Harmonic oscillator approximation

Equations to be solved

We are finding a minimum of the function

$$W(P_1, P_2, ..., P_N, Q_1, Q_2, ..., Q_N) = -\tfrac{1}{2}\ln(\text{Wigner function})$$

under the restriction

$$H(P_1, P_2, ..., P_N, Q_1, Q_2, ..., Q_N) = E$$

where

$$\begin{aligned} H &= \frac{1}{2}\sum_{i=1}^{N}\left[\frac{P_i^2}{m_i} + m_i\omega_i^{(0)2}\left(Q_i - Q_i^{(0)}\right)^2\right] \\ W &= \frac{1}{2}\sum_{i=1}^{N}\left[\frac{P_i^2}{m_i\omega_i^{(1)}} + m_i\omega_i^{(1)}\left(Q_i - Q_i^{(1)}\right)^2\right] \end{aligned}. \tag{1}$$

Scaling

To decrease number of parameters, let us perform scaling

$$\begin{aligned} q_i &= \sqrt{m_i}\omega_i^{(0)}\left(Q_i - Q_i^{(0)}\right) \\ q_i^{(1)} &= \sqrt{m_i}\omega_i^{(0)}\left(Q_i^{(1)} - Q_i^{(0)}\right) \\ p_i &= P_i / \sqrt{m_i} \\ \omega_i &= \omega_i^{(0)2} / \omega_i^{(1)} \end{aligned} \tag{2}$$

and rewrite (1) as

$$H = \frac{1}{2}\sum_{i=1}^{N}\left(p_i^2 + q_i^2\right)$$
$$W = \frac{1}{2}\sum_{i=1}^{N}\left[\frac{p_i^2}{\omega_i^{(1)}} + \frac{\left(q_i - q_i^{(1)}\right)^2}{\omega_i}\right]. \qquad (3)$$

Points of extremum

Extremum points are found from the equation $\vec{\nabla}W = \lambda\vec{\nabla}H$ that is equivalent to a set of equations

$$\begin{cases} \dfrac{p_i}{\omega_i^{(1)}} = \lambda p_i \\ \dfrac{q_i - q_i^{(1)}}{\omega_i} = \lambda q_i \end{cases} \quad (i = 1,2,...,N). \qquad (4)$$

The second equation of (4) is equivalent to

$$q_i = \frac{1}{1-\lambda\omega_i}q_i^{(1)}. \qquad (4a)$$

Note that $\frac{dW}{dE} = \sum_{i=1}^{N}\left(\frac{\partial W}{\partial p_i}\frac{dp_i}{dE} + \frac{\partial W}{\partial q_i}\frac{dq_i}{dE}\right) = \lambda\sum_{i=1}^{N}\left(\frac{\partial H}{\partial p_i}\frac{dp_i}{dE} + \frac{\partial H}{\partial q_i}\frac{dq_i}{dE}\right) = \lambda\frac{dH}{dE} = \lambda$.

Two kinds of extrema

If $p_1 \neq 0$ then

$$\lambda = 1/\omega_1^{(1)},$$
$$q_i = \frac{1}{1-\omega_i/\omega_1^{(1)}}q_i^{(1)} \quad (i = 1,2,...,N). \qquad (5)$$

Coordinates (5) correspond to real momentum p_1 if $\frac{1}{2}\sum_{i=1}^{N}q_i^2 \le E$.

If the coordinates are enumerated so that $\omega_1^{(1)} \geq \omega_2^{(1)} \geq ... \geq \omega_N^{(1)}$ then no other similar extremum for $p_k \neq 0$ where $k = 2,3,...,N$ can be a minimum of W because there exist a point with the same coordinates and interchanged momemta with less W.

Extremum points with all zero momenta can be found by solving an equation for λ,

$$\frac{1}{2}\sum_{i=1}^{N}\left(\frac{q_i^{(1)}}{1-\lambda\omega_i}\right)^2 = E \tag{6}$$

and then finding coordinates using eq. (4a).

Choosing minimum of *W*

Firstly, we choose an extremum with minimum W among the second kind of extrema (zero-momenta). If an extremum of the first kind (5) exists then its W should be compared with the second-kind minimum to make a proper choice of the global minimum. Consider here the first step in detail.

