x'\,C(\boldsymbol{x},\boldsymbol{x}',\beta_1)C(\boldsymbol{x}',\boldsymbol{x}'',\beta_2)=C(\boldsymbol{x},\boldsymbol{x}'',\beta_1+\beta_2). \tag{6}$$

The integration can be regarded at least formally as multiplication of the matrices $C(\beta_1)$ and $C(\beta_2)$ with indices $(\boldsymbol{x},\boldsymbol{x}')$ and $(\boldsymbol{x}',\boldsymbol{x}'')$, respectively, therefore equations (5) and (6) can be rewritten

$$C(\beta_1)C(\beta_2)=C(\beta_1+\beta_2) \tag{6a}$$

and

$$C(0)=I \tag{5a}$$

where I is the identity matrix with elements $\delta(\boldsymbol{x}-\boldsymbol{x}')$. Thus the matrices $C(\beta)$ form a semigroup.

Semiclassical or high temperature approximations to C have been given by ter Haar (1954) in the form

$$C(\boldsymbol{x}, \boldsymbol{x}', \beta) = C_0(\boldsymbol{x}, \boldsymbol{x}', \beta) \exp\left(\sum_{n=1}^{\infty} a_n \beta^n\right) \tag{7}$$

where C_0 is the free-particle expression

$$C_0(\boldsymbol{x}, \boldsymbol{x}', \beta) = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2} \exp\left(-\frac{m(\boldsymbol{x}-\boldsymbol{x}')^2}{2\beta\hbar^2}\right). \tag{8}$$

In the work of Bruch and Revercomb (1973) the coefficients a_n are presented in a form which is especially suited for our approach. Let us retain the term $a_1\beta$ in the exponent, and expand the higher terms as a power series of β. Using the expressions for the a_n and re-arranging the series according to powers of $\hbar^2$ we obtain up to terms of order $\hbar^2$:

$$C^{(2)}(\boldsymbol{x}, \boldsymbol{x}', \beta) = C_0(\boldsymbol{x}, \boldsymbol{x}', \beta) \exp(-\beta W(\boldsymbol{x}, \boldsymbol{x}'))\left(1 + \frac{\hbar^2}{2m}(\beta^3 K(\boldsymbol{x}, \boldsymbol{x}') - \beta^2 L(\boldsymbol{x}, \boldsymbol{x}'))\right) \tag{9}$$

where

$$W(\boldsymbol{x}, \boldsymbol{x}') = -a_1 = \int_0^1 \mathrm{d}\lambda\; V(\boldsymbol{u}(\lambda)) \tag{10a}$$

$$K(\boldsymbol{x}, \boldsymbol{x}') = 2\int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\mu\; \mu(1-\lambda)\nabla_{\boldsymbol{u}} V(\boldsymbol{u}(\mu)) \cdot \nabla_{\boldsymbol{u}} V(\boldsymbol{u}(\lambda)) \tag{10b}$$

$$L(\boldsymbol{x}, \boldsymbol{x}') = -\frac{2ma_2}{\hbar^2} = \int_0^1 \mathrm{d}\lambda\; \lambda(1-\lambda)\nabla_{\boldsymbol{u}}^2 V(\boldsymbol{u}(\lambda)) \tag{10c}$$

$$\boldsymbol{u}(\lambda) = \boldsymbol{x}' + \lambda(\boldsymbol{x} - \boldsymbol{x}'). \tag{10d}$$

We have used the notation $\boldsymbol{x} \cdot \boldsymbol{y} = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} x_{i\alpha} y_{i\alpha}$ where $x_{i\alpha}$ is the αth Cartesian component of $\boldsymbol{x}_i$. The coefficient a_3 is given by

$$a_3 = \frac{\hbar^2}{2m} K(\boldsymbol{x}, \boldsymbol{x}') + \mathrm{O}(\hbar^4).$$

$C^{(2)}$ is a good approximation to C if the change of the potential is small compared to β^{-1} over a distance equal to the thermal wavelength

$$\Lambda = (2\pi\beta\hbar^2/m)^{1/2}. \tag{11}$$

Concerning the first and the second derivatives of V this means

$$\Lambda|\nabla V|\beta \ll 1 \tag{12a}$$

$$\Lambda^2|\nabla^2 V|\beta \ll 1. \tag{12b}$$

Then, from the definitions of K and L, it is seen that the correction terms of equation (9) are small compared to unity.

It is the aim of the following to check the validity of relation (6) if $C^{(2)}$ is used instead of the exact expression which is unknown in general.

3. Asymptotic expansion of the semiclassical C matrix product

We shall evaluate the left-hand side of equation (6) assuming that for β_1 and β_2 conditions (12a, b) are met. Introducing

$$\beta = \max(\beta_1, \beta_2) \tag{13a}$$

$$0 \leqslant \tau_1 = \beta_1/\beta \leqslant 1 \tag{13b}$$

$$0 \leqslant \tau_2 = \beta_2/\beta \leqslant 1 \tag{13c}$$

we get

$$C^{(2)}(\boldsymbol{x}, \boldsymbol{x}', \beta_1) = (\tau_1\Lambda^2)^{-3N/2} \exp\left(-\frac{\pi(\boldsymbol{x}-\boldsymbol{x}')^2}{\tau_1\Lambda^2}\right) \exp(-\tau_1\beta W(\boldsymbol{x}, \boldsymbol{x}'))\left(1+\frac{\Lambda^2\tau_1^2\beta}{4\pi}(\tau_1\beta K - L)\right). \tag{9a}$$

A corresponding expression holds for $C^{(2)}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2)$. When $|\boldsymbol{x}-\boldsymbol{x}'|$ grows from zero to Λ the first exponential falls off rapidly while the remaining terms change only slowly. For the second exponential this follows from a Taylor series expansion of $V(\boldsymbol{u}(\lambda))$ about $\boldsymbol{x}$ which leads to

$$W(\boldsymbol{x}, \boldsymbol{x}') = V(\boldsymbol{x}) + \tfrac{1}{2}(\boldsymbol{x}'-\boldsymbol{x}) \cdot \nabla_x V(\boldsymbol{x}) + \ldots.$$

Due to (12a, b) W changes only little when $\boldsymbol{x}'$ runs through the domain $|\boldsymbol{x}-\boldsymbol{x}'| \leqslant \Lambda$. Therefore, it is advisable to perform the integral of equation (6) by an asymptotic expansion about the point $\boldsymbol{X}$ in $\boldsymbol{x}'$ space where, for $\boldsymbol{x}, \boldsymbol{x}''$ being fixed, the rapidly decreasing part of the integrand reaches its maximum value.

