Density matrix for a triatomic linear molecule model

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We find the unitary operator for diagonalizing the Hamiltonian of a triatomic linear molecule. The unitary operator is expressed in a coordinate representation that brings convenience for deriving the density matrix $\rho(x_1,x_2,x_3;x_1',x_2',x_3',\beta)$. The unitary transformation approach is simple because the derivation can be reduced to the calculation of two independent harmonic-oscillator density matrices and one free-particle density matrix. The average of the potential energy and the kinetic of the molecule is calculated by using the density matrix.

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I. INTRODUCTION

As Feynman pointed out, the concept of the density matrix plays a role in reformulate quantum mechanics because pure states are not general enough to describe a quantum-mechanical system [1]. The density matrix for a definite Hamiltonian H is defined as $\exp(-\beta H)=\rho$; here $\beta=(k_BT)^{-1}$ and k_B is the Boltzmann constant. The equation of motion of ρ in coordinate representation is given by

$$-\partial\rho(x,x';\beta)/\partial\beta=H_x(x,x',\beta) \tag{1}$$

with the initial condition $\rho(x,x';0)=\delta(x-x')$. An example showing how to use Eq. (1) to derive the density matrix for a harmonic oscillator is presented by Feynman. Although Eq. (1) offers a general approach for treating density matrices, only several problems can be solved exactly [2].

In this work we consider the density matrix for a more complicated system—the triatomic linear molecule whose Hamiltonian is given by [3]

$$\mathcal{H}=\sum_{i=1}^{3}\frac{\hat{P}_i^2}{2m_i}+\frac{k}{2}[(\hat{x}_2-\hat{x}_1-d)^2+(\hat{x}_3-\hat{x}_2-d)^2]\ ,$$
$$[\hat{x}_i,\hat{p}_j]=i\hbar\delta_{ij}\ , \tag{2}$$

where d is the distance between two adjacent atoms. Using the displacement operator $\exp(i\hat{P}_jd)$, we have $\exp(-i\hat{P}_jd)\hat{x}_j\exp(i\hat{P}_jd)=\hat{x}_j-d$. Therefore in the following we focus on dealing with the displaced Hamiltonian $H=H_0+H'$, where $H'=-k(\hat{x}_1\hat{x}_2+\hat{x}_2\hat{x}_3)$ and

$$H_0=\sum_{i=1}^{3}\frac{\hat{P}_i^2}{2m_i}+\frac{k}{2}(\hat{x}_1^2+\hat{x}_3^2)+k\hat{x}_2^2$$
$$=\hbar[\sqrt{k/m_1}(a_1^\dagger a_1+\tfrac{1}{2})+\sqrt{2k/m_2}(a_2^\dagger a_2+\tfrac{1}{2})$$
$$+\sqrt{k/m_3}(a_3^\dagger a_3+\tfrac{1}{2})]\ , \tag{3}$$

and we derive its density matrix. Instead of using Eq. (1), we adopt a unitary transformation approach. This is enlightened by our previous works [4], which solve the dynamics of N identically coupled oscillators by virtue of a unitary transformation. The present work is arranged as follows: In Sec. II we find the unitary operator U that can diagonalize the Hamiltonian H. It is worth pointing out that, although the eigenvalues of H have already been derived in [3] by performing some definite rotational transformations of the variables (the momentum $\hat{P}_i$ and position coordinate $\hat{x}_i$), to the best of our knowledge, the unitary operator that can directly diagonalize H has not been studied in the literature. As one will see in our later discussion (Sec. II), the unitary operator is quite complicated because it engenders not only rotation but also squeezing transformations; the latter originates from changes in masses and frequencies and must be involved in searching for the unitary transformation. In Sec. III, by virtue of the unitary operator in coordinate representation we can very easily work out the density matrix $\rho(\mathbf{x},\mathbf{x}';\beta)$, $\mathbf{x}\equiv(x_1,x_2,x_3)$. Then in Sec. IV we use $\rho(\mathbf{x},\mathbf{x},\beta)$ to calculate the average of potential energy and kinetic energy of the triatomic linear molecule. Our conclusion is that although the Hamiltonian H involves three coupling coordinates, it actually is equivalent to the motions of two independent harmonic oscillators and one free particle, and we obtain $\langle(\text{potential energy})\rangle=\langle(\text{kinetic energy})\rangle-1/2\beta$.