Let us define functions

$$\begin{aligned} F(\lambda) &= \frac{1}{2}\sum_{i=1}^{N}\left(\frac{q_i^{(1)}}{1-\lambda\omega_i}\right)^2 \\ U(\lambda) &= \frac{\lambda^2}{2}\sum_{i=1}^{N}\left(\frac{q_i^{(1)}}{1-\lambda\omega_i}\right)^2\omega_i \end{aligned}. \tag{7}$$

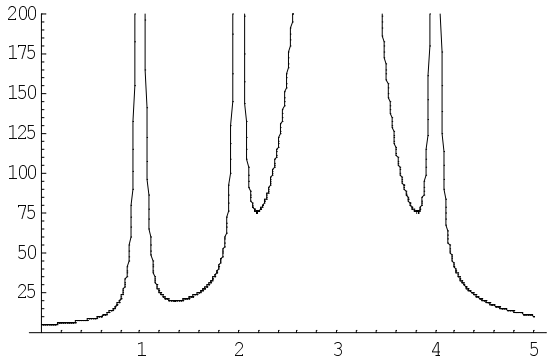
The problem of finding of the second-kind minimum reduces to finding a root of the equation $F(\lambda) = E$ with minimum of $U(\lambda)$ that is equivalent to minimum of the function $R(\lambda) = U(\lambda)/F(\lambda)$. In some regions, this function can be estimated as

$$R(\lambda) \sim \begin{cases} \overline{\omega}\lambda^2, & \lambda \to 0 \\ \omega_i^{-1}, & \lambda \to \omega_i^{-1} \\ \overline{\omega^{-1}}\lambda^2, & \lambda \to \infty \end{cases} \quad (i = 1,2,...,N). \tag{8}$$

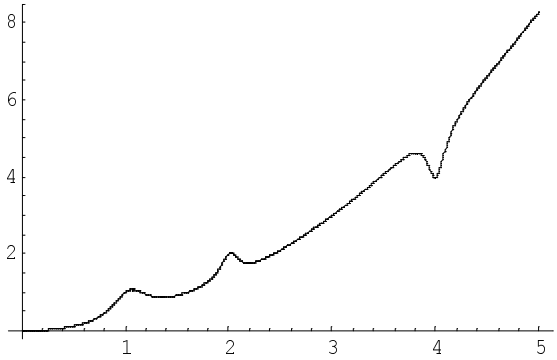
where $\overline{\omega} = \sum_{i=1}^{N} q_i^{(1)^2} \omega_i \,/ \sum_{i=1}^{N} q_i^{(1)^2}$ and $\overline{\omega^{-1}} = \sum_{i=1}^{N} q_i^{(1)^2} \omega_i^{-1} \,/ \sum_{i=1}^{N} q_i^{(1)^2}$.

For illustration, let us plot graphs of the functions taking for example $\{\omega_i\} = \{1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}\}$ and $\{q_i^{(1)}\} = \{1, \frac{1}{2}, 3, \frac{1}{4}\}$:

$F(\lambda)$



$R(\lambda)$



For example at $E = 50$ the equation $F(\lambda) = E$ has four real roots with minimum of $R(\lambda)$ (and hence $W = U(\lambda)$) for the smallest root ≈ 0.95.

Singularities of the function inverse to $F(\lambda)$, i.e. λ as a function of E are determined from the equation $\frac{d}{d\lambda} F(\lambda) = 0$. In a particular case of $N = 2$, there is one real singularity

$$\lambda_0 = \frac{\omega_1^{1/3} q_1^{(1)^{2/3}} + \omega_2^{1/3} q_2^{(1)^{2/3}}}{\omega_1^{1/3} \omega_2 q_1^{(1)^{2/3}} + \omega_1 \omega_2^{1/3} q_2^{(1)^{2/3}}} \tag{9}$$

and a pair of complex-conjugate singularities

$$\lambda_{1,2} = \frac{\omega_1^{1/3} q_1^{(1)\,2/3} + e^{\pm 2i\pi/3} \omega_2^{1/3} q_2^{(1)\,2/3}}{\omega_1^{1/3} \omega_2 q_1^{(1)\,2/3} + e^{\pm 2i\pi/3} \omega_1 \omega_2^{1/3} q_2^{(1)\,2/3}} \,. \tag{9a}$$