From equation (8) we obtain

$$C_0(\boldsymbol{x}, \boldsymbol{x}', \beta_1)C_0(\boldsymbol{x}', \boldsymbol{x}'', \beta_2) = (\tau_1\tau_2)^{-3N/2}\Lambda^{-6N} \exp\left(\frac{\pi}{\Lambda^2} f(\boldsymbol{x}')\right) \exp\left[-\frac{\pi}{\Lambda^2}\left(\frac{\boldsymbol{x}^2}{\tau_1}+\frac{\boldsymbol{x}''^2}{\tau_2}\right)\right] \tag{14}$$

where we have set

$$f(\boldsymbol{x}') = 2\boldsymbol{x}' \cdot \left(\frac{\boldsymbol{x}}{\tau_1}+\frac{\boldsymbol{x}''}{\tau_2}\right) - \gamma \boldsymbol{x}'^2 \tag{15}$$

$$\gamma = \frac{1}{\tau_1} + \frac{1}{\tau_2}. \tag{16}$$

For

$$\boldsymbol{x}' = \boldsymbol{X} \equiv \frac{\tau_2\boldsymbol{x} + \tau_1\boldsymbol{x}''}{\tau_1+\tau_2} \tag{17}$$

$f(\boldsymbol{x}')$ takes on its maximum

$$f(\boldsymbol{X}) = \frac{1}{\gamma}\left(\frac{\boldsymbol{x}}{\tau_1}+\frac{\boldsymbol{x}''}{\tau_2}\right)^2. \tag{18}$$

Thus $f(\boldsymbol{x}')$ can be rewritten

$$f(\boldsymbol{x}') = f(\boldsymbol{X}) - \gamma(\boldsymbol{x}'-\boldsymbol{X})^2. \tag{15a}$$

Then the left-hand side of equation (6) becomes

$$
\begin{aligned}
A^{(2)} &\equiv \int C^{(2)}(\boldsymbol{x}, \boldsymbol{x}', \beta_1) C^{(2)}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2)\, \mathrm{d}^{3N}x' \\
&= (\tau_1\tau_2)^{-3N/2} \Lambda^{-6N} \exp\left[-\frac{\pi}{\Lambda^2}\left(\frac{\boldsymbol{x}^2}{\tau_1} + \frac{\boldsymbol{x}''^2}{\tau_2} - f(\boldsymbol{X}) \right) \right] B \\
&= (\tau_1\tau_2)^{-3N/2} \Lambda^{-6N} \exp\left(-\frac{\pi(\boldsymbol{x}-\boldsymbol{x}'')^2}{\Lambda^2(\tau_1+\tau_2)} \right) B
\end{aligned}
\tag{19}
$$

where

$$
B \equiv \int \mathrm{d}^{3N}x' \exp\left(-\frac{\pi\gamma}{\Lambda^2}(\boldsymbol{x}'-\boldsymbol{X})^2 \right) \Phi(\boldsymbol{x}') \tag{20}
$$

with the slowly varying term

$$
\begin{aligned}
\Phi(\boldsymbol{x}') = {}& \exp(-\beta_1 W(\boldsymbol{x}, \boldsymbol{x}') - \beta_2 W(\boldsymbol{x}', \boldsymbol{x}''))\left(1 + \frac{\Lambda^2\tau_1}{4\pi}(\beta_1^2 K(\boldsymbol{x}, \boldsymbol{x}') - \beta_1 L(\boldsymbol{x}, \boldsymbol{x}')) \right) \\
& \times \left(1 + \frac{\Lambda^2\tau_2}{4\pi}(\beta_2^2 K(\boldsymbol{x}', \boldsymbol{x}'') - \beta_2 L(\boldsymbol{x}', \boldsymbol{x}'')) \right).
\end{aligned}
\tag{21}
$$

$\Phi(\boldsymbol{x}')$ is now expanded about $\boldsymbol{x}' = \boldsymbol{X}$

$$
\Phi(\boldsymbol{x}') = \Phi(\boldsymbol{X}) + (x'_{\alpha i} - X_{\alpha i})\frac{\partial\Phi(\boldsymbol{X})}{\partial X_{\alpha i}} + \tfrac{1}{2}(x'_{\alpha i} - X_{\alpha i})(x'_{\delta j} - X_{\delta j})\frac{\partial^2\Phi(\boldsymbol{X})}{\partial X_{\alpha i}\partial X_{\delta j}} + \dots \tag{22}
$$

where the summation convention over repeated indices is adopted. Using new integration variables

$$
\boldsymbol{y} \equiv (\pi\gamma)^{1/2}(\boldsymbol{x}' - \boldsymbol{X}) \tag{23}
$$

we find

$$
\begin{aligned}
B = {}& (\pi\gamma)^{-3N/2} \int \mathrm{d}^{3N}y \exp\left(-\frac{\boldsymbol{y}^2}{\Lambda^2} \right) \\
& \times \left(\Phi(\boldsymbol{X}) + (\pi\gamma)^{-1/2} y_{i\alpha}\frac{\partial\Phi}{\partial X_{i\alpha}} + \tfrac{1}{2}(\pi\gamma)^{-1} y_{i\alpha} y_{j\delta}\frac{\partial^2\Phi}{\partial X_{i\alpha}\,\partial X_{j\delta}} + \dots \right).
\end{aligned}
$$

Integrating over the whole $\boldsymbol{y}$ space the term linear in y gives no contribution while the second-order term vanishes excepting the case $\alpha = \delta$ and $i = j$. Thus

$$
B = \Lambda^{3N}\gamma^{-3N/2}\left(\Phi(\boldsymbol{X}) + \frac{\Lambda^2}{4\pi\gamma}\nabla_{\boldsymbol{X}}^2\Phi(\boldsymbol{X}) \right). \tag{24}
$$

Since in equation (21) terms of higher than second order of Λ have been neglected B is given to the same order by

$$
B = \Lambda^{3N}\gamma^{-3N/2}\left(R(\boldsymbol{X}) + \frac{\Lambda^2}{4\pi} Q(\boldsymbol{X}) \right) \tag{25}
$$

where

$$
R(\boldsymbol{X}) = \exp(-\beta_1 W(\boldsymbol{x}, \boldsymbol{X}) - \beta_2 W(\boldsymbol{X}, \boldsymbol{x}'')) \tag{26}
$$

$$Q(\boldsymbol{X})=R(\boldsymbol{X})[\tau_1\beta_1(\beta_1K(\boldsymbol{x},\boldsymbol{X})$$
$$-L(\boldsymbol{x},\boldsymbol{X}))+\tau_2\beta_2(\beta_2K(\boldsymbol{X},\boldsymbol{x}'')-L(\boldsymbol{X},\boldsymbol{x}''))]+\nabla_{\boldsymbol{X}}^2R(\boldsymbol{X})/\gamma. \tag{27}$$

Inserting expression (25) into equation (19) and using equations (8), (11), (13*b*, *c*), and (16) we find

$$A^{(2)}=C_0(\boldsymbol{x},\boldsymbol{x}'',\beta_1+\beta_2)\left(R(\boldsymbol{X})+\frac{\Lambda^2}{4\pi}Q(\boldsymbol{X})+\mathrm{O}(\Lambda^4)\right). \tag{28}$$

