

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

Journal of Physics and Chemistry of Solids 61 (2000) 1561-1566

www.elsevier.nl/locate/jpcs

A method for solving Bloch equation for Morse potential

B.S. Tošić^{1,a}, D. Popov^{b,*}

^aInstitute of Physics, Faculty of Sciences, 21000 Novi Sad, Trg Dositeja Obradovića 4, Yugoslavia ^bCatedra de Fizică, Universitatea "Politehnica" din Timişoara, Piața Horațiu No. 1, 1900 Timișoara, Romania

Received 8 December 1999; accepted 22 February 2000

Abstract

A method is presented for solving the Bloch equation for Morse potential, based on the application of Fourier transformation of the density matrix. The results obtained agree completely with the results obtained by other methods, however its advantage lies in its elegance and intuitivity of the approach. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bloch equation; Morse potential; Internuclear potential

1. Introduction

In order to obtain more correct estimate of the interaction potential in the case of diatomic molecule vibrations, several models of the internuclear potential were established during the decades [1-3]. Among many models for the potential function, a particular role is given to the potential proposed by Morse [4]:

$$V(r) = D[1 - \exp(-\alpha(r - r_{\rm e}))]^2,$$
(1)

where *r* represents the internuclear coordinate, $r_{\rm e}$ is the equilibrium position of the system of two nuclei in the diatomic molecule, α is Morse constant of the anharmonicity, and *D* is the dissociation energy of the diatomic molecule.

The arguments for such a statement are the following: (a) Morse potential allows for an analytical solution of the Schrödinger equation and is characterized by a finite number of bound states; (b) theoretical spectroscopic results obtained using Morse potential in the case of vibrational motion of diatomic [2] (as well as poliatomic) molecules, and also in the case of molecular collisions agree well with experimental data.

All this makes this potential a subject of numerous practical applications and related results are rather often quoted. We think that these are strong enough reasons to deal in more detail with another method for solving Bloch equation for Morse potential. The result obtained is in no way a new one, it has been known for a long time, however, we consider that each new approach to solving some problem can help clarifying some aspects, or even raising some new questions. From this point of view, the method proposed definitely broadens the scope of the application of the very model.

2. Bloch equation

Generally speaking, when one considers a quantum physical system characterized by a certain potential V(r), the first problem is to solve the corresponding Schrödinger equation for the stationary states:

$$\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(r)\right]\Psi_n(\vec{r}) = E_n\Psi_n(\vec{r}),\tag{2}$$

where $\Psi_n(\vec{r})$ denotes eigenfunctions, and E_n —energy eigenvalues of the system, while *n* denotes the set of all quantum numbers determining a particular state of the system.

The system which can be completely characterized by the eigenfunction $\Psi_n(\vec{r})$, i.e. when the information about the system is complete, is entitled as the *pure system*, and the corresponding states are *pure quantum states*. This implies that these states are of ideal character, since it is very difficult to obtain the complete information about any quantum system in practice.

In the case of realistic quantum systems it is generally impossible to obtain the complete information, so such systems are entitled *mixed systems*, and corresponding states are no more pure ones, but *mixed quantum states*. Mixed

^{*} Corresponding author. Fax: + 40-56-200-325.

E-mail address: dpopov@edison.et.utt.ro (D. Popov).

¹ Tel.: + 21-55-318; fax: + 21-55-662.

^{0022-3697/00/\$ -} see front matter @ 2000 Elsevier Science Ltd. All rights reserved. PII: \$0022-3697(00)00039-1\$

systems are not characterized by a eigenfunction, but by a *density matrix*.

