I. PERTURBATION THEORY FOR HARMONIC POTENTIAL WITH CUBIC ANHARMONICITY

Equations

$$\vec{\nabla} W = \lambda \vec{\nabla} H, \quad H = E \tag{1}$$

are solved here by perturbation theory, for specific functions $H = H^{(0)} + H^{(1)}\delta$, $W = W^{(0)} + W^{(1)}\delta$, where

$$H^{(0)} = \frac{1}{2}\sum_i x_i^2, \quad H^{(1)} = \frac{1}{6}\sum_{i,j,k} f_{ijk} x_i x_j x_k, \tag{2}$$

$$W^{(0)} = \frac{1}{2}\sum_i \alpha_i \bar{x}_i^2, \quad W^{(1)} = \frac{1}{6}\sum_{i,j,k} \beta_{ijk} \bar{x}_i \bar{x}_j \bar{x}_k. \tag{3}$$

Here, x_i are variables collecting coordinates and momenta, $\bar{x}_i = x_i - X_i$, X_i are corresponding displacements, and δ is a perturbation parameter. Eq. (1) is equivalent to

$$\alpha_i \bar{x}_i + \frac{\delta}{2}\sum_{j,k} \beta_{ijk} \bar{x}_j \bar{x}_k = \lambda \left(x_i + \frac{\delta}{2}\sum_{j,k} f_{ijk} x_j x_k \right), \tag{4}$$

$$\frac{1}{2}\sum_i x_i^2 + \frac{1}{6}\sum_{i,j,k} f_{ijk} x_i x_j x_k = E. \tag{5}$$

Unknown variables are x_i $(i = 1, ..., M)$ and Lagrange multiplier λ. They are searched in the form

$$x_i = x_i^{(0)} + x_i^{(1)}\delta + o(\delta), \tag{6}$$

$$\lambda = \lambda^{(0)} + \lambda^{(1)}\delta + o(\delta). \tag{7}$$

In zero order approximation ($\delta = 0$), Eq. (4), (5) are

$$\alpha_i \bar{x}_i^{(0)} = \lambda^{(0)} x_i^{(0)}, \quad (i = 1, ..., M)$$

$$\frac{1}{2}\sum_i x_i^{(0)2} = E, \tag{8}$$

where $\bar{x}_i^{(0)} = x_i^{(0)} - X_i$.

In the first order in δ, Eq. (4), (5) are

$$\alpha_i x_i^{(1)} + \frac{1}{2}\sum_{j,k}\beta_{ijk}\bar{x}_j\bar{x}_k = \lambda^{(0)}\left(x_i^{(1)} + \frac{1}{2}\sum_{j,k} f_{ijk}x_j^{(0)}x_k^{(0)}\right) + \lambda^{(1)}x_i^{(0)}, \quad (i = 1, ..., M) \quad (9)$$

$$\sum_i x_i^{(0)}x_i^{(1)} + \frac{1}{6}\sum_{i,j,k} f_{ijk}x_i^{(0)}x_j^{(0)}x_k^{(0)} = 0. \quad (10)$$

II. FINDING THE MINIMUM OF W IN HARMONIC APPROXIMATION

Let us rearrange variables (x_i, X_i, α_i) $(i = 1, 2, ..., M)$ so that α_1 the minimal among the set of all α_i. Let us define a function

$$F(\lambda) = \frac{1}{2}\sum_{i=1}^{M}\left(\frac{\alpha_i}{\alpha_i - \lambda}\right)^2 X_i^2. \quad (11)$$

We consider the function $F(\lambda)$ as a function defined on the interval $(-\infty, \alpha_1]$ where it monotonously increases from 0 to ∞ or to $E_1 = \frac{1}{2}\sum_{i=2}^{M}\left(\frac{\alpha_i}{\alpha_i-\alpha_1}\right)^2 X_i^2$ in a special case of $X_1 = 0$. According to results given in Appendix, finding the minimum is as follows. Let us consider separately two cases: (1) $X_1 \neq 0$ or $X_1 = 0$ and $E \leq E_1$, (2) a specific case when $X_1 = 0$ and $E > E_1$.

(1) Firstly, locate the point $\lambda_* = F^{-1}(E)$ where F^{-1} is a function inverse to F, i.e. solve the equation $F(\lambda_*) = E$. Since $F(\lambda)$ is a monotonous function, the point λ_* is defined uniquely. Coordinates of the minimum are expressed through λ_* as

$$x_i = \frac{\alpha_i}{\alpha_i - \lambda_*}X_i, \quad (12)$$

and minimum of the function W

$$W_{\min} = \frac{1}{2}\sum_{i=1}^{M}\alpha_i\left(\frac{\lambda_*}{\alpha_i - \lambda_*}\right)^2 X_i^2. \quad (13)$$

(2) Coordinates of the minimum are

$$x_i = \begin{cases} \pm\left[2\left(E - E_1\right)\right]^{1/2}, & i = 1 \\ \frac{\alpha_i}{\alpha_i-\alpha_1}X_i, & i \neq 1 \end{cases} \quad (14)$$

and minimum of the function W is

$$W_{\min} = \alpha_1 E - \frac{\alpha_1}{2} \sum_{i=2}^{M} \frac{\alpha_i X_i^2}{\alpha_i - \alpha_1}. \tag{15}$$

There are two symmetrical minima, in contrast to the case (1) when the global minimum is single.