4. Proof of zeroth- and second-order semigroup property

It is the aim of this section to cast equation (28) into a form that shows explicitly that

$$\int C^{(0)}(\boldsymbol{x},\boldsymbol{x}',\beta_1)C^{(0)}(\boldsymbol{x}',\boldsymbol{x}'',\beta_2)\,\mathrm{d}^{3N}x'=A^{(0)}=C^{(0)}(\boldsymbol{x},\boldsymbol{x}'',\beta_1+\beta_2)(1+\mathrm{O}(\hbar^2)) \tag{29}$$

and

$$\int C^{(2)}(\boldsymbol{x},\boldsymbol{x}',\beta_1)C^{(2)}(\boldsymbol{x}',\boldsymbol{x}'',\beta_2)\,\mathrm{d}^{3N}x'=A^{(2)}=C^{(2)}(\boldsymbol{x},\boldsymbol{x}'',\beta_1+\beta_2)(1+\mathrm{O}(\hbar^4)). \tag{30}$$

$C^{(0)}$ is the zeroth-order matrix which is obtained from $C^{(2)}$ by neglecting the term of order $\hbar^2$ in the large round brackets of equation (9).

4.1. Zeroth order

Consider first $R(\boldsymbol{X})$. From equation (17) we obtain

$$\boldsymbol{X}+\lambda(\boldsymbol{x}-\boldsymbol{X})=\boldsymbol{x}+\frac{\tau_1(1-\lambda)}{\tau_1+\tau_2}(\boldsymbol{x}''-\boldsymbol{x}) \tag{31a}$$

$$\boldsymbol{x}''+\mu(\boldsymbol{X}-\boldsymbol{x}'')=\boldsymbol{x}''+\frac{\mu\tau_2}{\tau_1+\tau_2}(\boldsymbol{x}-\boldsymbol{x}'') \tag{31b}$$

where $0\leqslant\lambda,\mu\leqslant1$. If we substitute (31*a*) for $\boldsymbol{u}(\lambda)$ in equation (10*a*) and introduce the new variable of integration

$$\lambda'=(\tau_1\lambda+\tau_2)/(\tau_1+\tau_2) \tag{32a}$$

we find

$$-\beta_1W(\boldsymbol{x},\boldsymbol{X})$$
$$=-\frac{\beta_1}{\tau}\int_{1-\tau}^{1}\mathrm{d}\lambda'\ V[\boldsymbol{x}+(1-\lambda')(\boldsymbol{x}''-\boldsymbol{x})]$$
$$=-(\beta_1+\beta_2)\int_{1-\tau}^{1}\mathrm{d}\lambda\ V[\boldsymbol{x}''+\lambda(\boldsymbol{x}-\boldsymbol{x}'')]$$

with

$$\tau\equiv\tau_1/(\tau_1+\tau_2). \tag{33}$$

In the same manner, setting

$$\mu'=\mu(1-\tau) \tag{32b}$$

we get from equation (31*b*)

$$-\beta_2 W(\boldsymbol{X}, \boldsymbol{x}'') = -\frac{\beta_2}{1-\tau}\int_0^{1-\tau} \mathrm{d}\mu'\ V[\boldsymbol{x}''+\mu'(\boldsymbol{x}-\boldsymbol{x}'')]$$

$$= -(\beta_1+\beta_2)\int_0^{1-\tau} \mathrm{d}\lambda\ V[\boldsymbol{x}''+\lambda(\boldsymbol{x}-\boldsymbol{x}'')].$$

Thus $R(\boldsymbol{X})$, equation (26), becomes

$$R(\boldsymbol{X}) = \exp\left(-(\beta_1+\beta_2)\int_0^1 \mathrm{d}\lambda\ V[\boldsymbol{x}''+\lambda(\boldsymbol{x}-\boldsymbol{x}'')]\right)$$

$$= \exp[-(\beta_1+\beta_2)W(\boldsymbol{x}, \boldsymbol{x}'')]. \tag{34}$$

Now it is seen readily that relation (29) holds. Since $C^{(0)}$ can be obtained from $C^{(2)}$ by formally letting $K = L = 0$ in equation (9) we gain $A^{(0)}$ from $A^{(2)}$, equation (28), by setting $Q(\boldsymbol{X}) = \nabla^2 R(\boldsymbol{X})/\gamma$. Then, with equation (34), we see that

$$A^{(0)} = C_0(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)R(\boldsymbol{X})\left(1+\Lambda^2\frac{\nabla^2 R(\boldsymbol{X})}{4\pi\gamma R(\boldsymbol{X})}\right)$$

$$= C^{(0)}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)(1+\mathrm{O}(\hbar^2)). \tag{35}$$

Thus we have shown that the zeroth order density matrix has semigroup property to zeroth order of $\hbar$.

If C were a regular function of $\hbar$ at $\hbar = 0$ it would be possible to expand

$$C(\boldsymbol{x}, \boldsymbol{x}', \beta) = C^{(0)}(\boldsymbol{x}, \boldsymbol{x}', \beta) + \mathrm{O}(\hbar^2)$$

with $C^{(0)}$ independent of $\hbar$. Then we could write

$$\int C(\boldsymbol{x}, \boldsymbol{x}', \beta_1)C(\boldsymbol{x}', \boldsymbol{x}'', \beta_2)\,\mathrm{d}^{3N}x' = \int C^{(0)}(\boldsymbol{x}, \boldsymbol{x}', \beta_1)C^{(0)}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2)\,\mathrm{d}^{3N}x' + \mathrm{O}(\hbar^2).$$

Since C is exact the left-hand side equals

$$C(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2) = C^{(0)}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2) + \mathrm{O}(\hbar^2).$$

Thus we could conclude

$$A^{(0)} = C^{(0)}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)$$

i.e. $C^{(0)}$ would have exact semigroup property.

Hence, it is just the singularity at $\hbar = 0$ that confines $C^{(0)}$ to have this property only to order $\hbar^0$.

4.2. Second order

In order to prove equation (30) we have to solve the much more laborious task of transforming $Q(\boldsymbol{X})$.