For arbitrary N, there is no closed-form formula. We can estimate minima and generally, complex stationary points of the function $F(\lambda)$ by assuming that they appear as a result of interference of some couple of neighbor poles, corresponding to a couple of terms in the sum (9). For example, for the above example with $N = 4$, the second local minimum of $F(\lambda)$ at $\lambda = 2.18788$ appears as a result of juxtaposition of two terms, the second and the third, and can be estimated using eq. (9) for the second and the third coordinates and disregarding another coordinates. It gives $\lambda_0 = 2.18773$ which is very close to the exact position of the minimum (at $\lambda = 2.18788$). The following table lists all singularities found by formula (9) in comparison with exact singularities.

Poles in (7) taken into account	1, 2	2, 3	3, 4
Singularities, eq. (9)	1.5 1.5 ± 0.866 i	2.1877 1.9244 ± 0.2434 i	3.8123 4.0756 ± 0.2434 i
Exact singularities	1.3566 0.8556 ± 0.4759 i	2.1879 1.9261 ± 0.2436 i	3.8123 4.0756 ± 0.2432 i

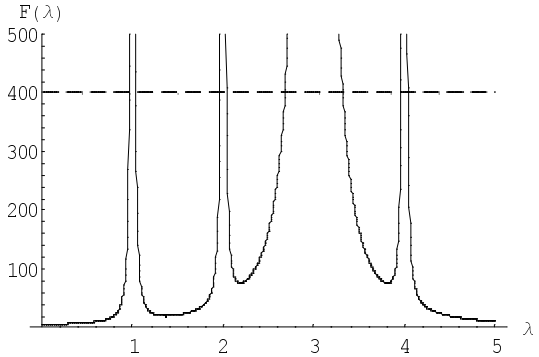
Our assumption gives accurate predictions for almost all singularities (except only one pair of singularities).

Large *E* behavior

At large energies, there are N pairs of extremum points,

$$\begin{aligned}
\lambda &= \frac{1}{\omega_i}\left[1+q_i^{(1)}\varepsilon\left(1+\tfrac{1}{2}\sum_{j\neq i}\left(\frac{q_j^{(1)}\omega_i}{\omega_i-\omega_j}\right)^2\varepsilon^2\right)\right]+O(\varepsilon^4),\\
q_i &= -\frac{1}{\varepsilon}+\tfrac{1}{2}\sum_{j\neq i}\left(\frac{q_j^{(1)}\omega_i}{\omega_i-\omega_j}\right)^2\varepsilon+O(\varepsilon^3)\\
q_j &= \frac{\omega_i q_j^{(1)}}{\omega_i-\omega_j}+\frac{\omega_i\omega_j q_i^{(1)}q_j^{(1)}}{(\omega_i-\omega_j)^2}\varepsilon+O(\varepsilon^2)\\
W &= \frac{1}{2\omega_i\varepsilon^2}+\frac{q_i^{(1)}}{\omega_i\varepsilon}+\frac{1}{2}\left(\frac{q_i^{(1)2}}{\omega_i}-\sum_{j\neq i}\frac{q_j^{(1)2}}{\omega_i-\omega_j}\right)+O(\varepsilon)
\end{aligned}, \qquad (10)$$

where $i=1,2,...,N$, $j\neq i$, and $\varepsilon=\pm 1/\sqrt{2E}$. As an illustration, in our previous example, there are four pairs of roots of the equation $F(\lambda)=E$ at $E=400$, and the smallest root corresponds to the minimum of W:



For $N=2$, radius of convergence of these expansions is distance from the origin to the most distant singularity,

$$E_* = \max_{n=0,1,2}\left|F(\lambda_n)\right| \qquad (11)$$

where λ_n are given by formulas (9). For arbitrary N, it can be estimated as $E_* = \max_{|i-j|=1} E_*^{(i,j)}$ where $E_*^{(i,j)}$ is the radius of convergence for $N=2$ with only two non-zero adjacent terms in (7) with indexes i and j (here, the frequencies are arranged in ascending or descending order).