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II. UNITARY OPERATOR U IN COORDINATE REPRESENTATION

Although the Hamiltonian H has no coupling term $\hat{x}_1\hat{x}_3$, fortunately we still find a unitary operator U that can diagonalize H. In coordinate respresentation U is expressed as

$$U=\left[\frac{2m_2m_3}{AB}\right]^{1/8}\int d^3\mathbf{x}\left|u\begin{bmatrix}x_1\\x_2\\x_3\end{bmatrix}\right\rangle\left\langle\begin{bmatrix}x_1\\x_2\\x_3\end{bmatrix}\right|, \tag{4}$$

$$\left|\begin{bmatrix}x_1\\x_2\\x_3\end{bmatrix}\right\rangle\equiv|x_1,\ x_2,\ x_3\rangle,$$

where

$$u=\begin{vmatrix} 1 & \frac{-1}{M}\left[\frac{2m_2}{A}\right]^{1/4}[(m_2+m_3)\cos\alpha+m_3\sin\alpha] & \frac{1}{M}\left[\frac{m_3}{B}\right]^{1/4}[(m_2+m_3)\sin\alpha-m_3\cos\alpha] \\ 1 & \frac{1}{M}\left[\frac{2m_2}{A}\right]^{1/4}(m_1\cos\alpha-m_3\sin\alpha) & -\frac{1}{M}\left[\frac{m_3}{B}\right]^{1/4}(m_1\sin\alpha+m_3\cos\alpha) \\ 1 & \frac{1}{M}\left[\frac{2m_2}{A}\right]^{1/4}[(m_1+m_2)\sin\alpha+m_1\cos\alpha] & \frac{1}{M}\left[\frac{m_3}{B}\right]^{1/4}[(m_1+m_2)\cos\alpha-m_1\sin\alpha] \end{vmatrix}, \tag{5}$$

$$\det u=(2m_2m_3/AB)^{1/4}, \tag{6}$$

$M=m_1+m_2+m_3$ is the total mass of the molecule, α satisfies the equation

$$(m_3^{-1}-m_1^{-1})\sin2\alpha=2m_2^{-1}\cos2\alpha, \tag{7}$$

and

$$\begin{aligned} A^{-1}&=\mu_1^{-1}\cos^2\alpha+\mu_2^{-1}\sin^2\alpha-m_2^{-1}\sin2\alpha, \\ B^{-1}&=\mu_1^{-1}\sin^2\alpha+\mu_2^{-1}\cos^2\alpha+m_2^{-1}\sin2\alpha, \\ \mu_1&=m_1m_2/(m_1+m_2),\quad \mu_2=m_2m_3/(m_2+m_3). \end{aligned} \tag{8}$$

$|x_i\rangle$ is the three-mode coordinate eigenstate. In the Fock space spanned by $|n_1n_2n_3\rangle$ (the eigenstate of H_0), $|x_i\rangle$ is expressed as

$$|x_i\rangle=\left[\frac{m_i\omega_i}{\pi\hbar}\right]^{1/4}\exp\left[-\frac{m_i\omega_i}{2\hbar}x_i^2+\left[\frac{2m_i\omega_i}{\hbar}\right]^{1/2}x_ia_i^\dagger-\tfrac{1}{2}a_i^{\dagger2}\right]|0\rangle_i$$

$$(\omega_1=\sqrt{k/m_1},\quad \omega_2=\sqrt{2k/m_2},\quad \omega_3=\sqrt{k/m_3}). \tag{10}$$

The factor $[2m_2m_3/(AB)]^{1/8}$ in Eq. (4) anticipates the unitarity of U. To see this, we use Eq. (6) to calculate

$$UU^\dagger=\left[\frac{2m_2m_3}{AB}\right]^{1/4}\int d^3\mathbf{x}\left|u\begin{bmatrix}x_1\\x_2\\x_3\end{bmatrix}\right\rangle\left\langle u\begin{bmatrix}x_1\\x_2\\x_3\end{bmatrix}\right|=1;$$

thus $U^\dagger=U^{-1}$. Using $\langle x_i|p_i\rangle=(2\pi\hbar)^{-1/2}\exp(ip_ix_i/\hbar)$, where $|p_i\rangle$ is the momentum eigenstate, we may set U in momentum representation,

$$U=\left[\frac{2m_2m_3}{AB}\right]^{1/8}\int d^3\mathbf{p}\left|\begin{bmatrix}p_1\\p_2\\p_3\end{bmatrix}\right\rangle\left\langle\tilde{u}\begin{bmatrix}p_1\\p_2\\p_3\end{bmatrix}\right|. \tag{11}$$