Using equation (31*a*) and the substitutions (32*a*) and

$$\mu' = 1-\tau(1-\mu) \tag{32c}$$

we find from (10*b*)

$$K(\boldsymbol{x},\boldsymbol{X})=\frac{2}{\tau^3}\int_{1-\tau}^{1}\mathrm{d}\lambda'\int_{1-\tau}^{\lambda'}\mathrm{d}\mu'(1-\lambda')\Big(1-\frac{1-\mu'}{\tau}\Big)\,\mathscr{F}(\lambda',\mu') \tag{36a}$$

where

$$\mathscr{F}(\lambda',\mu')\equiv\boldsymbol{F}[\boldsymbol{x}+\lambda'(\boldsymbol{x}-\boldsymbol{x}'')]\,.\,\boldsymbol{F}[\boldsymbol{x}''+\mu'(\boldsymbol{x}-\boldsymbol{x}'')] \tag{37}$$

$$\boldsymbol{F}(\boldsymbol{u})\equiv\nabla_{\boldsymbol{u}}V(\boldsymbol{u}). \tag{38}$$

Similarly, with (32*b*) and

$$\lambda'=\lambda(1-\tau) \tag{32d}$$

it follows from (31*b*) that

$$K(\boldsymbol{X},\boldsymbol{x}'')=\frac{2}{(1-\tau)^3}\int_0^{1-\tau}\mathrm{d}\lambda'\int_0^{\lambda'}\mathrm{d}\mu'\,\mu'\Big(1-\frac{\lambda'}{1-\tau}\Big)\,\mathscr{F}(\lambda',\mu'). \tag{36b}$$

Introducing

$$G(\boldsymbol{u})\equiv\nabla_{\boldsymbol{u}}^2V(\boldsymbol{u}) \tag{39}$$

and using (32*a*, *d*) we obtain

$$L(\boldsymbol{x},\boldsymbol{X})=\frac{1}{\tau^2}\int_{1-\tau}^{1}\mathrm{d}\lambda'\Big(1-\frac{1-\lambda'}{\tau}\Big)(1-\lambda')G[\boldsymbol{x}''+\lambda'(\boldsymbol{x}-\boldsymbol{x}'')] \tag{40a}$$

$$L(\boldsymbol{X},\boldsymbol{x}'')=\frac{1}{(1-\tau)^2}\int_0^{1-\tau}\mathrm{d}\lambda'\,\lambda'\Big(1-\frac{\lambda'}{1-\tau}\Big)G[\boldsymbol{x}''+\lambda'(\boldsymbol{x}-\boldsymbol{x}'')]. \tag{40b}$$

Furthermore we have to treat $\nabla^2R(\boldsymbol{X})$. Differentiating equation (26) with respect to $\boldsymbol{X}$ we find, noting equations (10*a*, *d*), (38), and (39):

$$\nabla^2R(\boldsymbol{X})=R(\boldsymbol{X})(D_1+D_2+D_3+D_4+D_5) \tag{41}$$

where the terms in brackets are given by

$$\begin{aligned}D_1&\equiv\Big(\beta_1\int_0^1\mathrm{d}\lambda\,(1-\lambda)\boldsymbol{F}[\boldsymbol{X}+\lambda(\boldsymbol{x}-\boldsymbol{X})]\Big)^2\\&=\beta_1^2\int_0^1\mathrm{d}\lambda\int_0^1\mathrm{d}\mu\,(1-\lambda)(1-\mu)\boldsymbol{F}[\boldsymbol{x}+\tau(1-\lambda)(\boldsymbol{x}''-\boldsymbol{x}')]\,.\,\boldsymbol{F}[\boldsymbol{x}+\tau(1-\mu)(\boldsymbol{x}''-\boldsymbol{x})]\\&=\frac{\beta_1^2}{\tau^4}\int_{1-\tau}^{1}\mathrm{d}\lambda'\int_{1-\tau}^{1}\mathrm{d}\mu'(1-\lambda')(1-\mu')\mathscr{F}(\lambda',\mu').\end{aligned} \tag{42a}$$

Substitutions (32*a*, *c*) have been used. Then with (32*a*, *b*)

$$\begin{aligned}D_2&\equiv2\beta_1\beta_2\int_0^1\mathrm{d}\lambda\,(1-\lambda)\boldsymbol{F}[\boldsymbol{X}+\lambda(\boldsymbol{x}-\boldsymbol{X})]\,.\int_0^1\mathrm{d}\mu\,\mu\boldsymbol{F}[\boldsymbol{x}''+\mu(\boldsymbol{X}-\boldsymbol{x}'')]\\&=2\beta_1\beta_2\int_0^1\mathrm{d}\lambda\,(1-\lambda)\int_0^1\mathrm{d}\mu\,\mu\boldsymbol{F}[\boldsymbol{x}+\tau(1-\lambda)(\boldsymbol{x}''-\boldsymbol{x})]\,.\,\boldsymbol{F}[\boldsymbol{x}''+(1-\tau)\mu(\boldsymbol{x}-\boldsymbol{x}'')]\\&=\frac{2\beta_1\beta_2}{\tau^2(1-\tau)^2}\int_{1-\tau}^{1}\mathrm{d}\lambda'(1-\lambda')\int_0^{1-\tau}\mathrm{d}\mu'\,\mu'\mathscr{F}(\lambda',\mu').\end{aligned} \tag{42b}$$

Using (32*b*, *d*) we find

$$D_3 \equiv \left(\beta_2 \int_0^1 \mathrm{d}\lambda\, \lambda \boldsymbol{F}[\boldsymbol{x}'' + \lambda(\boldsymbol{X} - \boldsymbol{x}'')]\right)^2$$

$$= \beta_2^2 \int_0^1 \mathrm{d}\lambda \int_0^1 \mathrm{d}\mu\, \lambda\mu\, \boldsymbol{F}[\boldsymbol{x}'' + (1-\tau)\lambda(\boldsymbol{x} - \boldsymbol{x}'')] \boldsymbol{.} \boldsymbol{F}[\boldsymbol{x}'' + (1-\tau)\mu(\boldsymbol{x} - \boldsymbol{x}'')]$$

$$= \frac{\beta_2^2}{(1-\tau)^4} \int_0^{1-\tau} \mathrm{d}\lambda' \int_0^{1-\tau} \mathrm{d}\mu'\, \mu'\lambda' \mathscr{F}(\lambda', \mu'). \tag{42c}$$

The last two terms of equation (41) are

$$D_4 \equiv -\beta_1 \int_0^1 \mathrm{d}\lambda\, (1-\lambda)^2 G[\boldsymbol{X} + \lambda(\boldsymbol{x} - \boldsymbol{X})]$$

$$= -\frac{\beta_1}{\tau^3} \int_{1-\tau}^1 \mathrm{d}\lambda' (1-\lambda')^2 G[\boldsymbol{x}'' + \lambda'(\boldsymbol{x} - \boldsymbol{x}'')] \tag{43a}$$

$$D_5 \equiv -\beta_2 \int_0^1 \mathrm{d}\lambda\, \lambda^2 G[\boldsymbol{x}'' + \lambda(\boldsymbol{X} - \boldsymbol{x}'')]$$

$$= -\frac{\beta_2}{(1-\tau)^3} \int_0^{1-\tau} \mathrm{d}\lambda'\, \lambda'^2 G[\boldsymbol{x}'' + \lambda'(\boldsymbol{x} - \boldsymbol{x}'')]. \tag{43b}$$

When expressions (36*a*, *b*), (40*a*, *b*), (42*a*, *b*, *c*), and (43*a*, *b*) are inserted into equation (27), it is convenient to group together certain terms.

