

CONSIDERATIONS CONCERNING THE QUANTUM GAS OF PSEUDOHARMONICAL OSCILLATORS

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Received 27 March 1995, revised 29 May 1995, accepted 31 May 1995

In the present paper we have examined some aspects of the pseudoharmonical oscillators quantum gas. After the deduction of the density matrix expression and the partition function, we calculated some characteristics of this gas: thermal moments of coordinate, internal energy, free energy, entropy and heat capacity. We verified the obtained results by passing to the harmonic limit.

1. Introduction

Usually, the research of the vibrational motion of diatomic molecules is performed by the model of three-dimensional quantum oscillator (HO-3). The advantages of this model are well-known, originating, above all, in the fact that the harmonic potential admits an exactly analytical solution of the Schrödinger's equation.

Recently, there has reappeared an interest for another potential, namely the potential of the pseudoharmonical oscillator (PHO) [1]:

$$V^{(p)}(r) = \frac{1}{8} m \omega^2 r_0^2 \left(\frac{r}{r_0} - \frac{r_0}{r} \right)^2 \quad (1)$$

when r_0 is the equilibrium distance between the nuclei. This potential admits, also, the exactly analytical solution of Schrödinger equation, being, in a certain sense, an intermediate potential between the harmonic potential (an ideal potential) and the anharmonic potentials (such as the Morse potential, the more realistic potential). A comparative analysis of potentials HO-3 and PHO is made in ref. [2].

Let us consider the system of identical pseudoharmonical oscillators (the quantum gas), without interactions, which are in thermodynamical equilibrium. Starting from the statistical operator, or the density matrix, we shall calculate the most important quantities for the pseudoharmonical quantum gas.

We shall check up the obtained expressions in two ways: by passing to the harmonic limit and, if it possible, by using the Hellmann-Feynman theorem.

2. Formulation of the problem in the density matrix approach

A quantum gas of oscillators, in thermodynamical equilibrium with the reservoir (thermostat) at temperature T , obeys the quantum canonical distribution. This is characterized by the statistical operator or the density operator ρ which satisfies the Bloch equation [3]. A representation of the density operator is called the density matrix. In the coordinate representation, the density matrix $\rho(\mathbf{r}, \mathbf{r}'; \beta)$ satisfies the Bloch equation:

$$-\frac{\partial}{\partial \beta} \rho(\mathbf{r}, \mathbf{r}'; \beta) = H(\mathbf{r}) \rho(\mathbf{r}, \mathbf{r}'; \beta) \tag{2}$$

with the limiting condition:

$$\lim_{\beta \rightarrow 0} \rho(\mathbf{r}, \mathbf{r}'; \beta) = \delta(\mathbf{r} - \mathbf{r}') \tag{3}$$

The density matrix may be defined as follows:

$$\rho(\mathbf{r}, \mathbf{r}'; \beta) = \sum_{vJM} \exp(-\beta E_{vJM}) \Psi_{vJM}(\mathbf{r}) \Psi_{vJM}^*(\mathbf{r}') \tag{4}$$

Here $\Psi_{vJM}(\mathbf{r})$ is the eigenfunction of the hamiltonian $H(\mathbf{r})$, corresponding to the eigenvalue E_{vJM} .

The density matrix is a very important concept, because its trace is just the partition function of the system:

$$Z(\beta) = \int \rho(\mathbf{r}, \mathbf{r}'; \beta) d\mathbf{r} \tag{5}$$

which contains all the statistical-thermodynamical information about the system.

For a central-type potential, like PHO, the eigenfunctions $\Psi_{vJM}^{(p)}(\mathbf{r})$ can be factorized into the radial part $R_{vJ}^{(p)}(r)$ and the angular one $Y_{JM}(\Theta, \varphi)$, so that the density matrix (4) can be written in the form:

$$\rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) = \frac{1}{4\pi} \sum_J (2J+1) P_J(\cos \gamma) \rho_J^{(p)}(r, r'; \beta), \tag{6}$$

where γ is the angle between the vectors \mathbf{r} and \mathbf{r}' , the index (p) refers to the characteristic quantities of PHO.