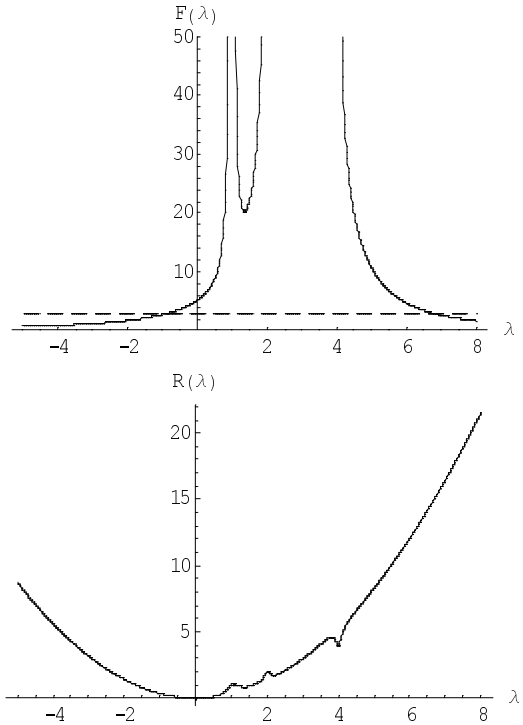
Small *E* behavior

At small energies, there is a pair of real extrema at

$$\begin{aligned} &\lambda = 1/\mu \\ &q_i = -\frac{q_i^{(1)}}{\omega_i}\mu \qquad\qquad , \\ &W = W_0 + \mu\sum_{i=1}^{N} {q_i^{(1)}}^2/\omega_i^2 \end{aligned} \tag{12}$$

where $W_0 = \frac{1}{2}\sum_{i=1}^{N}\frac{{q_i^{(1)}}^2}{\omega_i}$ and $\mu = \pm\sqrt{E/W_0}$ (negative sign corresponds to minimum of W). There are also $2N-2$ complex stationary points.

For the above example, appearance of two roots of the equation $F(\lambda) = E$ for small $E = 3$ is illustrated on the figure below (the lower graph of the function $R(\lambda)$ shows that the smallest root has minimum of W):



Almost classically allowed transition (small *W*)

If $E \to E_0 = V(q_1^{(1)}, q_2^{(1)}, ..., q_N^{(1)}) = \sum_{i=1}^{N} q_i^{(1)\,2}$, then the minimum is described by the following formulas.

$$\begin{aligned} &\lambda = \overline{\omega}^{-1}\delta, \\ &q_i = q_i^{(1)}\left(1 + \frac{\omega_i}{\overline{\omega}}\delta\right), \\ &W = \frac{E_0}{2\overline{\omega}}\delta^2 \end{aligned} \tag{13}$$

where $\delta = (E - E_0)/E_0$ and $\overline{\omega}$ was defined above.

Perturbation theory for an anharmonic Hamiltonian

Formal perturbation theory for general anharmonicity

To find stationary points, it is necessary to solve simultaneous equations

$$\begin{aligned} &\vec{\nabla} W = \lambda \vec{\nabla} H \\ &H = E \end{aligned}. \tag{14}$$

In this section, we consider an anharmonic Hamiltonian in the form $H = H^{(0)} + \varepsilon H^{(1)}$ where ε is a small parameter, $H^{(0)}$ and W are quadratic functions of momenta and coordinates given by formulas (3), and $H^{(1)}$ is some anharmonicity which is typically $\frac{1}{6}\sum_{i,j,k} f_{ijk} q_i q_j q_k + \frac{1}{24}\sum_{i,j,k,l} g_{ijkl} q_i q_j q_k q_l + \ldots$. Here, we expand unknown momenta, coordinates, and λ into power series

$$\begin{aligned}\vec{p} &= \vec{p}^{\,(0)} + \varepsilon\vec{p}^{\,(1)} + ... \\ \vec{q} &= \vec{q}^{\,(0)} + \varepsilon\vec{q}^{\,(1)} + ... \\ \lambda &= \lambda^{(0} + \varepsilon\lambda^{(1)} + ...\end{aligned} . \qquad (15)$$

The first-order corrections to harmonic approximation will be found here formally for a general anharmonicity.