Consider first terms containing $\mathscr{F}$. Noting that

$$1 - \frac{1-\mu}{\tau} = \mu - \frac{\tau_2(1-\mu)}{\tau_1}$$

$$1 - \frac{\lambda}{1-\tau} = 1 - \lambda - \frac{\tau_1}{\tau_2}\lambda$$

we can establish after some algebra

$$\tau_1\beta_1^2 K(\boldsymbol{x}, \boldsymbol{X}) + [(D_1 + D_2)/\gamma]$$

$$= 2\beta^2(\tau_1+\tau_2)^3 \int_{1-\tau}^1 \mathrm{d}\lambda\, (1-\lambda)\left[\int_0^1 \mu\mathscr{F}\, \mathrm{d}\mu + \frac{\tau_2}{2\tau_1}\left(\int_\lambda^1 \mathrm{d}\mu\, (1-\mu)\mathscr{F} - \int_{1-\tau}^\lambda \mathrm{d}\mu\, (1-\mu)\mathscr{F}\right)\right] \tag{44}$$

$$\tau_2\beta_2^2 K(\boldsymbol{X}, \boldsymbol{x}'') + (D_3/\gamma)$$

$$= 2\beta^2(\tau_1+\tau_2)^3 \int_0^{1-\tau} \mathrm{d}\lambda \left[\int_0^\lambda \mu(1-\lambda)\mathscr{F}\, \mathrm{d}\mu + \frac{\tau_1}{2\tau_2}\left(\int_\lambda^{1-\tau} \lambda\mu\mathscr{F}\, \mathrm{d}\mu - \int_0^\lambda \lambda\mu\mathscr{F}\, \mathrm{d}\mu\right)\right] \tag{45}$$

Reversing the order of integration we find

$$\int_{1-\tau}^1 \mathrm{d}\lambda \int_{1-\tau}^\lambda \mathrm{d}\mu\, g(\lambda, \mu) = \int_{1-\tau}^1 \mathrm{d}\mu \int_\mu^1 \mathrm{d}\lambda\, g(\lambda, \mu)$$

which is equal to

$$\int_{1-\tau}^{1} \mathrm{d}\lambda \int_{\lambda}^{1} \mathrm{d}\mu\, g(\lambda, \mu)$$

for any integrand $g(\lambda, \mu)$ symmetric with respect to interchange of λ and μ. Since this is the case for

$$g(\lambda, \mu) = (1-\lambda)(1-\mu)\mathscr{F}(\lambda, \mu)$$

the last two terms of equation (44) cancel each other. Similarly, the cancellation of the two last terms of equation (45) can be shown.

Adding equations (44) and (45) we thus get

$$\begin{aligned}\tau_1\beta_1^2K(\boldsymbol{x}, \boldsymbol{X}) &+ \tau_2\beta_2^2K(\boldsymbol{X}, \boldsymbol{x}'') + [(D_1+D_2+D_3)/\gamma] \\ &= 2\beta^2(\tau_1+\tau_2)^3 \int_0^1 \mathrm{d}\lambda\,(1-\lambda) \int_0^\lambda \mu\mathscr{F}(\lambda, \mu)\,\mathrm{d}\mu.\end{aligned} \tag{46}$$

For the terms containing $G = G[\boldsymbol{x}''+\lambda(\boldsymbol{x}-\boldsymbol{x}'')]$ we obtain

$$\begin{aligned}-\tau_1\beta_1L(\boldsymbol{x}, \boldsymbol{X}) &+ (D_4/\gamma) \\ &= -\beta(\tau_1+\tau_2)^2\Big(\int_{1-\tau}^1 \mathrm{d}\lambda\,(\tau_2/\tau_1)(1-\lambda)^2G \\ &\quad + \int_{1-\tau}^1 \mathrm{d}\lambda\,[\lambda-(\tau_2/\tau_1)(1-\lambda)](1-\lambda)G\Big) \\ &= -\beta(\tau_1+\tau_2)^2 \int_{1-\tau}^1 \mathrm{d}\lambda\,\lambda(1-\lambda)G.\end{aligned} \tag{47}$$

Correspondingly,

$$-\tau_2\beta_2L(\boldsymbol{X}, \boldsymbol{x}'') + (D_5/\gamma) = -\beta(\tau_1+\tau_2)^2 \int_0^{1-\tau} \mathrm{d}\lambda\,\lambda(1-\lambda)G, \tag{48}$$

thus

$$-\tau_1\beta_1L(\boldsymbol{x}, \boldsymbol{X}) - \tau_2\beta_2L(\boldsymbol{X}, \boldsymbol{x}'') + [(D_4+D_5)/\gamma] = -\beta(\tau_1+\tau_2)^2 \int_0^1 \mathrm{d}\lambda\,\lambda(1-\lambda)G. \tag{49}$$

Using equations (46) and (49) we finally get from equation (27):

$$\begin{aligned}\frac{\Lambda^2}{4\pi}Q(\boldsymbol{X}) &= \frac{\hbar^2}{2m}R(\boldsymbol{X})\Big(2(\beta_1+\beta_2)^3 \int_0^1 \mathrm{d}\lambda\,(1-\lambda) \int_0^\lambda \mu\mathscr{F}(\lambda, \mu)\,\mathrm{d}\mu \\ &\quad - (\beta_1+\beta_2)^2 \int_0^1 \mathrm{d}\lambda\,\lambda(1-\lambda)G\Big) \\ &= (\hbar^2/2m)R(\boldsymbol{X})[(\beta_1+\beta_2)^3K(\boldsymbol{x}, \boldsymbol{x}'') - (\beta_1+\beta_2)^2L(\boldsymbol{x}, \boldsymbol{x}'')]\end{aligned}$$

which shows together with equations (9), (28) and (34) the validity of equation (30).

5. Consideration of quantum statistics

By definition, the canonical density matrix $C^{\pm}$ for bosons (plus sign) or fermions (minus sign) is obtained from expression (3) by properly symmetrising the wavefunctions. However, $C^{\pm}$ can also be calculated from C without knowledge of individual wavefunctions.