If we consider a system characterized by the quantum canonical distribution, in the coordinate representation, \vec{r} , the density matrix $\rho(\vec{r}, \vec{r}'; \beta)$ is expressed in the following way:

$$\rho(\vec{r}, \vec{r}'; \beta) = \frac{1}{Z(\beta)} \sum_{n} e^{-\beta E_{n}} \Psi_{n}(\vec{r}) \Psi_{n}^{*}(\vec{r})$$
$$= \frac{1}{Z(\beta)} \sum_{n} e^{-\beta E_{n}} \rho_{n}(\vec{r}, \vec{r}').$$
(3)

The importance of the density matrix lies mostly in the fact that its *trace*, (or *Spur*) is so called partition function or sum (integral) of the states (depending on the character of the energy spectrum: discrete or continuous):

$$Z(\beta) = \int \rho(\vec{r}, \vec{r}; \beta) \, \mathrm{d}\vec{r}. \tag{4}$$

One can express all thermodynamical quantities characterizing particular quantum statistical system in terms of the partition function [5].

An alternative approach for the calculation of the density matrix is to solve the Bloch equation [6]:

$$-\frac{\partial}{\partial\beta}\rho(\vec{r},\vec{r}';\beta) = H(\vec{r})\rho(\vec{r},\vec{r}';\beta),$$
(5)

with the initial condition:

$$\lim_{\beta \to 0} \rho(\vec{r}, \vec{r}'; \beta) = \delta(\vec{r} - \vec{r}').$$
(6)

In our opinion, this is more elegant way, since in this case one generally avoids direct solving of Schrödinger equation, i.e. this method does not assume the knowledge of energy eigenvalues. However, Bloch equation is a partial differential equation, whose solving in the majority of cases represents a complex mathematical problem, and makes the problem more challenging.

In the case of the harmonic oscillator potential, the Bloch equation was solved by Feynman [5]. Applying this method, this equation was solved for somewhat more complicated case of the rotational harmonic oscillator [7].

The problems becomes complicated when the potentials of anharmonic character are taken into account, since, in most of the cases, the partial differential equation can not be solved exactly analytically.

3. The statement of the problem

We are interested in solving the Bloch equation for the case of one-dimensional Morse potential:

$$-\frac{\partial}{\partial\beta}\rho(x,x';\beta) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + D(1-e^{-\alpha x})^2\right]\rho(x,x';\beta),$$
(7)

with the initial condition:

$$\lim_{\beta \to 0} \rho(x, x'; \beta) = \delta(x - x').$$
(8)

We assume that it is worth looking for a compact *analytical* solution (i.e. in terms of some special analytical functions), of Bloch equation for Morse potential, since this would open the door to *new, anharmonic (Morse) spectroscopy* (\equiv [*MS*]), which would include as the limiting case (for *x* small) *the present harmonic spectroscopy* (\equiv [*HS*]):

$$\lim_{\to 0; (x\ll)} [MS] = [HS],\tag{9}$$

having in mind the limit for the potentials:

$$\lim_{x \to 0; (x \ll)} V_{\text{Morse}} = V_{\text{harmonic}}.$$
 (10)

In this way, numerous calculations of spectroscopic quantities would be simplified and also their analytical expressions could be derived, which would make easier the estimate of various physical parameters entering these analytical expressions.

In the paper [7] the case with present rotation was discussed (quantum rotational number $J \neq 0$) for Morse oscillator, in the manner in which it was done in the work of Pauling and Wilson [8] for the rotationless case. The following expression was obtained for the diagonal elements of the density matrix:

$$\rho_{vJ}(z) = \frac{\alpha \Gamma\left(\frac{c}{d} - v\right)}{v! \Gamma\left(\frac{c}{d} - 2v - 1\right) \Gamma\left(\frac{c}{d} - 2v\right)} e^{-z_z (c/d) - 2v - 1} \times \left[F\left(-v, \frac{c}{d} - 2v; z\right)\right]^2, \tag{11}$$