The radial density matrix will be:

$$\rho_J^{(p)}(r, r'; \beta) = \sum_v \exp(-\beta E_{vJ}^{(p)}) R_{vJ}^{(p)}(r) R_{vJ}^{(p)*}(r') \tag{7}$$

The functions $R_{vJ}^{(p)}(r)$ have been calculated in [1]:

$$R_{vJ}^{(p)}(r) = \left[\frac{\left(\frac{m\omega}{\hbar}\right)^{\frac{3}{2}} v!}{2^{\alpha J} \Gamma(\alpha J + v + 1)} \right]^{\frac{1}{2}} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} r \right]^{\alpha J - \frac{1}{2}} \exp\left(-\frac{m\omega}{4\hbar} r^2\right) L_v^{\alpha J} \left(\frac{m\omega}{2\hbar} r^2\right) \tag{8}$$

Here $\Gamma(x)$ is Euler's gamma function, $L_v^\alpha(z)$ - Laguerre's polynomial and

$$\alpha_J = \left[\left(J + \frac{1}{2}\right)^2 + \left(\frac{m\omega}{2\hbar} r_0^2\right)^2 \right]^{\frac{1}{2}} \tag{9}$$

The eigenvalue of energy is:

$$E_{vJ}^{(p)} = \hbar\omega \left(v + \frac{1}{2}\right) + \frac{\hbar\omega}{2} \alpha_J - \frac{m\omega^2}{4} r_0^2 \tag{10}$$

Evidently, for the central field potential, like PHO, the Bloch equation (2) can be reduced as follows:

$$-\frac{\partial}{\partial \beta} \rho_J^{(p)}(r, r'; \beta) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V^{(p)}(r) + \frac{\hbar^2}{2m} \frac{J(J+1)}{r^2} \right] \rho_J^{(p)}(r, r'; \beta) \tag{11}$$

Using the substitution

$$g_J^{(p)}(r, r'; \beta) = r r' \rho_J^{(p)}(r, r'; \beta), \tag{12}$$

it is easy to obtain the Bloch equation in the form:

$$-\frac{\partial}{\partial \beta} g_J^{(p)}(r, r'; \beta) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V^{(p)}(r) + \frac{\hbar^2}{2m} \frac{J(J+1)}{r^2} \right] g_J^{(p)}(r, r'; \beta), \tag{13}$$

which, in absence of rotation ($J = 0$), is formally identical with the Bloch equation of the one-dimensional motion.

In a previous paper (ref. [4]) we have deduced the expression of the density matrix (6) by calculating the radial density matrix with eq. (7) and using the Hille-Hardy relation [5]:

$$\sum_{v=0}^{\infty} \frac{v! L_v^\alpha(x) L_v^\alpha(y)}{\Gamma(\alpha + v + 1)} z^{-v} = \frac{(xyz)^{-\frac{\alpha}{2}}}{1-z} \exp\left(-z \frac{x+y}{1-z}\right) I_\alpha\left(2 \frac{\sqrt{xyz}}{1-z}\right), \tag{14}$$

where I_α is the modified Bessel function.

The radial density matrix becomes:

$$\rho_J^{(p)}(r, r'; \beta) = \exp\left(\beta \frac{m\omega^2}{4} r_0^2\right) \frac{1}{sh \beta \frac{\hbar\omega}{2}} \frac{1}{\left(r r'\right)^{\frac{1}{2}}} \times \exp\left[-\frac{m\omega}{4\hbar} (r^2 + r'^2) ct h \beta \frac{\hbar\omega}{2}\right] I_{\alpha_J} \left(\frac{m\omega}{2\hbar} r r'\right) \tag{15}$$

and the total density matrix (4) will be [4]:

$$\rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) = \frac{1}{4\pi} \exp\left(\beta \frac{m\omega^2}{4} r_0^2\right) \frac{1}{sh \beta \frac{\hbar\omega}{2}} \frac{m\omega}{2\hbar} \exp\left[-\frac{m\omega}{4\hbar} (r^2 + r'^2) ct h \beta \frac{\hbar\omega}{2}\right]$$

$$\times \sum_{J=0}^{\infty} (2J+1) P_J(\cos \gamma) I_{\alpha_J} \left(\frac{m\omega r r'}{2\hbar} \frac{1}{sh\beta \frac{\hbar\omega}{2}} \right) \quad (16)$$

The reduced radial density matrix (12) can be obtained also directly, by solving the Bloch equation (13) by standard methods for the Green function, path integrals [6] or by hybrid methods (shape invariant potentials and a time transformation of variables [7]).