Let $\boldsymbol{\xi}_i = (\boldsymbol{x}_i, s_i)$, s_i being the spin variable of the ith particle, and $\boldsymbol{\xi} = (\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_N)$. By means of the symmetriser $(+)$ or antisymmetriser $(-)$

$$\hat{S}^{\pm}_{\boldsymbol{\xi}} \equiv \frac{1}{N!} \sum_{\mathcal{P}} (\pm 1)^{p} \hat{P}_{\boldsymbol{\xi}}$$

where $\hat{P}_{\boldsymbol{\xi}}$ is associated with a permutation $\mathcal{P}$ of the $\boldsymbol{\xi}_i$ such that $\hat{P}_{\boldsymbol{\xi}} G(\boldsymbol{\xi}) = G(\mathcal{P}\boldsymbol{\xi})$ (G arbitrary) the exact density matrix is given by

$$C^{\pm}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta) = \sum_{j} \Psi^{\pm *}_{j}(\boldsymbol{\xi}') \Psi^{\pm}_{j}(\boldsymbol{\xi}) \exp(-\beta E_j)$$

$$= \exp(-\beta \hat{H}) \sum_{j} \hat{S}^{\pm}_{\boldsymbol{\xi}'} \Psi^{*}_{j}(\boldsymbol{\xi}') \hat{S}^{\pm}_{\boldsymbol{\xi}} \Psi_{j}(\boldsymbol{\xi}) = \exp(-\beta \hat{H}) \hat{S}^{\pm}_{\boldsymbol{\xi}'} \hat{S}^{\pm}_{\boldsymbol{\xi}} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}').$$

$\hat{H}$ is supposed here to be spin independent. $\Psi^{\pm}_{j}$ are the properly symmetrised eigenfunctions obtained from the unsymmetrised Ψ_j by application of $\hat{S}^{\pm}_{\boldsymbol{\xi}}$. In the last line the completeness relation of the Ψ_j was used:

$$\sum_{j} \Psi^{*}_{j}(\boldsymbol{\xi}') \Psi_{j}(\boldsymbol{\xi}) = \delta(\boldsymbol{\xi} - \boldsymbol{\xi}') \equiv \delta(\boldsymbol{x} - \boldsymbol{x}') \delta_{s,s'} \equiv \prod_{i=1}^{N} \delta(\boldsymbol{x}_i - \boldsymbol{x}'_i) \delta_{s_i, s'_i}.$$

From $\hat{P}_{\boldsymbol{\xi}} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}') = \hat{P}^{-1}_{\boldsymbol{\xi}'} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}')$ it follows that

$$\hat{S}^{\pm}_{\boldsymbol{\xi}} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}') = \hat{S}^{\pm}_{\boldsymbol{\xi}'} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}'). \qquad (50)$$

Since $\hat{S}^{\pm}_{\boldsymbol{\xi}}$ is idempotent we find

$$C^{\pm}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta) = \exp(-\beta \hat{H}) \hat{S}^{\pm}_{\boldsymbol{\xi}} \delta(\boldsymbol{\xi} - \boldsymbol{\xi}') = \hat{S}^{\pm}_{\boldsymbol{\xi}} C(\boldsymbol{x}, \boldsymbol{x}', \beta) \delta_{s,s'} \qquad (51)$$

because $\hat{S}^{\pm}_{\boldsymbol{\xi}}$ commutes with $\hat{H}$. Equivalently we can write

$$C^{\pm}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta) = \hat{S}^{\pm}_{\boldsymbol{\xi}'} C(\boldsymbol{x}, \boldsymbol{x}', \beta) \delta_{s,s'} \qquad (51a)$$

which is seen immediately from equations (50) and (51).

Let us now turn to the semiclassical approximation. According to equation (51), the lth order approximation to $C^{\pm}$ is

$$C^{\pm(l)}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta) = \hat{S}^{\pm}_{\boldsymbol{\xi}} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta) \delta_{s,s'} \qquad (l = 0, 2) \qquad (52)$$

where $C^{(2)}$ is given by equations (9) and (10a)–(10d), and $C^{(0)}$ is obtained from $C^{(2)}$ by neglecting the quantum correction in the large round brackets of equation (9).

Instead of equation (52) we may write alternatively

$$C^{\pm(l)}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta) = \hat{S}^{\pm}_{\boldsymbol{\xi}'} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta) \delta_{s,s'} \qquad (l = 0, 2). \qquad (52a)$$

To see this let us factorise $\hat{P}_{\boldsymbol{\xi}} = \hat{P}_{x} \hat{P}_{s}$ where $\hat{P}_{x}$ and $\hat{P}_{s}$ permute spatial and spin coordinates, respectively. First we show that

$$\hat{P}_{x} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta) = \hat{P}^{-1}_{x'} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta), \qquad (53)$$

Obviously, this relation holds for $C_0(\boldsymbol{x}, \boldsymbol{x}', \beta)$, equation (8). Further we note that for an arbitrary function $r(\boldsymbol{u}(\lambda))$, where $\boldsymbol{u}(\lambda)$ is defined by equation (10d), the relation

$$\hat{P}_{\boldsymbol{x}} r(\boldsymbol{u}(\lambda)) = r\{\mathscr{P}[\mathscr{P}^{-1}\boldsymbol{x}' + \lambda(\boldsymbol{x} - \mathscr{P}^{-1}\boldsymbol{x}')]\} = \hat{P}_{\boldsymbol{x}'}^{-1} r(\mathscr{P}\boldsymbol{u}(\lambda))$$

holds. If r is identified with the potential which is symmetric with respect to permutation of particles we get

$$\hat{P}_{\boldsymbol{x}} V(\boldsymbol{u}(\lambda)) = \hat{P}_{\boldsymbol{x}'}^{-1} V(\boldsymbol{u}(\lambda))$$

whence it follows from equation (10a) that

$$\hat{P}_{\boldsymbol{x}} W(\boldsymbol{x}, \boldsymbol{x}') = \hat{P}_{\boldsymbol{x}'}^{-1} W(\boldsymbol{x}, \boldsymbol{x}'). \tag{54}$$

To show the same property for $K(\boldsymbol{x}, \boldsymbol{x}')$, equation (10$b$), let $\boldsymbol{u}'(\mu) = \mathscr{P}\boldsymbol{u}(\mu)$. Then

$$\begin{aligned}
&\hat{P}_{\boldsymbol{x}}(\nabla_{\boldsymbol{u}(\mu)} V(\boldsymbol{u}(\mu)) \cdot \nabla_{\boldsymbol{u}(\lambda)} V(\boldsymbol{u}(\lambda))) \\
&\quad = \hat{P}_{\boldsymbol{x}'}^{-1} (\nabla_{\boldsymbol{u}'(\mu)} V(\boldsymbol{u}'(\mu)) \cdot \nabla_{\boldsymbol{u}'(\lambda)} V(\boldsymbol{u}'(\lambda))) \\
&\quad = \hat{P}_{\boldsymbol{x}'}^{-1} \sum_{j=1}^{N} \nabla_{\boldsymbol{u}'_j(\mu)} V(\boldsymbol{u}(\mu)) \cdot \nabla_{\boldsymbol{u}'_j(\lambda)} V(\boldsymbol{u}(\lambda)) \\
&\quad = \hat{P}_{\boldsymbol{x}'}^{-1} \sum_{i=1}^{N} \nabla_{\boldsymbol{u}_i(\mu)} V(\boldsymbol{u}(\mu)) \cdot \nabla_{\boldsymbol{u}_i(\lambda)} V(\boldsymbol{u}(\lambda))
\end{aligned}$$

where we have summed over $i = \mathscr{P}j$ in the third line. Therefore

$$\hat{P}_{\boldsymbol{x}} K(\boldsymbol{x}, \boldsymbol{x}') = \hat{P}_{\boldsymbol{x}'}^{-1} K(\boldsymbol{x}, \boldsymbol{x}'). \tag{55}$$