The standard notation used here is:

$$\frac{c}{d} = \frac{2y_{\rm e}}{\alpha\sqrt{D}} \frac{D - \frac{\sigma}{\alpha r_{\rm e}} \left(2 - \frac{3}{\alpha r_{\rm e}}\right) J(J+1)}{\left[D + \frac{\sigma}{\alpha r_{\rm e}} \left(-1 + \frac{3}{\alpha r_{\rm e}}\right) J(J+1)\right]^{1/2}}, \quad (12)$$

$$z = 2 \frac{\sqrt{2m}}{\alpha \hbar} \left[D + \sigma J (J+1) \left(-\frac{1}{\alpha r_{\rm e}} + \frac{3}{\alpha^2 r_{\rm e}^2} \right) \right]^{1/2} {\rm e}^{-\alpha (r-r_{\rm e})},$$
(13)

$$y_{\rm e} = \frac{\sqrt{2mD}}{\hbar}, \qquad \sigma = \frac{\hbar^2}{2mr_{\rm e}^2}.$$
 (14)

From here on, *v* represents quantum vibrational number, $\Gamma(t)$ —Euler function of II order, and $F(-v, \gamma; z)$ —degenerated hypergeometrical function.

By solving the Schrödinger equation for Morse potential

[8], energy eigenvalues were obtained:

$$E_{\nu J} = D + \sigma J (J+1) \left(1 - \frac{3}{\alpha r_{\rm e}} + \frac{3}{\alpha^2 r_{\rm e}^2} \right) - \left(\frac{\alpha \hbar}{2\sqrt{2m}} \right)^2 \left(\frac{c}{d} - 2\nu - 1 \right)^2, \tag{15}$$

as well as eigenfunctions:

$$\Psi_{vJ}(z) = \left[\frac{\alpha \Gamma\left(\frac{c}{d} - v\right)}{v! \Gamma\left(\frac{c}{d} - 2v - 1\right) \Gamma\left(\frac{c}{d} - 2v\right)}\right]^{1/2} \times e^{(-1/2)z} z^{((1/2)((c/d) - 2v - 1))} F\left(-v, \frac{c}{d} - 2v; z\right).$$
(16)

So, on the basis of the Eqs. (3), (15) and (16) there exist some vague indications how the function $\rho(x, x'; \beta)$ should look like.

4. Solving method

We shall try to apply the method of Fourier transformation, so we first introduce dimensionless quantities:

$$y = \frac{\sqrt{2mD}}{\hbar}x; \ f = \beta D; \ \lambda = -i\frac{\alpha\hbar}{\sqrt{2mD}} \equiv -i\gamma,$$
 (17)

and then introduce Fourier transformation for the function $\rho(y, y'; f)$:

$$F(k,k';f) \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i(ky-k'y')} \rho(y,y';f) \, dy \, dy'.$$
(18)

In this way we obtain the following differential-difference equation related to the Bloch partial differential equation (7):

$$-\frac{\partial}{\partial f}F(k,k';f) = (k^2+1)F(k,k';f) - 2F(k+\lambda,k';f)$$
$$+F(k+2\lambda,k';f)$$
(19)

which we try to solve by the method of separation of variables. For this purpose we treat the function F(k, k'; f) in the form of an infinite sum of the products of two functions with different variables:

$$F(k,k';f) = \sum_{\nu} A_{\nu}(k) B_{\nu}(k';f),$$
(20)

where v = 0, 1, 2, ... After substituting Eq. (20) into Eq. (19), we have:

$$-A_{\nu}(k)\frac{\partial B_{\nu}(k';f)}{\partial f}$$

= $B_{\nu}(k';f)[k^{2}A_{\nu}(k) + A_{\nu}(k) + A_{\nu}(k+2\lambda) - 2A_{\nu}(k+\lambda)].$
(21)

After the separation of variables, we arrive to two separate equations:

$$\frac{A_{\nu}(k+2\lambda) - 2A_{\nu}(k+\lambda)}{A_{\nu}k} + 1 + k^{2}$$
$$= -\frac{1}{B_{\nu}(k';f)} \frac{\partial B_{\nu}(k';f)}{\partial f} \equiv p.$$
(22)