For shortness, momenta and coordinates will be unified to a single $2N$-component set $(X_1, X_2, ..., X_{2N}) = (p_1, p_2, ..., p_N, q_1, q_2, ..., q_N)$, so eq. (14) are rewritten as

$$\begin{aligned}&\frac{\partial}{\partial X_i} W(X) = \lambda \frac{\partial}{\partial X_i} H(X), \quad i = 1,2,...,2N \\ &H(X) = E\end{aligned} . \qquad (16)$$

Now, both sides of eq. (16) will be expanded in powers of ε.

In the second equation of (16),

$$\begin{aligned}H(X) = H^{(0)}(X^{(0)} + \varepsilon X^{(1)} + ...) + \varepsilon H^{(1)}(X^{(0)} + \varepsilon X^{(1)} + ...) + ... = \\ H^{(0)}(X^{(0)}) + \varepsilon\left[\sum_i \frac{\partial}{\partial X_i} H^{(0)}(X^{(0)}) X_i^{(0)} + H^{(1)}(X^{(0)})\right] + ...\end{aligned} . \qquad (17)$$

For shortness, let us write everywhere for some function $A(X)$, $A(X^{(0)}) = A$, $\frac{\partial}{\partial X_i} A(X^{(0)}) = A_i$, $\frac{\partial^2}{\partial X_i \partial X_j} A(X^{(0)}) = A_{i,j}$. The second equation of (16) now reads

$$H^{(0)} + \varepsilon\left[\sum_i H_i^{(0)} X_i^{(1)} + H^{(1)}\right] + ... = E . \qquad (18)$$

In zero order, it is equivalent to unperturbed equation $H^{(0)} = E$, and in the first order,

$$\sum_i H_i^{(0)} X_i^{(1)} + H^{(1)} = 0 . \qquad (19)$$

In a similar manner, the first equation of (16) is expanded as

$$W_i + \varepsilon \sum_j W_{i,j} X_j^{(1)} + ... = \lambda^{(0)} H_i^{(0)} + \varepsilon \left[\lambda^{(0)} \sum_j H_{i,j}^{(0)} X_j^{(1)} + \lambda^{(1)} H_i^{(0)} + \lambda^{(0)} H_i^{(1)} \right]. \quad (20)$$

In zero order, it is equivalent to unperturbed equation $W_i = \lambda^{(0)} H_i^{(0)}$, and in the first order,

$$\sum_j \left(W_{i,j} - \lambda^{(0)} H_{i,j}^{(0)} \right) X_j^{(1)} = \lambda^{(1)} H_i^{(0)} + \lambda^{(0)} H_i^{(1)}. \quad (21)$$

Solution of (21) is

$$X_i^{(1)} = \sum_j G_{ij} \left(\lambda^{(1)} H_j^{(0)} + \lambda^{(0)} H_j^{(1)} \right), \quad (22)$$

where $\{G_{ij}\}$ is a matrix reciprocal to $\left\{ W_{i,j} - \lambda^{(0)} H_{i,j}^{(0)} \right\}$. By substituting eq. (22) into eq. (19), we arrive to

$$\sum_{i,j} G_{ij} H_i^{(0)} \left(\lambda^{(1)} H_j^{(0)} + \lambda^{(0)} H_j^{(1)} \right) + H^{(1)} = 0. \quad (23)$$

From eq. (23), $\lambda^{(1)}$ is determined as

$$\lambda^{(1)} = - \frac{H^{(1)} + \lambda^{(0)} \sum_{i,j} G_{ij} H_i^{(0)} H_j^{(1)}}{\sum_{i,j} G_{ij} H_i^{(0)} H_j^{(0)}}. \quad (24)$$

Summary of results for an anharmonic perturbation

For general anharmonic correction $H^{(1)}$, the first anharmonic correction to coordinates of points of launch is determined as follows. At the first step, unperturbed coordinates $X_i^{(0)}$ together with $\lambda^{(0)}$ are calculated according to the preceding chapter. Then, the matrix of the second derivatives $\left\{ W_{i,j} - \lambda^{(0)} H_{i,j}^{(0)} \right\}$ at the point $X = X^{(0)}$ is calculated, and its inverse matrix $\{G_{ij}\}$ is

found. After that, the correction $\lambda^{(1)}$ is calculated by formula (24). Finally, corrections $X_i^{(1)}$ are calculated by formula (22).