III. THE FIRST CORRECTION TO THE HARMONIC APPROXIMATION

A. Case (1)

Unperturbed coordinates and the Lagrange multiplier are

$$x_i^{(0)} = \frac{\alpha_i}{\alpha_i - \lambda_*} X_i, \quad \lambda^{(0)} = \lambda_*, \tag{16}$$

where λ_* is the minimal root of an equation $\frac{1}{2}\sum_i \left(\frac{\alpha_i}{\alpha_i - \lambda}\right)^2 X_i^2 = E$.

Now, let us find $x_i^{(1)}$ and $\lambda^{(1)}$ using Eq. (9) and (10). It follows from (9) that

$$x_i^{(1)} = \frac{1}{\alpha_i - \lambda_*} \left[\frac{1}{2} \sum_{j,k} \left(\lambda_* f_{ijk} x_j^{(0)} x_k^{(0)} - \beta_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} \right) + \lambda^{(1)} x_i^{(0)} \right], \tag{17}$$

or alternatively after substitution of (16) into (17)

$$x_i^{(1)} = \frac{\lambda_*}{2(\alpha_i - \lambda_*)} \sum_{j,k} \frac{X_j X_k}{(\alpha_j - \lambda_*)(\alpha_k - \lambda_*)} \left(f_{ijk} \alpha_j \alpha_k - \beta_{ijk} \lambda_* \right) + \frac{\alpha_i}{(\alpha_i - \lambda_*)^2} X_i \lambda^{(1)}. \tag{18}$$

Inserting (17) into (10), we find

$$\lambda^{(1)} = \frac{1}{6} \left(\sum_i \frac{x_i^{(0)2}}{\alpha_i - \lambda_*} \right)^{-1} \sum_{i,j,k} \frac{x_i^{(0)}}{\alpha_i - \lambda_*} \left[3\beta_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} - 2(\lambda_* + \alpha_i) f_{ijk} x_j^{(0)} x_k^{(0)} \right], \tag{19}$$

or alternatively, after substitution of $x_i^{(0)}$ and $x_i^{(1)}$ into (19)

$$\lambda^{(1)} = \left(\sum_i \frac{\alpha_i^2 X_i^2}{(\alpha_i - \lambda_*)^3} \right)^{-1} \tag{20}$$

$$\times \sum_{i,j,k} \left(\frac{\lambda_*^2}{2} \beta_{ijk} - \frac{2\lambda_* + \alpha_i}{6} \alpha_i \alpha_j f_{ijk} \right) \frac{\alpha_i X_i X_j X_k}{(\alpha_i - \lambda_*)^2 (\alpha_j - \lambda_*)(\alpha_k - \lambda_*)}. \tag{21}$$

We can in principle find an expression of $x_i^{(1)}$ through λ_* by substituting (19) or (20) into (17) or (18). Finally, expanding minimum of the function W into power series $W_{\min} = W_{\min}^{(0)} + W_{\min}^{(1)} \delta + O(\delta^2)$, we find that $W_{\min}^{(0)}$ is given by a formula (13), and

$$W_{\min}^{(1)} = \sum_i \alpha_i \bar{x}_i^{(0)} x_i^{(1)} + \frac{1}{6} \sum_{i,j,k} \beta_{ijk} \bar{x}_i^{(0)} \bar{x}_j^{(0)} \bar{x}_k^{(0)}. \tag{22}$$

B. Case (2)

Unperturbed coordinates and the Lagrange multiplier are

$$x_i^{(0)} = \begin{cases} \pm\left[2\left(E - E_1\right)\right]^{1/2}, & i = 1 \\ \frac{\alpha_i}{\alpha_i - \alpha_1} X_i, & i \neq 1 \end{cases}, \quad \lambda^{(0)} = \alpha_1. \tag{23}$$

For this case, it follows from (9) for $i = 1$ that

$$\lambda^{(1)} = \frac{1}{2x_1^{(0)}} \sum_{j,k} \left(\beta_{1jk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} - \alpha_1 f_{1jk} x_j^{(0)} x_k^{(0)} \right), \tag{24}$$

and from (9) for $i \neq 1$ that

$$x_i^{(1)} = \frac{1}{\alpha_i - \alpha_1} \left[\frac{1}{2} \sum_{j,k} \left(\alpha_1 f_{ijk} x_j^{(0)} x_k^{(0)} - \beta_{ijk} \bar{x}_j^{(0)} \bar{x}_k^{(0)} \right) + \lambda^{(1)} x_i^{(0)} \right], \quad i \neq 1. \tag{25}$$

Finally, the remaining unknown variable $x_1^{(1)}$ can be found by substituting (25) into (10),

$$x_1^{(1)} = \frac{1}{x_i^{(0)}} \left[\sum_{i \neq 1} \bar{x}_i^{(0)} x_i^{(1)} + \frac{1}{6} \sum_{i,j,k} f_{ijk} x_i^{(0)} x_j^{(0)} x_k^{(0)} \right]. \tag{26}$$

The second case differs from the first case in the order in which the unknown variables are found. The variable $\lambda^{(1)}$ is determined before the variable $x_1^{(1)}$. It is similar to the zero-order calculations of $\lambda^{(0)}$ and $x_1^{(0)}$: for the case (1) we find firstly an expression of all x_i through λ, and then find λ, but for the case (2) we find firstly λ, and finally x_1.

In zero order (harmonic approximation), there are two points of minimum differing by a sign of x_1, see Eq. (14) with the same $W_{\min}$ given by (15). In the first order approximation, $W_{\min}$ is given by (22), and it is no longer the same for the two points, corresponding to different signs in Eq. (14). So, a true minimum is the one for which (22) is smaller.