Now we have to solve the equation:

$$-\frac{1}{B_{\nu}(k';f)}\frac{\partial B_{\nu}(k';f)}{\partial f} = p;$$

$$\frac{\partial B_{\nu}(k';f)}{\partial f} + 0\frac{\partial B_{\nu}(k';f)}{\partial k'} = -pB_{\nu}(k';f),$$
(23)

meaning that we should have:

$$\frac{df}{1} = \frac{dk'}{0}; \quad \frac{df}{1} = -\frac{1}{p} \frac{dB_{\nu}(k';f)}{B_{\nu}(k';f)};$$

$$\frac{dB_{\nu}(k';f)}{B_{\nu}(k';f)} = -p df; \quad B_{\nu}(k';f) = C_{1;\nu} e^{-pf},$$
(24)

leading to:

∂f

$$dk' = 0; \ k' = C_2; \ C_{1;\nu} = \Phi_{\nu}(C_2).$$
 (25)

So we obtain:

$$B_{\nu}(k';f) = \Phi_{\nu}(k') e^{-pf},$$
 (26)

where, at the moment, Φ is an arbitrary function. It will be determined later when we discuss the problem of the symmetry of the function F(k; k'; f) with respect to variables k and k', i.e. the symmetry of the density matrix (which in this case is a real function), with respect to variables x and x'.

In order to solve the equation with the variable *k*:

$$A_{\nu}(k+2\lambda) - 2A_{\nu}(k+\lambda) + k^{2}A_{\nu}(k) = pA_{\nu}(k)$$
(27)

we multiply it by e^{iky} and integrate the result over k from $-\infty$ to $+\infty$:

$$\int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k+2\lambda) - 2 \int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k+\lambda) + \int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k) + \int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} k^{2} A_{\nu}(k) = p \int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k).$$
(28)

We introduce a new function:

$$\int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k) = a_{\nu}(x) \tag{29}$$

and derive it twice:

$$\int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} k^2 A_{\nu}(k) = -\frac{\mathrm{d}^2 a_{\nu}(y)}{\mathrm{d}y^2}.$$
 (30)

After the substitution $k + \tau = q$, dk = dq, $k = q - \tau$, we

obtain:

$$\int_{-\infty}^{+\infty} dk \, \mathrm{e}^{\mathrm{i}ky} A_{\nu}(k+\tau) = \int_{-\infty}^{+\infty} dq \, \mathrm{e}^{\mathrm{i}qy} \, e^{-\mathrm{i}\tau x} A_{\nu}(q)$$
$$= \mathrm{e}^{-\mathrm{i}\tau x} \int_{-\infty}^{+\infty} dq \, \mathrm{e}^{\mathrm{i}qy} A_{\nu}(q) = \mathrm{e}^{-\mathrm{i}\tau y} a_{\nu}(y). \tag{31}$$

The above equations lead to a new one:

$$\frac{d^2 a_{\nu}(y)}{dy^2} - (e^{-2i\lambda y} - 2e^{-i\lambda y} - p + 1)a_{\nu}(y) = 0.$$
(32)

Taking into account that according to Eq. (17), $i\lambda = \gamma$, the above equation can be written in the following way:

$$-\frac{d^2 a_v(y)}{dy^2} + (1 - 2e^{-\gamma y} + e^{-2\gamma y})a_v(y) = pa_v(y).$$
(33)

This equation is, in fact, the Schrödinger equation for the stationary states for Morse potential, if one sets $\hbar^2/2m = 1$ and D = 1.