In order to know how $\hat{x}_i$ and $\hat{p}_i$ change under the U transformation we first calculate

$$u^{-1}=\begin{vmatrix} \frac{m_1}{M} & \frac{m_2}{M} & \frac{m_3}{M} \\ -\left[\frac{A}{2m_2}\right]^{1/4}\cos\alpha & \left[\frac{A}{2m_2}\right]^{1/4}(\cos\alpha-\sin\alpha) & \left[\frac{A}{2m_2}\right]^{1/4}\sin\alpha \\ \left[\frac{B}{m_3}\right]^{1/4}\sin\alpha & -\left[\frac{B}{m_3}\right]^{1/4}(\sin\alpha+\cos\alpha) & \left[\frac{B}{m_3}\right]^{1/4}\cos\alpha \end{vmatrix}. \tag{12}$$

Using the orthonormal relation $\langle x_i|x_i'\rangle=\delta(x_i-x_i')$ we can deduce

$$U\hat{x}_iU^{-1}=\det u\int d^3\mathbf{x}\left|u\left|\begin{matrix}x_1\\x_2\\x_3\end{matrix}\right\rangle\left\langle\begin{matrix}x_1\\x_2\\x_3\end{matrix}\right|\right|x_i'\int d^3\mathbf{x}'\left|\left|\begin{matrix}x_1'\\x_2'\\x_3'\end{matrix}\right\rangle\left\langle u\begin{matrix}x_1'\\x_2'\\x_3'\end{matrix}\right|\right|$$

$$=\det u\int d^3\mathbf{x}\left|u\left|\begin{matrix}x_1\\x_2\\x_3\end{matrix}\right\rangle\left\langle u\begin{matrix}x_1\\x_2\\x_3\end{matrix}\right|\right|x_i=\sum_{j=1}^{3}(u^{-1})_{ij}\hat{x}_j\ . \tag{13}$$

In a similar manner, in terms of the momentum representation of U we obtain

$$U\hat{P}_iU^{-1}=\det u\int d^3\mathbf{p}\left|\left|\begin{matrix}p_1\\p_2\\p_3\end{matrix}\right\rangle\left\langle\tilde{u}\begin{matrix}p_1\\p_2\\p_3\end{matrix}\right|\right|\hat{P}_i\int d^3\mathbf{p}'\left|\tilde{u}\left|\begin{matrix}p_1'\\p_2'\\p_3'\end{matrix}\right\rangle\left\langle\begin{matrix}p_1'\\p_2'\\p_3'\end{matrix}\right|\right|=\sum_{j=1}^{3}\tilde{u}_{ij}\hat{p}_j\ . \tag{14}$$

Comparing Eqs. (12) and (13) with (14), we see that the U operator causes not only rotation transformation but also squeezing transformation. For example, as the factor $(B/m_3)^{1/4}$ appears in $U\hat{x}_3U^{-1}$, its inverse $(m_3/B)^{1/4}$ appears in $U\hat{P}_3U^{-1}$, which means the squeezing [4] for the coordinate and its canonical conjugate momentum are mutual inverse. This squeezing originates from the change of masses and frequencies [see also Eq. (16)]. Combining the results (13) and (14), we can prove that H is diagonalized as

$$H=U\left[\frac{\omega_A}{\omega_2}\left[\frac{\hat{p}_2^2}{2m_2}+kx_2^2\right]+\frac{\omega_B}{\omega_3}\left[\frac{\hat{p}_3^2}{2m_3}+\frac{k}{2}x_3^2\right]+\frac{\hat{p}_1^2}{2M}\right]U^{-1}$$

$$=U\left[\left[\omega_A(a_2^\dagger a_2+\tfrac{1}{2})+\omega_B(a_3^\dagger a_3+\tfrac{1}{2})\right]\hbar+\frac{\hat{p}_1^2}{2M}\right]U^{-1}\ , \tag{15}$$

where

$$\omega_A=\sqrt{k/A}\ ,\quad \omega_B=\sqrt{k/B}\ ,\quad \omega_2=\sqrt{2k/m_2},\quad \omega_3=\sqrt{k/m_3}\ , \tag{16}$$