Generally, for $J \neq 0$, the use of eq. (16) generates some mathematical difficulties and this is the reason why a simplification of this equation is necessary, if it is possible. A function can be developed into a series of Lagrange polynomials as follows:

$$f(x, t) = \sum_{J=0}^{\infty} (2J+1) P_J(x) f_J(t) \quad (17)$$

$$f_J(t) = \frac{1}{2} \int_{-1}^1 f(x, t) P_J(x) dx \quad (18)$$

By comparing these expressions and the sum of eq. (16), we use the following integral representation for the modified Bessel function $I_{\alpha_J}(t)$ [8]:

$$f_J(t) \equiv I_{\alpha_J}(t) = \frac{\left(\frac{t}{2}\right)^{\alpha_J}}{\sqrt{\pi} \Gamma(\alpha_J + \frac{1}{2})} \int_{-1}^1 e^{xt} (1-x^2)^{\alpha_J - \frac{1}{2}} dx \quad (19)$$

It is easy to obtain the result:

$$f(x, t) P_J(t) = \frac{2 \left(\frac{t}{2}\right)^{\alpha_J}}{\sqrt{\pi} \Gamma(\alpha_J + \frac{1}{2})} e^{xt} (1-x^2)^{\alpha_J - \frac{1}{2}} \quad (20)$$

We may use the development:

$$\frac{1}{(1-2\lambda x + \lambda^2)^{\frac{1}{2}}} = \sum_{J=0}^{\infty} P_J(x) \lambda^J \quad (21)$$

By multiplying eq. (20) by λ^J , where $|\lambda| < 1$ is a dimensionless parameter (naming it anharmonicity) and after summation, we obtain:

$$f(x, t) = \frac{2}{\sqrt{\pi}} e^{xt} \left(\frac{1-2\lambda x + \lambda^2}{1-x^2} \right)^{\frac{1}{2}} \sum_{J=0}^{\infty} \lambda^J \left[\frac{t}{2} (1-x^2) \right]^{\alpha_J} \Gamma(\alpha_J + \frac{1}{2}) \quad (22)$$

where the following notations have been used:

$$x = \cos \gamma; \quad t = \frac{m\omega}{2\hbar} \frac{r r'}{sh\beta \frac{\hbar\omega}{2}} \quad (23)$$

In conclusion, the total density matrix (16) becomes:

$$\rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) = \frac{1}{\pi^{\frac{3}{2}} \sin \gamma sh\beta \frac{\hbar\omega}{2}} \left(\frac{1-2\lambda \cos \gamma + \lambda^2}{r r'} \right)^{\frac{1}{2}}$$

$$\times \exp \left\{ -\frac{m\omega}{4\hbar} \left[(r^2 + r'^2) ct\hbar\beta \frac{\hbar\omega}{2} - 2 \frac{\cos \gamma}{sh\beta \frac{\hbar\omega}{2}} r r' \right] \right\}$$

$$\times \exp \left(\beta \frac{m\omega - r_0^2}{4\hbar} \right) \sum_{J=0}^{\infty} \frac{\lambda^J}{\Gamma(\alpha_J + \frac{1}{2})} \left(\frac{m\omega}{4\hbar} \frac{r r' \sin^2 \gamma}{sh\beta \frac{\hbar\omega}{2}} \right)^{\alpha_J} \quad (24)$$

It is useful to observe here, that at the harmonical limit, defined as:

$$\begin{aligned} \lim_{r_0 \rightarrow 0} A^{(p)} &\equiv \lim_{HO} A^{(p)} = A^{(0)} \\ \alpha_J &= J + \frac{1}{2} \\ \omega &= 2\omega_0 \\ \lambda &\rightarrow 0 \end{aligned} \quad (25)$$

and taking into consideration the expression [5]:

$$e^{-z \cos \gamma} = \left(\frac{\pi}{2z} \right)^{\frac{1}{2}} \sum_{J=0}^{\infty} (2J+1) P_J(\cos \gamma) I_{J+\frac{1}{2}}(z) \quad (26)$$

the density matrix (16) for PHO passes into the density matrix $\rho^{(0)}(\mathbf{r}, \mathbf{r}'; \beta)$ for isotropic HO-3:

$$\rho^{(0)}(\mathbf{r}, \mathbf{r}'; \beta) = \left(\frac{m\omega_0}{2\pi\hbar} \right)^{\frac{3}{2}} \frac{1}{(sh\beta\hbar\omega_0)^{\frac{3}{2}}} \times \exp \left\{ -\frac{m\omega_0}{2\hbar} \left[(r^2 + r'^2) ct\hbar\beta\hbar\omega_0 - \frac{2 \cos \gamma}{sh\beta\hbar\omega_0} r r' \right] \right\} \quad (27)$$