So, the solution of this equation for the domain of discrete energy values is [8]:

$$a_{\nu}(y) = C_{\nu} e^{-(1/\gamma)e^{-\gamma y}} e^{-y\sqrt{1-p}} F\left(-\nu, 1-\frac{2}{\gamma}\sqrt{1-p}; \frac{2}{\gamma} e^{-\gamma y}\right),$$
(34)

where F(...) is the degenerated hypergeometric function, and this form of the solution is valid if the following condition is fulfilled:

$$\sqrt{1-p} = 1 - \gamma \left(v + \frac{1}{2} \right).$$
 (35)

So, the number v has the meaning of the principal quantum number and for the bound states of two nuclei of a diatomic molecule, it can have a limited number of values, corresponding to the maximal number of the bound states v_{max} :

$$v = 0, 2, 3, \dots v_{\max} = \left[\frac{1}{\gamma} - \frac{1}{2}\right],$$
 (36)

where the symbol [...] implies an integer number of the quantity within brackets.

Taking into account the condition for the quantity p, the solution can be written in another way:

$$a_{\nu}(y) = C_{\nu} e^{-(1/\gamma)e^{-\gamma y}} e^{-[1-\gamma(\nu+(1/2))]y} F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} e^{-\gamma y}\right).$$
(37)

Following the definition, the function $A_{\nu}(k)$ is expressed in the following way:

$$A_{\nu}(k) = \frac{C_{\nu}}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy \, e^{-(1/\gamma)e^{-\gamma y}} \, e^{-[ik+1-\gamma(\nu+(1/2))]y} \\ \times F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} \, e^{-\gamma y}\right),$$
(38)

but the integral will not be calculated for the moment.

In order to assure the above mentioned symmetry we choose:

$$\Phi_{\nu}(k') = A_{\nu}(k'), \tag{39}$$

so that the function F(k, k'; f) will have the following structure:

$$F(k,k';f) = \sum_{\nu=0}^{\nu_{\max}} e^{-f[2\gamma(\nu+(1/2))-\gamma^2(\nu+(1/2))^2]} A_{\nu}(k) A_{\nu}(k').$$
(40)

Substituting the corresponding expressions for these functions, the function F(k, k'; f) can be written as:

$$F(k, k'; f) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dy \, dy' \, e^{-i(ky+k'y')}$$

$$\times \sum_{\nu=0}^{\nu_{max}} C_{\nu}^{2} \, e^{-f[2\gamma(\nu+(1/2))-\gamma^{2}(\nu+(1/2))^{2}]} \, e^{-(1/\gamma)(e^{-\gamma\nu}+e^{-\gamma\nu'})}$$

$$\times \, e^{-[1-\gamma(\nu+(1/2))](y+y')} F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} \, e^{-\gamma y}\right)$$

$$\times F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} \, e^{-\gamma y'}\right). \tag{41}$$

Comparing this equation with Eq. (18), the density matrix is obtained as:

$$\rho(y, y'; f) = \sum_{\nu=0}^{\nu_{\text{max}}} C_{\nu}^{2} e^{-f[2\gamma(\nu + (1/2)) - \gamma^{2}(\nu + (1/2))^{2}]} e^{-(1/\gamma)(e^{-\gamma \nu} + e^{-\gamma \nu'})}$$
$$\times e^{-[1 - \gamma(\nu + (1/2))](y + y')} F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} e^{-\gamma \nu}\right)$$
$$\times F\left(-\nu, \frac{2}{\gamma} - 2\nu; \frac{2}{\gamma} e^{-\gamma \nu'}\right). \tag{42}$$

If we return now to the initial variables, x and β and substitute the constant γ :

$$x = \frac{\hbar}{\sqrt{2mD}}y, \quad \beta = \frac{1}{D}f, \quad \gamma = \frac{\alpha\hbar}{\sqrt{2mD}},$$
 (43)

we can write the density matrix in the following way:

$$\rho(x, x'; \beta) = \sum_{\nu=0}^{\nu_{\max}} e^{-\beta E_{\nu}} \rho_{\nu}(x, x').$$
(44)