Perturbation of harmonic potential by a cubic polynomial

Matrixes of the second derivatives of H and W (see formulas (3)) are diagonal, $H_{ij}^{(0)} = \delta_{ij}$, and $W_{ij} = \frac{1}{\omega_i}\delta_{ij}$ where $i, j = 1,..., N$ (we disregard here derivatives over momenta because we shall consider perturbation independent of momenta, so all matrixes have size NxN instead of 2Nx2N).

For the case when the perturbation term contains only coordinates and has a form of a general cubic polynomial,

$$H^{(1)} = \frac{1}{6}\sum_{i,j,k} f_{ijk} q_i q_j q_k \ , \tag{25}$$

the first derivatives of H are

$$H_i^{(1)} = \frac{1}{2}\sum_{i,j,k} f_{ijk} q_j q_k \ . \tag{26}$$

Eq. (24) and (22) are considerably simplified in our case,

$$\begin{aligned} \lambda^{(1)} &= -\frac{1}{6}\frac{\sum_{i,j,k}\left(1+3\lambda^{(0)} g_i\right) f_{ijk} q_i^{(0)} q_j^{(0)} q_k^{(0)}}{\sum_i g_i {q_i^{(0)}}^2} \\ q_i^{(1)} &= g_i\left(\lambda^{(1)} q_i^{(0)} + \frac{1}{2}\lambda^{(0)}\sum_{j,k} f_{ijk} q_j^{(0)} q_k^{(0)}\right) \end{aligned} \ . \tag{27}$$

where $g_i = \frac{\omega_i}{1-\omega_i\lambda^{(0)}}$ are diagonal matrix elements of the matrix G from the previous section, and $q_i^{(1)}$ stands for the coordinate correction, not the displacement.

Application to benzene molecule

Physical parameters

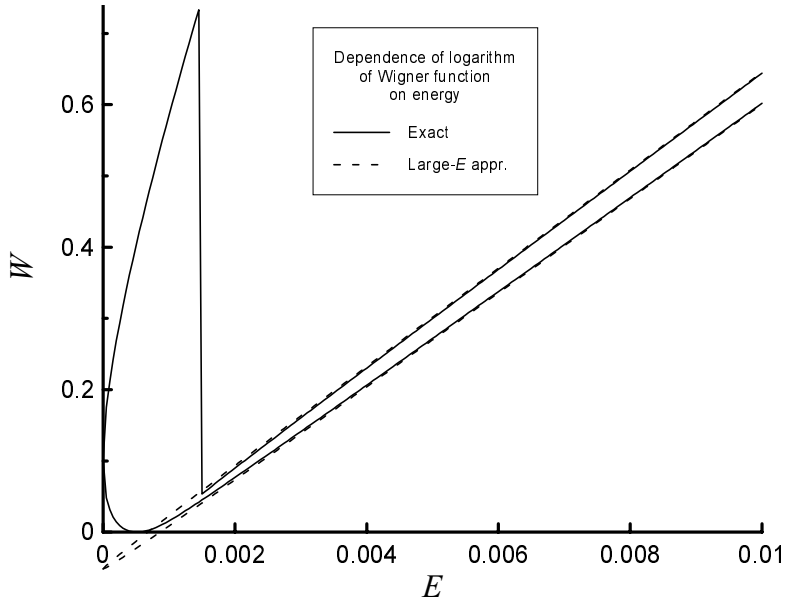
We choose a sample molecular system to test above approximations and to estimate their applicability range. Let us consider two-mode system with the following physical parameters

$$\begin{array}{l} Q_1^{(0)} = 1.397\ \text{Å} \\ Q_2^{(0)} = 1.084\ \text{Å} \\ Q_1^{(1)} = 1.432\ \text{Å} \\ Q_2^{(1)} = 1.086\ \text{Å} \end{array}, \quad \begin{array}{l} m_1 = 11016\, m_e \\ m_2 = 1836\, m_e \end{array}, \quad \begin{array}{l} \omega_1^{(0)} = 1008\ \text{cm}^{-1} \\ \omega_2^{(0)} = 3191\ \text{cm}^{-1} \\ \omega_1^{(1)} = 923\ \text{cm}^{-1} \\ \omega_2^{(1)} = 3130\ \text{cm}^{-1} \end{array} \tag{28}$$