Taking into consideration this fact, the eq. (24) can be written in a simplified manner:

$$\rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) = \rho^{(0)}(\mathbf{r}, \mathbf{r}'; \beta) \left[\frac{(1-2\lambda \cos \gamma + \lambda^2) sh\beta \frac{\hbar\omega}{2}}{\frac{m\omega}{2\hbar} r r' \sin^2 \gamma} \right]^{\frac{1}{2}} \times \sum_{J=0}^{\infty} \frac{\lambda^J}{\Gamma(\alpha_J + \frac{1}{2})} \left(\frac{m\omega}{4\hbar} \frac{r r' \sin^2 \gamma}{sh\beta \frac{\hbar\omega}{2}} \right)^{\alpha_J} \quad (28)$$

Due to eq. (9) for the α_J parameter, eq. (28) cannot further be simplified. In this stage, the formulation of the problem in the density matrix approach is finished, $\rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta)$ being the central concept of the theory.

3. Calculation of the thermal moments and thermodynamical functions

Generally, the expected value for a certain physical observable $A^{(p)}$, which characterizes the pseudoharmonical oscillator gas is:

$$\langle A^{(p)} \rangle = \frac{1}{Z^{(p)}(\beta)} \int A^{(p)}(\mathbf{r}') \rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) |\mathbf{r}' = \mathbf{r} \rangle d\mathbf{r} \quad (29)$$

where the succession of operations is the following: first, the operator $A^{(p)}$ acts on the function $\rho^{(p)}$ (acting only on the dashed variables), then the dash is deleted. Finally, the integration is performed over the variables without the dash [9], [10]. Of course, when the operator $A^{(p)}$ has a multiplicative character, diagonal elements of the density matrix will appear directly in the last formula.

Some important observables which characterize the quantum oscillator gas are the coordinate thermal moments, because the two first moments can be determined experimentally [11]. The n -order moment is the expected value of the displacement from the equilibrium position:

$$\langle (\Delta r)^n \rangle^{(p)} = \langle (r - r_0)^n \rangle^{(p)} \quad (30)$$

$$\langle r^n \rangle^{(p)} = \lim_{\gamma \rightarrow 0} \frac{\int r^n \rho^n(\mathbf{r}, \mathbf{r}; \beta) d\mathbf{r}}{\int \rho^{(p)}(\mathbf{r}, \mathbf{r}; \beta) d\mathbf{r}} \quad (31)$$

The integral from the denominator is just the statistical sum (partition function) (3). The integral is of the following kind [5]:

$$\int_0^\infty r^b \exp(-ar^2) dr = \frac{1}{2} \frac{\Gamma(\frac{b+1}{2})}{a^{\frac{b+1}{2}}} \quad (32)$$

Here $\Gamma(x)$ are the Euler's gamma functions, and:

$$a = \frac{m\omega}{2\hbar} \frac{1}{sh\beta \frac{\hbar\omega}{2}} \left(ch\beta \frac{\hbar\omega}{2} - \cos\gamma \right) > 0 \quad (33)$$

$$b = 2\alpha_J + n + 1 \quad (34)$$

After the integration, the following notation is used:

$$S_{(\alpha_J)}^{(n+1)} = \sum_{J=0}^\infty \lambda^J \frac{\Gamma(\alpha_J + 1 + \frac{n}{2})}{\Gamma(\alpha_J + \frac{1}{2})} u^{2\alpha_J} \quad (35)$$

where the new variable is:

$$u = \frac{\sin\gamma}{2sh\beta \frac{\hbar\omega}{4}} = u(\beta; \gamma) \quad (36)$$

The partition function corresponds to the value $n=0$:

$$Z^{(p)}(\beta) = \frac{2}{\sqrt{\pi}} \exp\left(\beta \frac{m\omega^2}{4} r_0^2\right) \frac{1-\lambda}{(2sh\beta \frac{\hbar\omega}{4})^2} \lim_{\gamma \rightarrow 0} \frac{S_{(\alpha_J)}^{(1)}}{\sin\gamma} \quad (37)$$