Let us now write down the normalizing integral for the density matrix:

$$\int_{-\infty}^{+\infty} \rho(x, x; \beta) \, dx$$

= $\sum_{\nu=0}^{\nu_{\text{max}}} e^{-\beta D[2(\alpha \hbar/\sqrt{2mD})(\nu + (1/2)) - (\alpha^2 \hbar^2/2mD)(\nu + (1/2))^2]} \equiv Z(\beta),$
(45)

where $Z(\beta)$ is the statistical sum. Now we can derive the normalizing constant C_{ν} from the condition:

$$\int_{-\infty}^{+\infty} \rho_{\nu}(x, x) \, \mathrm{d}x = 1.$$
(46)

1564

This integral can be most easily evaluated if we use the variable *z* (for the case J = 0 in Eq. (13), i.e. in the rotation-less case):

$$z = 2\frac{\sqrt{2mD}}{\alpha\hbar} e^{-\alpha x} = \frac{2}{\gamma} e^{-\alpha x}, \qquad (47)$$

so we obtain:

$$C_{\nu}^{2} \frac{1}{\alpha} \left(\frac{\gamma}{2}\right)^{((2/\gamma)-2\nu-1)} \int_{0}^{\infty} dz \, e^{-z} z^{((2/\gamma)-2\nu-1)-1} \left[F\left(-\nu,\frac{2}{\gamma};z\right)\right]^{2} = 1.$$
(48)

The integrals of this kind are solved, among others, in the annex of Landau and Lifshitz textbook [9]. We wrote in the paper [6] this result in a more compact form:

$$J_{\nu} = \int_{0}^{\infty} dz \ e^{-z} z^{\nu-1} [F(-\nu,\delta;z)]^{2}$$
$$= \frac{\nu! \Gamma(\nu) \Gamma(\delta)}{\Gamma(\nu+\delta)} \sum_{k=0}^{\nu} \frac{\binom{\nu}{k} \binom{\delta-\nu-1}{k} \binom{\delta-\nu-1+k}{k}}{\binom{\delta-1+k}{k}},$$
(49)

Identifying the exponents:

$$\nu = \frac{2}{\gamma} - 2\nu - 1, \qquad \delta = \frac{2}{\gamma} - 2\nu \tag{50}$$

we finally find the normalizing constant:

$$C_{\nu} = \left[\frac{\alpha \Gamma\left(\frac{2}{\gamma} - \nu\right)}{\nu! \Gamma\left(\frac{2}{\gamma} - 2\nu - 1\right) \Gamma\left(\frac{2}{\gamma} - 2\nu\right)}\right]^{1/2}.$$
 (51)

. ...

In this way, the solution of Bloch equation for Morse potential, i.e. the density matrix has the following form:

$$\rho(x, x'; \beta) = \sum_{\nu=0}^{\nu_{max}} e^{-\beta E_{\nu}} \frac{\alpha \Gamma(b_{\nu} + \nu + 1)}{\nu! \Gamma(b_{\nu}) \Gamma(b_{\nu} + 1)}$$
$$\times e^{-(K/2)(e^{-\alpha x} + e^{-\alpha x'})} (e^{-\alpha x} e^{-\alpha x'})^{(1/2)b_{\nu}}$$
$$\times F(-\nu, b_{\nu}; K e^{-\alpha x}) F(-\nu, b_{\nu}; K e^{-\alpha x'}),$$
(52)

where we have introduced the new notation for the sake of simplification:

$$K = \frac{2}{\gamma} = 2 \frac{\sqrt{2mD}}{\alpha \hbar}, \qquad b_v = K - 2v - 1.$$
 (53)

