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Abstract

Full Text

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PHYSICS

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VIBRATIONAL RELAXATION OF OSCILLATORS WITH CLOSE FREQUENCIES

(Presented by Academician V. N. Kondrat' ev, 18 VII 1968)

1. The problem of vibrational relaxation in a system of harmonic oscillators is relevant to many kinetic processes. As an example one may cite the exchange of vibrational and translational energy in a diatomic gas, intramolecular redistribution of energy induced by collisions, etc. The derivation of equations for the mean values of microscopic quantities (for example, the mean vibrational energy E_{vib}) is, as a rule, based on investigation of the system of equations for the populations of individual states. The transition probabilities entering this system either remain free parameters or are calculated in first order of perturbation theory with respect to the interaction inducing relaxation. Violation of the conditions for applicability of perturbation theory most often arises in those cases when the collisions are nonadiabatic in character, i.e., when the Massey parameter $\xi = \Delta E/\hbar a v$ is small ([1,2]). Here ΔE denotes the energy transferred by partners with vibrational degrees of freedom into translational ones, $1/a$ is the radius of action of the intermolecular forces, and v is the velocity of the partners. Going beyond perturbation theory without introducing indefinite parameters proves possible in practice in two cases: either for a diffusion mechanism of relaxation (the condition $\xi \ll 1$ is ensured by the small ratio of the reduced mass of the partners μ to the reduced mass M of the relaxing molecule) ([3]), or for relaxation of a system of identical oscillators (the condition $\xi \ll 1$ is satisfied as a result of exact resonance $\Delta E = 0$) ([4]).

In the present work the case of exchange of vibrational energy of diatomic molecules AB and CD in collisions is considered. No conditions are imposed on the Massey parameter ξ or on the intensity of the interaction; however, the molecules are modeled by harmonic oscillators with close frequencies. This last assumption makes it possible to single out the case in which exchange of vibrational energy between AB and CD occurs faster than the conversion of the vibrational energy of each molecule into translational energy, and thus makes it possible to consider only this stage of relaxation. The derivation of a closed relaxation equation for the mean vibrational energy proves possible owing to

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the observed analogy between beats of oscillators with a time-dependent coupling and the rotation of a magnetic moment in a variable field. The principal characteristics of the solution of the latter problem are known sufficiently well ([5]).

2. Let us consider the collision of two diatomic molecules AB and CD, modeled by harmonic oscillators with frequencies ω_a and ω_b. We write the potential of interaction between the molecules in the form of an expansion in the deviations of the internuclear distances r_a and r_b from the equilibrium positions $r_{a,c}$ and $r_{b,c}$, putting $x_a = r_a - r_{a,c}$, $x_b = r_b - r_{b,c}$,

$$V(R, x_a, x_b) = V_0(R) + V_a x_a + V_b x_b + \frac{1}{2} V_{aa} x_a^2 + V_{ab} x_a x_b + \frac{1}{2} V_{bb} x_a^2, \quad (1)$$

where $V_0, V_{aa}, V_{ab}, V_{bb}$ are the expansion coefficients of the interaction $V(R, x_a, x_b)$ depending on the intermolecular distance R.

The relative motion of the molecules is assumed to be classical; therefore by R is meant some function $R(t)$, to which the trajectory of the relative motion corresponds. As follows from the selection rules for matrix elements of the coordinate of a harmonic oscillator, in expansion (1) the linear terms are responsible for one-quantum transitions only in one partner. By assumption, such transitions are ineffective in relaxation, since the collisions are adiabatic in character with respect to these transitions: the vibrational frequencies ω_a and ω_b are assumed to be large in comparison with the inverse collision time τ_0. Therefore the probabilities of one-quantum transitions are proportional to $\exp(-\omega_a \tau_0)$ and $\exp(-\omega_b \tau_0)$ and are negligibly small, and the linear terms in (1) may be omitted. The terms quadratic in x_a and x_b give two-quantum transitions, as well as a shift of the energy levels during a collision. Owing to the adiabaticity condition, two-quantum transitions are neglected; however, corrections to the energy must be retained. Finally, the bilinear term $x_a x_b$ causes simultaneous one-quantum transitions in AB and CD. Among these, transitions are possible in which the energy changes by $\hbar(\omega_a + \omega_b)$ (simultaneous excitation or deactivation) and by $\hbar(\omega_a - \omega_b)$ (quasiresonant energy transfer). Of these, only the latter are taken into account, for which the characteristic nonadiabaticity parameter $\xi = |\omega_a - \omega_b|/\alpha v$, generally speaking, is not large. Thus, we take into account only transitions between the group of energy levels of the two oscillators that would be degenerate in the case of equality of the frequencies ω_a and ω_b.