In a manner quite similar we find

$$\hat{P}_{\boldsymbol{x}} L(\boldsymbol{x}, \boldsymbol{x}') = \hat{P}_{\boldsymbol{x}'}^{-1} L(\boldsymbol{x}, \boldsymbol{x}'). \tag{56}$$

Thus, using equations (54), (55) and (56) we arrive at equation (53) which immediately leads to

$$\begin{aligned}
&\hat{S}_{\boldsymbol{\xi}}^{\pm} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta)\delta_{s,s'} \\
&\quad = \frac{1}{N!} \sum_{\mathscr{P}} (\pm 1)^p \hat{P}_s \delta_{s,s'} \hat{P}_{\boldsymbol{x}} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta) \\
&\quad = \frac{1}{N!} \sum_{\mathscr{P}} (\pm 1)^p \hat{P}_{s'}^{-1} \delta_{s,s'} \hat{P}_{\boldsymbol{x}'}^{-1} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta) \\
&\quad = \hat{S}_{\boldsymbol{\xi}'}^{\pm} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta)\delta_{s,s'}
\end{aligned} \tag{57}$$

and hence to equation (52a).

After these preliminaries we are able to evaluate

$$A^{\pm(l)} \equiv \sum_{s'} \int \mathrm{d}^{3N}x' \, C^{\pm(l)}(\boldsymbol{\xi}, \boldsymbol{\xi}', \beta_1) C^{\pm(l)}(\boldsymbol{\xi}', \boldsymbol{\xi}'', \beta_2)$$

by inserting equation (52) for the first factor of the integrand and equation (52a) for the second. The symmetrisers can be taken out of the integral sign. Using equations (29) and (30) we obtain

$$\begin{aligned}
A^{\pm(l)} &= \hat{S}_{\boldsymbol{\xi}}^{\pm} \hat{S}_{\boldsymbol{\xi}''}^{\pm} \sum_{s'} \delta_{s,s'} \delta_{s',s''} \int \mathrm{d}^{3N}x' \, C^{(l)}(\boldsymbol{x}, \boldsymbol{x}', \beta_1) C^{(l)}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2) \\
&= \hat{S}_{\boldsymbol{\xi}}^{\pm} \hat{S}_{\boldsymbol{\xi}''}^{\pm} \delta_{s,s''} C^{(l)}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1 + \beta_2)(1 + \mathrm{O}(\hbar^{l+2})).
\end{aligned} \tag{58}$$

This is the quantum statistical equivalent to relations (29) and (30). Since, however, the term $O(\hbar^{l+2})$ depends on $\boldsymbol{x}$ and $\boldsymbol{x}''$ too, the right-hand side of equation (58) cannot be cast into the form

$$C^{\pm(l)}(\boldsymbol{\xi}, \boldsymbol{\xi}'', \beta_1+\beta_2)(1+O(\hbar^{l+2}))$$

in constrast to equations (29) and (30) valid for classical statistics.

6. Application to the high temperature approximation appearing in the Trotter formula

The Trotter formula expresses $\exp(-\beta\hat{H})$ where $\hat{H}=\hat{T}+\hat{V}$ and $[\hat{T}, \hat{V}]\neq 0$ as an infinite product

$$\exp[-\beta(\hat{T}+\hat{V})] = \lim_{n\to\infty} [\exp(-\beta\hat{V}/n)\exp(-\beta\hat{T}/n)]^n.$$

In an approximation scheme, we can choose for a given value of β a finite n such that $\beta'=\beta/n$ satisfies (12a) and (12b). Thus in the coordinate representation we start from a high temperature approximation

$$\begin{aligned}\tilde{C}(\boldsymbol{x}, \boldsymbol{x}', \beta') &= \langle \boldsymbol{x}|\exp(-\beta'\hat{V})\exp(-\beta'\hat{T})|\boldsymbol{x}'\rangle \\ &= C_0(\boldsymbol{x}, \boldsymbol{x}', \beta')\exp(-\beta' V(\boldsymbol{x}))\end{aligned} \tag{58a}$$

and have to calculate matrix products, i.e. integrals of the form

$$\tilde{A} \equiv \int \mathrm{d}^{3N}x'\, \tilde{C}(\boldsymbol{x}, \boldsymbol{x}', \beta_1)\tilde{C}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2).$$

In the frame of the present work we are interested in the deviation of $\tilde{A}$ from $\tilde{C}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)$. A derivation quite analogous to that given in § 3 yields

$$\tilde{A} = C_0(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)(R(\boldsymbol{X})+O(\hbar^2))$$

where R is now given by

$$R(\boldsymbol{X}) = \exp(-\beta_1 V(\boldsymbol{x})-\beta_2 V(\boldsymbol{X})).$$

Thus we obtain

$$\int \mathrm{d}^{3N}x'\, \tilde{C}(\boldsymbol{x}, \boldsymbol{x}', \beta_1)\tilde{C}(\boldsymbol{x}', \boldsymbol{x}'', \beta_2) = \tilde{C}(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)(U+O(\hbar^2)) \tag{59a}$$

with

$$U = \exp[-\beta_2(V(\boldsymbol{X})-V(\boldsymbol{x}))]. \tag{60a}$$

If we use as an initial high temperature approximation instead of equation (58a) the expression (Storer 1968a):

$$\begin{aligned}\tilde{C}_s(\boldsymbol{x}, \boldsymbol{x}', \beta') &= \langle \boldsymbol{x}|\exp(-\beta'\hat{V}/2)\exp(-\beta'\hat{T})\exp(-\beta'\hat{V}/2)|\boldsymbol{x}'\rangle \\ &= C_0(\boldsymbol{x}, \boldsymbol{x}', \beta')\exp[-\beta'(V(\boldsymbol{x})+V(\boldsymbol{x}'))/2]\end{aligned} \tag{58b}$$

which is symmetric with respect to interchange of $\boldsymbol{x}$ and $\boldsymbol{x}'$, we find

$$\int \mathrm{d}^{3N}x'\tilde{C}_s(\boldsymbol{x}, \boldsymbol{x}', \beta_1)\tilde{C}_s(\boldsymbol{x}', \boldsymbol{x}'', \beta_2) = \tilde{C}_s(\boldsymbol{x}, \boldsymbol{x}'', \beta_1+\beta_2)(U_s+O(\hbar^2)) \tag{59b}$$

where

$$U_s = \exp[-\tfrac{1}{2}(\beta_1+\beta_2)V(\boldsymbol{X})+\tfrac{1}{2}(\beta_2 V(\boldsymbol{x})+\beta_1 V(\boldsymbol{x}''))]. \tag{60b}$$

Therefore, the high temperature expressions which are used in the Trotter product representation have semigroup property not even to zeroth order of $\hbar$ excepting the diagonal elements ($\boldsymbol{x}=\boldsymbol{x}''$) as is seen from the definition of $\boldsymbol{X}$, equation (17).