If we use Laguerre polynomials instead of degenerated hypergeometric function, according to the relation (see for example, Ref. [10]):

$$L_{\nu}^{b\nu}(z) = \frac{\Gamma(b_{\nu} + \nu + 1)}{\nu! \Gamma(b_{\nu} + 1)} F(-\nu, b_{\nu} + 1; z),$$
(54)

than the expression for the density matrix can be written in a

more compact way:

$$\rho(x, x'; \beta) = \exp\left[-\beta D - \frac{K}{2}(e^{-\alpha x} + e^{-\alpha x'})\right]$$

$$\times \sum_{\nu=0}^{\nu_{\max}} \frac{\alpha \nu! b_{\nu} \exp\left(\beta \frac{D}{K^2} b_{\nu}^2\right)}{\Gamma(b_{\nu} + \nu + 1)} (e^{-\alpha x} e^{-\alpha x'})^{(1/2)b_{\nu}}$$

$$\times L_{\nu}^{b_{\nu}}(K e^{-\alpha x}) L_{\nu}^{b_{\nu}}(K e^{-\alpha x'}).$$
(55)

In this way the problem stated is solved.

5. Conclusion

There is no doubt that the result obtained is not a new one, it is already known in the literature. What we consider to be new is the method applied, i.e. the method based on the application of Fourier transformation of the density matrix. In this way, on one hand we broaden the scope of the application of the method to quantum statistical physics, and on the other hand we include this method in the line with other methods for the derivation of density matrix of Morse oscillator, together with the "classical" method, based on Eq. (3) [6], method of Feynman path integrals [11], Green's function method [12], or, hybrid method of combining Laplace transform and Green's function [13].

The problem of the direct solution of the Bloch equation for Morse potential still remains open, in the sense of obtaining one closed (compact) analytical function, as in the case of the harmonic oscillator, a function that would satisfy the following limit:

$$\lim_{x \to 0: x \ll} \rho_{\text{Morse}} = \rho_{\text{harmonic}}.$$
 (56)

This would open the door to new, anharmonic (Morse) spectroscopy ($\equiv [MS]$), which would include, as the limiting case for small values of the variable *x*, the present, harmonic spectroscopy.

The interest for Morse potential is governed by its applications: the system of coupled Morse oscillators is convenient for the description of molecular vibrations [14]; the description of the potential energy surface—PES and vibrations of the O–H bond is also performed in terms of the Morse potential [15] etc.

References

- [1] Y.P. Varshni, Rev. Mod. Phys. 29 (1957) 664.
- [2] D. Steele, E.R. Lipincott, J.K. Vanderslice, Rev. Mod. Phys. 34 (2) (1962) 239.
- [3] E.S. Kryachko, Preprint, ITF-80-II 4R, Kiev, 1980.
- [4] P.M. Morse, Phys. Rev. 34 (1929) 57.
- [5] R.P. Feynman, Statistical Mechanics, Benjamin, Massachussets, 1972.
- [6] F. Bloch, Z. Phys. 74 (1932) 295.
- [7] D. Popov, Description of the Multielectron Systems by the

Density Matrix Method, PhD thesis, University of Craiova, Romania, 1986 (in Romanian, unpublished).

- [8] L. Pauling, E.B. Wilson Jr., Introduction to Quantum Mechanics, McGraw-Hill, New York, 1935.
- [9] L. Landau, E. Lifchitz, Mécanique quantique, Théorie non relativiste, Mir, Moscow, 1967.
- [10] I.S. Gradshteyn, I.M. Ryzhik, Table of Integrals, Series and Products, 5th ed., Academic Press, Boston, 1994.
- [11] C. Grosche, Ann. Phys. (N.Y.) 187 (1) (1988) 110.
- [12] L. Chetouani, T.F. Hammann, Nuovo Cimento 92B (1) (1986) 106.
- [13] D. Popov, Bul. St. si Tehnic al Univ. Tehnice Timişoara, Seria Matem. Fizica 37(51) (1992) 115.
- [14] M. Bancewicz, Chem. Phys. 203 (1996) 93.
- [15] D. Malzahn, V. May, Chem. Phys. 197 (1995) 1.