Let us represent the wave function of the colliding oscillators in the form of the expansion

$$\Phi(x_a, x_b, t) = \sum_{n,m} a_{n,m}(t) \varphi_n^a(x_a) \varphi_m^b(x_b), \quad (2)$$

where the summation extends over those values of the indices n and m which correspond to the above-mentioned group of levels, and φ_n^a and φ_m^b denote the

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functions of the isolated oscillators. Substituting (2) into the nonstationary Schrödinger equation for the system under consideration, we obtain equations for the coefficients a_{nm}:

$$i\hbar\dot{a}_{nm} = V_{ab}y_a y_b\sqrt{n+1}\sqrt{m}\,a_{n+1,m-1}+\left[V_{aa}y_a^2\left(n+\frac{1}{2}\right)+\left(n+\frac{1}{2}\right)\hbar\omega_a+\left(m+\frac{1}{2}\right)\hbar\omega_b\right]a_{nm}+V_{ab}y_a y_b\sqrt{n}\sqrt{m} \tag{3}$$

where the notation has been introduced

$$y_a = (\hbar/2M_{AB}\omega_a)^{1/2}, \qquad y_b = (\hbar/2M_{CD}\omega_b)^{1/2}. \tag{4}$$

Introducing a new numbering of the levels and new amplitudes $C_M^{(N)}$, which take into account the common displacement of the levels during a collision and are defined by the relations

$$n+m = 2N, \qquad n-m = 2M,$$

$$a_{nm} = a_{N-M,N+M} = C_M^{(N)}\exp\left[-\frac{i}{\hbar}\left(N+\frac{1}{2}\right)\int^t \Psi\,dt\right], \tag{5}$$

$$\Psi = V_{aa}y_a^2 + V_{bb}y_b^2 + \hbar\omega_a + \hbar\omega_b,$$

we obtain a system of equations for $C_M^{(N)}$, which contains the effective Hamiltonian H,

$$i\hbar\dot{C}_M^{(N)} = \sum_{M'} H_{MM'}(t)C_{M'}^{(N)}, \qquad \mathbf{H} = \mathbf{L}\mathbf{B}(t). \tag{6}$$

Here $\mathbf{L}$ denotes the angular-momentum operator, the eigenvalue of whose square is equal to $\hbar^2 N(N+1)$, and $\mathbf{B}(t)$ is a time-dependent vector.

with components

$$\begin{gathered} B_x = f(t) = 2V_{ab}(t)y_a y_b, \\ B_y = 0, \\ B_z = \varphi(t) = \left(V_{aa}y_a^2 - V_{bb}y_b^2 + \hbar\Delta\omega\right), \\ \Delta\omega = \omega_a - \omega_b. \end{gathered} \tag{7}$$

The indices M are now interpreted as the magnetic quantum numbers of the vector $\mathbf{L}$ with respect to the z axis, and $C_M^{(N)}$ as the amplitudes of the corresponding states. The z axis is distinguished here by the fact that both before

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and after the collision there remains one component of the vector $\mathbf{B}$ different from zero ($B_z = \hbar(\omega_a - \omega_b)$).

Let us consider the change in the mean energy of a system of two oscillators in one collision,

$$\Delta E = \sum_{n,m} [\hbar\omega_a(n+1/2) + \hbar\omega_b(m+1/2)]\left[|a^+_{nm}|^2 - |a^-_{nm}|^2\right] = \hbar\Delta\omega\left(\bar{L}^+_z - \bar{L}^-_z\right), \tag{8}$$

where the signs $-$ and $+$ indicate that the corresponding quantities are taken before and after the collision. It is seen that ΔE is determined by the change in the projection $\bar{L}_z$ as a result of the collision; therefore it is desirable to obtain an equation describing the time variation of $\bar{L}_z$. The mean value of each component of the vector $\mathbf{L}$ satisfies equations obtained by direct averaging of the equation for the operator L, written in the Heisenberg representation:

$$\dot{\bar{\mathbf{L}}} = [\mathbf{B}(t)\bar{\mathbf{L}}]. \tag{9}$$

In contrast to system (6), consisting of $2N+1$ equations, system (9) contains 3 equations for the mean projections of the vector $\mathbf{L}$. A further simplification consists in reducing the 3 equations for the real quantities $\bar{L}_x, \bar{L}_y, \bar{L}_z$ to 2 equations for complex quantities.