For sufficiently small $|\boldsymbol{x}-\boldsymbol{x}''|$ we can expand $V(\boldsymbol{x})$ and $V(\boldsymbol{x}'')$ about $\boldsymbol{X}$. We get

$$\begin{aligned} V(\boldsymbol{x}) &= V(\boldsymbol{X})+(x_{\alpha i}-X_{\alpha i})\frac{\partial V(\boldsymbol{X})}{\partial X_{\alpha i}}+\tfrac{1}{2}(x_{\alpha i}-X_{\alpha i})(x_{\delta j}-X_{\delta j})\frac{\partial^2 V(\boldsymbol{X})}{\partial X_{\alpha i}\,\partial X_{\delta j}}+\dots \\ &= V(\boldsymbol{X})+\frac{\beta_1}{\beta_1+\beta_2}(x_{\alpha i}-x''_{\alpha i})\frac{\partial V(\boldsymbol{X})}{\partial X_{\alpha i}} \\ &\quad +\frac{1}{2}\left(\frac{\beta_1}{\beta_1+\beta_2}\right)^2(x_{\alpha i}-x''_{\alpha i})(x_{\delta j}-x''_{\delta j})\frac{\partial^2 V(\boldsymbol{X})}{\partial X_{\alpha i}\,\partial X_{\delta j}}+\dots . \end{aligned}$$

A corresponding Taylor series holds for $V(\boldsymbol{x}'')$. Inserting these into equations (60*a*) and (60*b*) we obtain

$$U=\exp\left(+\frac{\beta_1\beta_2}{\beta_1+\beta_2}(x_{\alpha i}-x''_{\alpha i})\frac{\partial V(\boldsymbol{X})}{\partial X_{\alpha i}}+\mathrm{O}(|\boldsymbol{x}-\boldsymbol{x}''|^2)\right) \tag{61a}$$

and

$$U_s=\exp\left(\frac{\beta_1\beta_2}{4(\beta_1+\beta_2)}(x_{\alpha i}-x''_{\alpha i})(x_{\delta j}-x''_{\delta j})\frac{\partial^2 V(\boldsymbol{X})}{\partial X_{\alpha i}\,\partial X_{\delta j}}+\mathrm{O}(|\boldsymbol{x}-\boldsymbol{x}''|^3)\right) \tag{61b}$$

showing explicitly that semigroup condition equation (6) to order $\hbar^0$ is satisfied only for constant V in the case of equation (58*a*) and for linear V in the case of equation (58*b*) unless $\boldsymbol{x}=\boldsymbol{x}''$.

7. Conclusions

It has been shown by use of asymptotic analysis that the canonical density matrix $C(\boldsymbol{x}, \boldsymbol{x}', \beta)$ in semiclassical approximation to orders $\hbar^0$ and $\hbar^2$ satisfies the semigroup condition, equation (6), to orders $\hbar^0$ and $\hbar^2$, respectively. These results suggest that equation (6) is satisfied to nth order of $\hbar^2$ if the corresponding nth order semiclassical approximation is inserted. Since, however, the calculation becomes very intricate the above analysis has not been extended to higher n.

If the particles obey classical statistics equations (29) and (30) are valid. Especially, for the zeroth-order approximation $C^{(0)}$ equation (35) gives the second-order deviation from perfect semigroup property. It is noteworthy that $C^{(0)}$ had that property exactly if $C^{(0)}$ were regular at $\hbar=0$.

For bosons or fermions similar relations, see equation (58), can be derived from the case of classical statistics. However, equation (58) cannot be brought to a form that is entirely equivalent to expressions (29) or (30).

The foregoing analysis has also been applied to those high temperature approximations of the density matrix which are used as a starting point in evaluations of the Trotter formula. As is seen from equations (59*a*), (60*a*) and (59*b*), (60*b*), the semigroup property to order $\hbar^0$ is in general satisfied only along the diagonal. Therefore it might be advantageous in a numerical application of Trotter's formula to start with the proper semiclassical expansion of equation (9) instead of expressions (58*a*) or (58*b*).

In a preliminary calculation the formalism has been applied to the linear harmonic oscillator for control. The low temperature density matrix has been determined by iterative matrix multiplication starting from the semiclassical approximation, equations (9) and (10*a*)–(10*d*), and from the more conventional approximation, equation (58*b*), as well. The expressions obtained in this manner have been used then, by means of a projecting technique to be described elsewhere, to get the lowest ten energy levels. It turns out that the relative errors of the approximate eigenvalues are smaller by a factor of about 30–100 if the quantum corrected semiclassical expression is used instead of equation (58*b*). This supports strongly the assumption of improved convergence also in other cases. However, a general proof of convergence is not known so far, neither for the series equation (9) nor for the Wigner–Kirkwood expansion that emerges from equation (9) if $\boldsymbol{x}' = \boldsymbol{x}$.

The integrals involved in the high temperature expansion of the density matrices can be explicitly evaluated for a large class of potential functions, e.g. polynomials, hyperbolic functions, trigonometric sums the latter describing periodic potentials.

In deriving the semiclassical approximation it has been assumed that the potential is smooth. Therefore, this approximation scheme cannot be applied directly to potentials having cusps, discontinuities, or singularities. Nevertheless, if V tends to $+\infty$ at some point, meaningful results can yet be obtained from equation (9) (as is the case, e.g. for the Lennard-Jones potential at $r = 0$), since the factor $\exp(-\beta W)$ tends much faster to zero than the correction terms can diverge.

In general it is possible, however, to attack potentials which are not smooth using an indirect approach by combining the semiclassical approximation with a modified perturbation theory. The underlying idea is as follows. In many cases $V(\boldsymbol{x})$ can be approximated by a smooth potential $\bar{V}(\boldsymbol{x})$ for which the expansion equation (9) does exist yielding $\bar{C}^{(2)}$ if higher correction terms are disregarded. From $\bar{C}^{(2)}$ an effective potential $\bar{V}_{\text{eff}}(\boldsymbol{x}, \boldsymbol{x}', \beta)$ can then be specified explicitly such that the Bloch equation written down with $\bar{V}_{\text{eff}}$ has the exact solution $\bar{C}^{(2)}$. $C^{(2)}$ belonging to V is then obtained by low-order perturbation theory where $\bar{C}^{(2)}$ is taken to be the unperturbed matrix. The perturbation $V - \bar{V}_{\text{eff}}$ is, of course, much smaller than V itself, V being the perturbation if one starts from the free-particle matrix as unperturbed quantity.

For example, the attractive Coulomb potential $V(r) = -e^2/r$ can be approximated by the smooth potential $\bar{V}(r) = -e^2 \tanh(cr)/r$ where the parameter c is still adjustable. If c is chosen appropriately $\bar{V}$ is a good approximation to V except in the small region near $r = 0$. Since, however, in a perturbational treatment spatial integrations are involved the contribution even of the Coulomb singularity remains finite due to the factor r^2 of the volume element. Details of this procedure will be published in the near future.

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