in fact, using (14), (16), and (5), as well as the relations

$$\frac{1}{A}\cos^2\alpha+\frac{1}{B}\sin^2\alpha=\frac{1}{\mu_1},\quad \frac{1}{A}\sin^2\alpha+\frac{1}{B}\cos^2\alpha=\frac{1}{\mu_2},\quad \sin\left[\frac{1}{A}-\frac{1}{B}\right]\sin2\alpha=-\frac{2}{m_2}\ , \tag{17}$$

which are deduced from Eqs. (7)–(9), and doing some lengthy but straightforward calculations, we obtain

$$U\left[\frac{\omega_A}{\omega_2}\frac{\hat{p}_2^2}{2m_2}+\frac{\omega_B}{\omega_3}\frac{\hat{p}_3^2}{2m_3}+\frac{\hat{p}_1^2}{2M}\right]U^{-1}=\sum_{i=1}^{3}\frac{\hat{p}_i^2}{2m_i}\ . \tag{18}$$

On the other hand, using (13) and (16) we have

$$U\left[\frac{\omega_A}{\omega_2}\hat{x}_2^2+\frac{\omega_B}{\omega_3}\frac{\hat{x}_3^2}{2}\right]U^{-1}=(\hat{x}_1-\hat{x}_2)^2+(\hat{x}_3-\hat{x}_2)^2\ ; \tag{19}$$

thus Eq. (15) is proved.

III. DENSITY MATRIX IN COORDINATE REPRESENTATION

The coordinate representation of U provides us with a convenient way to derive $\rho(\mathbf{x},\mathbf{x}',\beta)$. Since by use of Eq. (4) we have

$$\left\langle\begin{matrix}x_1\\x_2\\x_3\end{matrix}\right|U=\left[\frac{2m_2m_3}{AB}\right]^{1/8}\int d^3x'\delta\left[\begin{matrix}x_1\\x_2\\x_3\end{matrix}-u\begin{matrix}x_1'\\x_2'\\x_3'\end{matrix}\right]\left\langle\begin{matrix}x_1'\\x_2'\\x_3'\end{matrix}\right|=\left[\frac{AB}{2m_2m_3}\right]^{1/8}\langle y_1,y_2,y_3|\ , \tag{20}$$

where y_i are defined by

$$y_i=\sum_{j=1}^{3}(u^{-1})_{ij}x_j\ . \tag{21}$$

Therefore as a result of (15) and (20) we get

$$\rho(\mathbf{x},\mathbf{x}',\beta)=\langle x_1,x_2,x_3|e^{-\beta H}|x_1',x_2',x_3'\rangle$$

$$=\left[\frac{AB}{2m_2m_3}\right]^{1/4}\langle y_1,y_2,y_3|\exp\left\{-\beta\left[\hbar\omega_A(a_2^\dagger a_2+\tfrac{1}{2})+\hbar\omega_B(a_3^\dagger a_3+\tfrac{1}{2})+\frac{\hat{p}_1^2}{2M}\right]\right\}|y_1',y_2',y_3'\rangle\equiv\rho(\mathbf{y},\mathbf{y}',\beta)\ , \tag{22}$$

which shows that the calculation for the three coupled oscillators' density matrix now reduces to the simple calculation of two independent harmonic oscillators' density matrices and one free particle's density matrix. Because Feynman already gave the density matrices both for a harmonic oscillator with frequency ω_1 and mass m_1,

$$\langle x_1|\exp[-\beta\hbar\omega_1(a_1^\dagger a_1+\tfrac{1}{2})]|x_1'\rangle=\left[\frac{m_1\omega_1}{2\pi\hbar\sinh(2f_1)}\right]^{1/2}\exp\left\{-\frac{m_1\omega_1}{2\hbar\sinh(2f_1)}[(x_1^2+x_1'^2)\cosh(2f_1)-2x_1x_1']\right\},$$

$$f_1\equiv\frac{\hbar\omega_1}{2}\beta\ , \tag{23}$$

and for a free particle with mass M,

$$\langle x_1|\exp\left[-\beta\frac{\hat{p}_1^2}{2M}\right]|x_1'\rangle=\left[\frac{M}{2\pi\hbar^2\beta}\right]^{1/2}\exp\left[-\left[\frac{M}{2\hbar^2\beta}\right](x_1-x_1')^2\right]\ , \tag{24}$$

we can immediately write down

$$\rho(\mathbf{y},\mathbf{y}',\beta)=\rho_1\rho_2\rho_3\ , \tag{25}$$

$$\rho_1=\langle y_1|\exp\left[-\beta\frac{\mathbf{p}_1^2}{2M}\right]|y_1'\rangle=\left[\frac{M}{2\pi\hbar^2\beta}\right]^{1/2}\exp\left[-\frac{M}{2\hbar^2\beta}(y_1-y_1')^2\right]\ , \tag{26}$$