3. Let us introduce a two-component matrix ρ, written in terms of the Pauli matrices σ_i and the projections $\bar{L}_x, \bar{L}_y, \bar{L}_z$, putting, for normalization, $x = \bar{L}_x/N,\ y = \bar{L}_y/N'$ and $z = \bar{L}_z/N$:

$$\rho = 1/2 + x\sigma_x + y\sigma_y + z\sigma_z. \tag{10}$$

System (9) is equivalent to an equation for the density matrix ρ, whose evolution is described by the Hamiltonian

$$H_{\text{eff}} = \begin{pmatrix} B_z(t) & B_x + iB_y \\ B_x - iB_y & -B_z(t) \end{pmatrix}, \tag{11}$$

and the mean instantaneous value $\bar{L}_z$ is given by the relation $\bar{L}_z = z(t)N$. The matrices ρ^+ and ρ are related by

$$\rho^+ = S\rho^- S^{-1}, \tag{12}$$

where S is the scattering matrix for the problem with two states described by Hamiltonian (11). Thus, to calculate ρ^+ one may use known results from the theory of nonadiabatic transitions for a two-term system.

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The study of $z(t)$ over a time including many collisions is substantially simplified because the diagonal elements of ρ vanish upon averaging, which is due to the completely uncorrelated distribution of the phases of the colliding oscillators. This means that equation (9) is solved for each subsequent collision with the initial conditions $x = 0$ and $y = 0$. As for z, from (12) we obtain:

$$z^{+} = [S_{11}S_{11}^{*} + S_{12}S_{12}^{*} - S_{22}S_{22}^{*} - S_{21}S_{21}^{*}] + z^{-}\frac{1}{2}\left[S_{11}S_{11}^{*} - S_{12}S_{12}^{*} + S_{22}S_{22}^{*} - S_{21}S_{21}^{*}\right]. \tag{13}$$

Averaging this relation over all parameters of one collision, we rewrite it in the form

$$z_k = \gamma + Az_{k-1}, \tag{14}$$

where γ and A denote the mean values of the first and second coefficients in (13), and z_k is the value of the parameter z after the k-th collision. The solution of this recurrence relation gives

$$z_k = A^k\left(z_0 - \frac{\gamma}{1-A}\right) + \frac{\gamma}{1-A}. \tag{15}$$

The quantity $z(t)$ at a given time t is obtained by summing (15) over all possible realizations of k successive collisions. Using the known expression P_k for the probability that k collisions occur in time t, we have

$$z(t) = \sum_k z_k P_k(t) = \sum_k z_k \frac{(zt)^k}{k!}\exp(-zt) =$$

$$= \left(z_0 - \frac{\gamma}{1-A}\right)\exp[-z(t)(1-A)] + \frac{\gamma}{1-A}. \tag{16}$$

From the form of this relation it is clear that the last term must be assigned the meaning of the asymptotic equilibrium value z_∞. As for $1 - A$, from (13) and from the meaning of the off-diagonal elements of the scattering matrix it follows that

$$1 - A = \frac{1}{2}\left[\langle S_{12}S_{12}^{*}\rangle + \langle S_{21}S_{21}^{*}\rangle\right] = \frac{1}{2}\left[P_{12} + P_{21}\right], \tag{17}$$

where P_{12} and P_{21} are the averaged transition probabilities in one collision for the Hamiltonian H_{eff}. Rewritten in the variables of energy ΔE, number of collisions z, and mean transition probabilities P_{12} and P_{21}, equation (16) takes the form

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$$\Delta E(t) = (\Delta E_0 - \Delta E_\infty) \exp[-zt(P_{12} + P_{21})/2] + \Delta E_\infty. \tag{18}$$

This relation describes the equalization of the mean vibrational energies of two diatomic components of a gas mixture due to the partial conversion of the vibrational energy of the partners into their kinetic energy at each collision event, if at the initial moment the difference of the vibrational energies was equal to ΔE_0.

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Note: Figure translations are in progress. See original paper for figures.

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