The n -order moment will be:

$$\langle r^n \rangle^{(p)} = \left(\frac{2\hbar}{m\omega} ch\beta \frac{\hbar\omega}{4} \right)^{\frac{n}{2}} \lim_{\gamma \rightarrow 0} \frac{S_{(\alpha_J)}^{(n+1)}}{S_{(\alpha_J)}^{(1)}} \quad (38)$$

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For $n=2$, the expected value will be:

$$\left\langle \frac{1}{r^2} \right\rangle^{(p)} = \frac{m\omega}{2\hbar} th\beta \frac{\hbar\omega}{4} \lim_{\gamma \rightarrow 0} \frac{S_{(\alpha_J)}^{(-1)}}{S_{(\alpha_J)}^{(1)}} \quad (39)$$

This expression is useful in evaluating the contribution of the centrifugal term. The $n=1$ and $n=2$ - orders moments will be:

$$\langle r \rangle^{(p)} = \left(\frac{2\hbar}{m\omega} ch\beta \frac{\hbar\omega}{4} \right)^{\frac{1}{2}} \lim_{\gamma \rightarrow 0} \frac{S_{(\alpha_J)}^{(2)}}{S_{(\alpha_J)}^{(1)}} \quad (40)$$

$$\langle r^2 \rangle^{(p)} = \left(\frac{2\hbar}{m\omega} ch\beta \frac{\hbar\omega}{4} \right) \lim_{\gamma \rightarrow 0} \frac{S_{(\alpha_J)}^{(3)}}{S_{(\alpha_J)}^{(1)}} \quad (41)$$

For the calculation of the thermodynamical functions it is useful to write the partition function which corresponds to an oscillator as follows:

$$Z^{(p)}(\beta) = Z^{(0)}(\beta) \frac{2(1-\lambda)}{\sqrt{\pi}} \exp\left(\beta \frac{m\omega^2}{4} r_0^2\right) \lim_{u \rightarrow 0} \frac{S_{(\alpha_J)}^{(1)}}{u} \quad (42)$$

This makes evident the contribution of the anharmonicity.

For the system of the N oscillators (quantum gas), the partition function is (when the interactions are absent):

$$Z_{\text{system}}^{(p)}(\beta) = [Z^{(p)}(\beta)]^N \quad (43)$$

According to the fundamental principle of statistical mechanics, it is possible to determine all the thermodynamical properties of the system, as soon as the partition function is known [10].

The free energy of the gas is:

$$F^{(p)} = -\frac{1}{\beta} \ln Z_{\text{system}}^{(p)}(\beta) = F^{(0)} - \frac{N}{\beta} \ln \frac{2(1-\lambda)}{\sqrt{\pi}} - N \frac{m\omega^2}{4} r_0^2 - \frac{N}{\beta} \lim_{u \rightarrow 0} \left[\ln \frac{S_{(\alpha_J)}^{(1)}}{u} \right] \quad (44)$$

The internal energy is:

$$U^{(p)} = -N \frac{\partial}{\partial \beta} \ln Z^{(p)}(\beta) = U^{(0)} - N \frac{m\omega^2}{4} r_0^2 - N \frac{\partial}{\partial \beta} \ln \left[\lim_{u \rightarrow 0} \frac{S_{(\alpha_J)}^{(1)}}{u} \right] \quad (45)$$

where, using the fact that

$$\frac{\partial}{\partial \beta} = -\frac{\hbar\omega}{4} ch\beta \frac{\hbar\omega}{4} u \frac{\partial}{\partial u}, \quad (46)$$

after the elementary operations, eq. (45) can be written as:

$$U^{(p)} = U^{(0)} - N \frac{m\omega^2}{4} r_0^2 - N \frac{\hbar\omega}{4} \operatorname{cth}\beta \frac{\hbar\omega}{4} \left[1 - \lim_{u \rightarrow 0} u \frac{\partial}{\partial u} \ln S^{(1)}_{(\alpha_j)} \right] \quad (47)$$

The entropy of the gas $S^{(p)}$ can be easily calculated by using the previous results

$$S^{(p)} = k\beta(U^{(p)} - F^{(p)}), \quad (48)$$

and so we obtain

$$S^{(p)} = S^{(0)} + kN \left[\ln \frac{2(1-\lambda)}{\sqrt{\pi}} + \lim_{u \rightarrow 0} \ln \frac{S^{(1)}_{(\alpha_j)}}{u} \right] - kN\beta \frac{\hbar\omega}{4} \operatorname{cth}\beta \frac{\hbar\omega}{4} \left[1 - \lim_{u \rightarrow 0} u \frac{\partial}{\partial u} \ln S^{(1)}_{(\alpha_j)} \right] \quad (49)$$