$$\rho_2=\langle y_2|\exp[-\beta\hbar\omega_A(a_2^\dagger a_2+\tfrac{1}{2})]|y_2'\rangle\left[\frac{A}{2m_2}\right]^{1/4}$$

$$=\langle y_2|\exp[-\beta_2\hbar\omega_2(a_2^\dagger a_2+\tfrac{1}{2})]|y_2'\rangle\left[\frac{A}{2m_2}\right]^{1/4}$$

$$=\left[\frac{m_2\omega_2}{2\pi\hbar\sinh(2f_2)}\right]^{1/2}\left[\frac{A}{2m_2}\right]^{1/4}\exp\left\{-\frac{m_2\omega_2}{2\hbar\sinh(2f_2)}[(y_2^2+y_2'^2)\cosh(2f_2)-2y_2y_2']\right\}$$

$$=\left[\frac{A\omega_A}{2\pi\hbar\sinh(2f_2)}\right]^{1/2}\exp\left\{-\frac{A\omega_A}{2\hbar\sinh(2f_2)}[(\bar{y}_2^2+\bar{y}_2'^2)\cosh(2f_2)-2\bar{y}_2\bar{y}_2']\right\}, \tag{27}$$

where

$$f_2=\frac{\hbar\omega_2}{2}\beta_2,\quad \beta_2=\beta\frac{\omega_A}{\omega_2},\quad \bar{y}_2=\left[\frac{2m_2}{A}\right]^{1/4}y_2\ , \tag{28}$$

and

$$\rho_3=\langle y_3|\exp[-\beta\hbar\omega_B(a_3^\dagger a_3+\tfrac{1}{2})]|y_3'\rangle\left[\frac{B}{m_3}\right]^{1/4}$$

$$=\left[\frac{B\omega_B}{2\pi\hbar\sinh(2f_3)}\right]^{1/2}\exp\left\{-\frac{B\omega_B}{2\hbar\sinh(2f_3)}[(\bar{y}_3^2+\bar{y}_3'^2)\cosh(2f_3)-2\bar{y}_3\bar{y}_3']\right\}, \tag{29}$$

where

$$f_3=\frac{\hbar\omega_3}{2}\beta_3,\quad \beta_3=\beta\frac{\omega_B}{\omega_3},\quad \bar{y}_3=\left[\frac{m_3}{B}\right]^{1/4}y_3\ . \tag{30}$$

IV. AVERAGE OF POTENTIAL ENERGY AND KINETIC ENERGY

Now we can analyze the average of potential energy and kinetic energy of the molecule. Using Eqs. (21)–(30) we first evaluate the average of $\langle \hat{x}_i^2 \rangle$,

$$\langle \hat{x}_i^2 \rangle = \frac{\int d^3\mathbf{x}\, x_i^2 \rho(\mathbf{x},\mathbf{x},\beta)}{\int d^3\mathbf{x}\, \rho(\mathbf{x},\mathbf{x},\beta)} = \frac{\int d^3\mathbf{y} \left[\sum_{j=1}^{3} u_{ij} y_j \right]^2 \rho(\mathbf{y},\mathbf{y},\beta)}{\int d^3\mathbf{y}\, \rho(\mathbf{y},\mathbf{y},\beta)} . \tag{31}$$

Because of

$$\int d^3\mathbf{y}\, y_i y_j \rho(\mathbf{y},\mathbf{y},\beta) = 0 \quad (i \neq j) , \tag{32}$$

Eq. (31) thus becomes

$$\langle \hat{x}_i^2 \rangle = \sum_{j=1}^{3} u_{ij}^2 g_j , \tag{33}$$

where

$$g_j \equiv \frac{\int dy_j \rho_j(y_j,y_j,\beta) y_j^2}{\int dy_j \rho_j(y_j,y_j,\beta)} ; \qquad g_2 = \frac{\hbar}{2m_2\omega_2 \tanh f_2}, \quad g_3 = \frac{\hbar}{2m_3\omega_3 \tanh f_3} . \tag{34}$$

Next we calculate the average of the coupling operators. Using (21) we have

$$\langle \hat{x}_i \hat{x}_j \rangle = \sum_{k=1}^{3} u_{ij} u_{jk} g_k . \tag{35}$$