(these data are for $S_1 \to S_0$ transition in benzene molecule, with coordinates 1 and 2 corresponding to CC and CH bonds). Scaled parameters are

$$\begin{array}{l} q_1^{(1)} = 0.0319 \\ q_2^{(1)} = 0.0024 \end{array}, \quad \begin{array}{l} \omega_1^{(1)} = 0.0042 \\ \omega_2^{(1)} = 0.0143 \\ \omega_1 = 0.0050 \\ \omega_2 = 0.0148 \end{array}, \tag{29}$$

in atomic units. Note that disregarding the displacements (that is justified for large energies), we have $W = E/\omega$ where ω is a maximum of four frequencies from (29), i.e. ω_2. It means that momenta and the first coordinate are zero, and only q_2 is non-zero. For small displacements (or large energy), solution is given by equations (10) with $i = 2$ and $\varepsilon = -1/\sqrt{2E}$. The expansion converges when energy is larger than 0.0015. Sum of three terms of the expansion (Eq. (10)) for W is shown on the following figure, together with the exact W.



There, it is shown also the second stationary point above the minimum. For the physical energy $E = 0.177$, the large-energy approximation is very accurate.

As an example of the system with four variables, we considered nonsymmetrical vibrational modes e_{2g} with frequencies ω_0 608, 3056, 1599, 1178 and ω_1 522, 3077, 1454, 1148 cm^{-1}. Since all displacements for that modes are zero, the solution is simply given by the first term of the large-energy approximation. We considered a hypothetical system with the same frequencies and four equal non-zero displacements 0.0319, the same as $q_1^{(1)}$ from the first example. We found that large-energy expansion converges for this system for energies larger than 0.032, so that physical energy ~0.1 lies within the range of applicability of this approximation.

These two examples show that the radius of applicability is of order of 0.01 for typical molecules.

Appendix. Proof of a mathematical inequality

Let us prove that if $F(\lambda_1) = F(\lambda_2)$ and $\lambda_1 < \lambda_2$ then $U(\lambda_1) < U(\lambda_2)$, where functions $F(\lambda)$ and $U(\lambda)$ are defined by Eq. (7) (as a consequence of this inequality, the root of the equation $F(\lambda) = E$ with minimum of $U(\lambda)$ is the minimal root).

Introducing symmetrical variables $s=\lambda_1+\lambda_2$ and $t=\lambda_1\lambda_2$, we rewrite increments of the functions as

$$\begin{aligned} F(\lambda_2)-F(\lambda_1)&=\frac{\lambda_2-\lambda_1}{2}\sum_{i=1}^{N}A_i(2-\omega_i s)\\ U(\lambda_2)-U(\lambda_1)&=\frac{\lambda_2-\lambda_1}{2}\sum_{i=1}^{N}A_i(s-2\omega_i t)\end{aligned}, \tag{A1}$$

where $A_i=\dfrac{q_i^{(1)^2}\omega_i}{(1-\omega_i\lambda_1)^2(1-\omega_i\lambda_2)^2}$. Multiplying the equation $F(\lambda_2)-F(\lambda_1)=0$ by $s/2$, we arrive to an equation

$$\frac{\lambda_2-\lambda_1}{2}\sum_{i=1}^{N}A_i(s-\omega_i s^2/2)=0\,. \tag{A2}$$

Since $(\lambda_1-\lambda_2)^2=s^2-4t>0$, then $s^2/2>2t$, and $-\omega_i s^2/2<-2\omega_i t$. Substituting the latter inequality into Eq. (A2) and taking into account that $A_i>0$, we find

$$\frac{\lambda_2-\lambda_1}{2}\sum_{i=1}^{N}A_i(s-2\omega_i t)>0\,. \tag{A3}$$

Comparing (A3) with the second equation in (A1) we conclude that $U(\lambda_2)-U(\lambda_1)>0$ (end of the proof).