Finally, we will also calculate the molar heat capacity at the constant volume:

$$C_V^{(p)} = \frac{1}{\nu} \frac{dU^{(p)}}{dT} = -\frac{R}{N} \beta^2 \frac{\partial U^{(p)}}{\partial \beta} \quad (50)$$

By using eqs. (47) and (46), we obtain its expression:

$$C_V^{(p)} = C_V^{(0)} - R \left(\beta \frac{\hbar\omega}{4} \right)^2 \frac{1}{(sh\beta \frac{\hbar\omega}{4})^2} \left[1 - \lim_{u \rightarrow 0} u \frac{\partial}{\partial u} \ln S^{(1)}_{(\alpha_j)} \right] + R \left(\beta \frac{\hbar\omega}{4} \right)^2 \left(\operatorname{cth}\beta \frac{\hbar\omega}{4} \right)^2 \lim_{u \rightarrow 0} \left[u \frac{\partial}{\partial u} \left(u \frac{\partial}{\partial u} \ln S^{(1)}_{(\alpha_j)} \right) \right] \quad (51)$$

In the final eqs. (42), (44), (47), (49) and (51) we have separated, (denoted by index (0)), the corresponding quantities of the three-dimensional isotropic HO.

The explicit expressions of these quantities will be given in the next chapter.

4. Verification of the obtained results

Since the problem of the harmonic oscillator is a completely solvable problem, to verify the obtained results, we address ourselves to the harmonic limit defined by eq. (25).

We use the relations [12]:

$$\Gamma \left(J + \frac{3}{2} \right) = \frac{\sqrt{\pi}}{2} \frac{1}{2^{2J}} \frac{(2J+1)!}{J!} \quad (52)$$

$$\sum_{J=0}^{\infty} \frac{(2J+1)!}{(J!)^2} x^J = \frac{1}{(1-4x)^{\frac{3}{2}}}, \quad |x| \leq \frac{1}{4} \quad (53)$$

$$\sum_{J=0}^{\infty} \frac{\Gamma(J+\nu)}{J!} x^J = \frac{\Gamma(\nu)}{(1-x)^\nu}, \quad |x| < 1. \quad (54)$$

In eq. (28), the infinite sum represents an exponential which has the harmonic limit equal to 1, so that

$$\lim_{HO} \rho^{(p)}(\mathbf{r}, \mathbf{r}'; \beta) = \rho^{(0)}(\mathbf{r}, \mathbf{r}'; \beta), \quad (55)$$

i.e. just eq. (27).

In order to find the limit of the partition function, but also for other expressions, it is useful to write the particular value of the sum $S^{(n+1)}_{(\alpha_j)}$:

$$S^{(n+1)}_{(J+\frac{1}{2})} = \Gamma \left(\frac{n+3}{2} \right) \frac{u}{(1-\lambda u^2)^{\frac{n+3}{2}}} \quad (56)$$

Thus eq. (42) becomes:

$$\lim_{HO} Z^{(p)}(\beta) = Z^{(0)}(\beta) = \frac{1}{(2sh\beta \frac{\hbar\omega_0}{2})^3} \quad (57)$$

We write also expressions of the other thermodynamical functions (internal energy, free energy, entropy and molar heat capacity, respectively):

$$\lim_{HO} F^{(p)} = F^{(0)} = 3N \left[\frac{\hbar\omega_0}{2} + \frac{1}{\beta} \ln(1 - e^{-\beta\hbar\omega_0}) \right], \quad (58)$$

$$\lim_{HO} U^{(p)} = U^{(0)} = 3N \left[\frac{\hbar\omega_0}{2} + \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} \right], \quad (59)$$

$$\lim_{HO} S^{(p)} = S^{(0)} = 3kN \left(\beta \frac{\hbar\omega_0}{2} \operatorname{cth}\beta \frac{\hbar\omega_0}{2} - \ln 2sh\beta \frac{\hbar\omega_0}{2} \right), \quad (60)$$

$$\lim_{HO} C_V^{(p)} = C_V^{(0)} = 3R \left(\beta \frac{\hbar\omega_0}{2} \right)^2 \frac{1}{(sh\beta \frac{\hbar\omega_0}{2})^2} \quad (61)$$