Thus the average of potential energy is

$$\langle v \rangle \equiv \tfrac{1}{2} k \langle (\hat{x}_1 - \hat{x}_2)^2 + (\hat{x}_2 - \hat{x}_3)^2 \rangle = \tfrac{1}{2} k \left\{ [(u_{12}-u_{22})^2 + (u_{22}-u_{32})^2] g_2 + [(u_{13}-u_{23})^2 + (u_{23}-u_{33})^2] g_3 \right\} . \tag{36}$$

Substituting (5) and (34) into Eq. (36) we have

$$\langle v \rangle = (\omega_A \coth f_2 + \omega_B \coth f_3)\hbar/4 . \tag{37}$$

In order to derive the average of kinetic energy we transform the density matrix into a momentum representation. With the aid of (15) and (11) we have

$$\rho(\mathbf{p},\mathbf{p}',\beta) = \left[\frac{2m_2 m_3}{AB} \right]^{1/4} \langle \mathcal{P}_1,\mathcal{P}_2,\mathcal{P}_3 | \exp\left\{ -\beta \left[\hbar\omega_A (a_2^\dagger a_2 + \tfrac{1}{2}) + \hbar\omega_B (a_3^\dagger a_3 + \tfrac{1}{2}) + \frac{\hat{p}_1^2}{2M} \right] \right\} | \mathcal{P}_1',\mathcal{P}_2',\mathcal{P}_3' \rangle , \tag{38}$$

where

$$\mathcal{P}_i = \sum_{j=1}^{3} \tilde{u}_{ij} p_j . \tag{39}$$

$\rho(\mathbf{p},\mathbf{p}',\beta)$ can also be decomposed as $\rho(\mathbf{p},\mathbf{p}',\beta) = \rho_1' \rho_2' \rho_3'$,

$$\rho_1' = \langle \mathcal{P}_1 | \exp\left[-\beta \frac{\hat{\rho}_1^2}{2M} \right] | \mathcal{P}_1' \rangle = \exp\left[-\frac{\beta \mathcal{P}_1^2}{2M} \right] \delta(\mathcal{P}_1 - \mathcal{P}_1') \tag{40}$$

$$\rho_2' = [2\pi\hbar A \omega_A \sinh(2f_2)]^{-1/2} \exp\left\{ -\frac{1}{2m_2\omega_2\hbar \sinh(2f_2)} [(\mathcal{P}_2^2 + \mathcal{P}_2'^2)\cosh(2f_2) - 2\mathcal{P}_2\mathcal{P}_2'] \right\} , \tag{41}$$

$$\rho_3' = [2\pi\hbar B \omega_B \sinh(2f_3)]^{-1/2} \exp\left\{ -\frac{1}{2m_3\omega_3\hbar \sinh(2f_3)} [(\mathcal{P}_3^2 + \mathcal{P}_3'^2 \cosh(2f_3) - 2\mathcal{P}_3\mathcal{P}_3'] \right\} . \tag{42}$$

Similar in spirit as deriving Eq. (37), we can obtain the average of kinetic energy

$$\left\langle \sum_{i=1}^{3} \frac{\hat{p}_i^2}{2m_i} \right\rangle = \frac{1}{2\beta} + \frac{\hbar}{4} [\omega_A \coth(f_2) + \omega_B \coth(f_3)] . \tag{43}$$

Comparing (37) and (43) we have the relation

$$\langle (\text{potential energy}) \rangle = \langle (\text{kinetic energy}) \rangle - \frac{1}{2\beta} . \tag{44}$$

This is in accord with Eq. (15), which states that the Hamiltonian is unitary equivalent to that of two independent harmonic oscillators and a free particle.

In summary, we have found the unitary operator for diagonalizing the Hamiltonian of a triatomic linear molecule and we have derived the corresponding density matrix with which the average of distribution of energy of the molecule is calculated.

[1] R. P. Feynman, *Statistical Mechanics* (Benjamin, New York, 1972).

[2] K. H. Yeon *et al.*, Phys. Rev. A **38**, 6224 (1988).

[3] S. Flügge, *Practical Quantum Mechanics* II (Springer-Verlag, Berlin, 1974), p. 41.

[4] Fan Hong-yi, Phys. Rev. A **42**, 4377 (1990); **47**, 2379 (1993).

[5] See, e.g., B. L. Schumaker, Phys. Rep. **135**, 317 (1985); D. F. Walls, Nature **306**, 141 (1983).