The harmonic limit of the n-order moment is obtained from eq. (38), taking into account eq. (52) ÷ (54):

$$\lim_{HO} \langle (\Delta r)^n \rangle^{(p)} = \langle r^n \rangle^{(0)} = \left(\frac{\hbar}{m\omega_0} \operatorname{cth}\beta \frac{\hbar\omega_0}{2} \right)^{\frac{n}{2}} \frac{\Gamma \left(\frac{n+3}{2} \right)}{\Gamma \left(\frac{3}{2} \right)} \quad (62)$$

with the evident particularizations for $n=2; 1; 2$.

The verification of the results for the moments can also be made if we calculate again the moments in rotation - vibration states $|nJ\rangle$ and the statistical average:

$$\langle r^n \rangle^{(p)} = \frac{1}{Z^{(p)}(\beta)} \sum_{J=0}^{\infty} (2J+1) \sum_{v=0}^{\infty} e^{-\beta E_{vJ}^{(p)}} \langle r^n \rangle_{vJ}^{(p)} \quad (63)$$

The expected values for $n=2$ and -2 can be calculated by using the Hellmann-Feynman theorem [10]:

$$\left\langle \frac{\partial H}{\partial a_i} \right\rangle_{vJ}^{(p)} = \frac{\partial E_{vJ}^{(p)}}{\partial a_i} \quad (64)$$

where a_i are the parameters involved in the hamiltonian H . From eqs. (1) and (10), for $a_i = r_0$, we obtain:

$$\left\langle \frac{1}{r^2} \right\rangle_{vJ}^{(p)} = \frac{m\omega}{2\hbar} \frac{1}{\alpha J} \quad (65)$$

and for $a_i = \omega$:

$$\langle r^2 \rangle_{vJ}^{(p)} = 4 \frac{\hbar}{m\omega} \left(v + \frac{1}{2} \right) + 2 \frac{\hbar}{m\omega} \alpha J \quad (66)$$

By substituting these values into eq. (63), we obtain eq. (39), respectively eq. (41), which have the limit given by the eq. (62).

5. Conclusions

The main reason why the study of the pseudoharmonical oscillators quantum gas is interesting is because this type of anharmonic potential permits an exactly analytical solution of the Schrödinger's equation, or the Bloch equation.

It is necessary to use an anharmonic potential for real diatomic molecules. In the present paper this is the PHO, because: it is asymmetric with respect to r_0 ; it is a more physically realistic potential in comparison with the HO; it becomes infinite in the origin of the coordinate r ; it is extended only in the physical region ($0 < r < \infty$); it admits an exact solution of the Schrödinger equation.

We have obtained a series of expressions for the coordinate moments and for some thermodynamical functions which characterize the pseudoharmonical oscillators quantum gas. At the harmonic limit, all these expressions go over into the corresponding expressions for HO.

References

- [1] M. Sage: *Chem. Phys.* **87** (1984) 431;
- [2] M. Sage, J. Goodisman: *Am. J. Phys.* **53** (1985) 4, 350;
- [3] F. Bloch: *Z. Phys.* **74** (1932) 295;
- [4] D. Popov: in "Proceedings of the Fifth Symposium of Mathematics and its Applications", october 1993, Timişoara, Romania;
- [5] I.S. Gradshteyn, I.M. Ryzhik: "Table of Integrals, Series and Products", Academic Press, London, New York, 1980;
- [6] C. Grosche, F. Steiner: *Z. Phys.* **C 36** (1987) 699;
- [7] C.J. Efthimiou: "A Comment on the Propagator of the Radial Oscillator", preprint CLNS-93/1206;
- [8] A. Nikiforov, V. Ouharov: "Elements de la theorie des fonctions speciales", Mir, Moscow, 1976;
- [9] P.O. Löwdin: *Phys. Rev.* **97** (1955) 6, 1474;
- [10] R.P. Feynman: "Statistical Mechanics", Benjamin, New York, 1972;
- [11] S.I. Gyvin: "Vibration of Molecules and the Mean Square Amplitudes", Mir, Moscow, 1971 (in Russian);
- [12] A.P. Proudnikov, Yu.A. Brychkov, O.I. Marichev: "Integrals and Series, Elementary Functions", Nauka, Moscow, 1981 (in Russian)