Many-body expansion of molecular clusters' energies

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8th October 2018

Abstract

Suppose we have a cluster made of $(M+1)$ molecules labelled 0, 1, …, M. The number of atoms in each molecule is N_i, $i = 0, 1, \ldots M$. Try to use many-body expansion of potential energy surface (PES) to accelerate the Quantum Vibrational Perturbation (QVP) Theory solving.

In system containing N atoms, the total number of degrees of freedom is $3N$ with $(3N-6)$ intramolecular ones. Over all these dimensions, one of them is of great importance which we call the quantal one, Q_0, while the others treated as chemical environment, Q_i, $i = 1, 2, \ldots, (3N-7)$. If we set the energy of an isolated atom 0, we can easily write down the total energy E in terms of these dimensions,

$$\mathcal{E}(Q_0; Q_1, \ldots, Q_{3N-7}) = \sum_{i=0}^{3N-7} V_i(Q_i) + \sum_{i=0}^{3N-7} \sum_{j=i+1}^{3N-7} V_{ij}(Q_i, Q_j) + \sum_{i=0}^{3N-7} \sum_{j=i+1}^{3N-7} \sum_{k=j+1}^{3N-7} V_{ijk}(Q_i, Q_j, Q_k) + \ldots \quad (1)$$

Luckily, in fact, we only need the terms actually related to Q_0, which shows in the Hamiltonian. Total energy can be then written as

$$\mathcal{E}(Q_0; Q_1, \ldots, Q_{3N-7}) = \mathcal{V}(Q_0) + \mathcal{V}'(Q_1, \ldots, Q_{3N-7}). \quad (2)$$

$\mathcal{V}'$ can be though as a constant since it do not effect the final wave functions. Then total effective potential reads

$$\begin{aligned}
\mathcal{V}(Q_0) &= V_0(Q_0) + \sum_{j=1}^{3N-7} V_{0j}(Q_0, Q_j) + \sum_{j=1}^{3N-7} \sum_{k=j+1}^{3N-7} V_{0jk}(Q_0, Q_j, Q_k) + \ldots \\
&= V_0 + \sum_{j=1}^{3N-7} V_{0j} + \sum_{j=1}^{3N-7} \sum_{k=j+1}^{3N-7} V_{0jk} + \ldots
\end{aligned} \quad (3)$$

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Now we deal with the situation where all the atoms are grouped into M 'molecules'. We use 'molecule 0-fixed' frame to satisfy the description of QVP theory, where vibration degrees of system is represented as normal coordinates, and the important quantal Q_0 is inside molecule 0. Vibrational degrees of freedom are labelled as

$$\underbrace{0,1,2,\ldots,3N_0-7}_{3N_0-6}, \underbrace{3N_0-6,3N_0-5,\ldots,3(N_0+N_1)-7}_{3N_1}, \ldots, \ldots, \underbrace{3\sum_{i=0}^{M}N_i-7}_{3N_M}. \tag{4}$$

It is straightforward that if only molecule 0 is in the system. The effect potential is

$$\mathcal{V}_0(Q_0) = V_0 + \sum_{j=1}^{3N_0-7} V_{0j} + \sum_{j=1}^{3N_0-7}\sum_{k=j+1}^{3N_0-7} V_{0jk} + \ldots, \tag{5}$$

and if both molecules 0 and 1 are in the system, we have

$$\mathcal{V}_{01}(Q_0) = V_0$$
$$+ \sum_{j=1}^{3N_0-7} V_{0j} + \sum_{j=3N_0-6}^{3(N_0+N_1)-7} V_{0j}$$
$$+ \sum_{j=1}^{3N_0-7}\sum_{k=j}^{3N_0-7} V_{0jk} + \sum_{j=1}^{3N_0-7}\sum_{k=3N_0-6}^{3(N_0+N_1)-7} V_{0jk} + \sum_{j=3N_0-6}^{3(N_0+N_1)-7}\sum_{k=j+1}^{3(N_0+N_1)-7} V_{0jk} + \ldots. \tag{6}$$

If both molecules 0 and 2 are in the system, we have

$$\mathcal{V}_{02}(Q_0) = V_0$$
$$+ \sum_{j=1}^{3N_0-7} V_{0j} + \sum_{j=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0j}$$
$$+ \sum_{j=1}^{3N_0-7}\sum_{k=j+1}^{3N_0-7} V_{0jk} + \sum_{j=1}^{3N_0-7}\sum_{k=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0jk} + \sum_{j=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7}\sum_{k=j+1}^{3(N_0+N_1+N_2)-7} V_{0jk} + \ldots. \tag{7}$$

If molecules 0, 1 and 2 are all in the system, we have

$$\mathcal{V}_{012}(Q_0) = V_0$$
$$+ \sum_{j=1}^{3N_0-7} V_{0j} + \sum_{j=3N_0-6}^{3(N_0+N_1+N_2)-7} V_{0j}$$
$$+ \sum_{j=1}^{3N_0-7}\sum_{k=j+1}^{3N_0-7} V_{0jk} + \sum_{j=1}^{3N_0-7}\sum_{k=3N_0-6}^{3(N_0+N_1+N_2)-7} V_{0jk} + \sum_{j=3(N_0-6}^{3(N_0+N_1+N_2)-7}\sum_{k=j+1}^{3(N_0+N_1+N_2)-7} V_{0jk} + \ldots. \tag{8}$$

Further, we have

$$
\begin{aligned}
\mathscr{V}_{012}(Q_0) = V_0 \\
+ \sum_{j=1}^{3N_0-7} V_{0j} + \sum_{j=3N_0-6}^{3(N_0+N_1)-7} V_{0j} + \sum_{j=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0j} \\
+ \sum_{j=1}^{3N_0-7}\sum_{k=j+1}^{3N_0-7} V_{0jk} + \sum_{j=1}^{3N_0-7}\sum_{k=3N_0-6}^{3(N_0+N_1)-7} V_{0jk} + \sum_{j=1}^{3N_0-7}\sum_{k=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0jk} \\
+ \sum_{j=3N_0-6}^{3(N_0+N_1)-7}\sum_{k=j+1}^{3(N_0+N_1)-7} V_{0jk} + \sum_{j=3N_0-6}^{3(N_0+N_1)-7}\sum_{k=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0jk} \\
+ \sum_{j=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7}\sum_{k=j+1}^{3(N_0+N_1+N_2)-7} V_{0jk} + \ldots \\
= \mathscr{V}_0 + (\mathscr{V}_{01} - \mathscr{V}_0) + (\mathscr{V}_{02} - \mathscr{V}_0) + \sum_{j=3N_0-6}^{3(N_0+N_1)-7}\sum_{k=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0jk} + \ldots \\
= \mathscr{V}_{01} + \mathscr{V}_{02} - \mathscr{V}_0 + \sum_{j=3N_0-6}^{3(N_0+N_1)-7}\sum_{k=3(N_0+N_1)-6}^{3(N_0+N_1+N_2)-7} V_{0jk} + \ldots.
\end{aligned}
\tag{9}
$$

We coloured the terms to clarify the origins of terms.

Here we conclude that up to the two-body term, we can accelerate the computation without further approximation. However, when three-body terms matters, the expansion breaks down.

Note that the perturbation energy reads

$$
\mathscr{V}'_{012}(Q_0) = \mathscr{V}_{012}(Q_0) - \mathscr{V}_{\text{ref}}(Q_0).
\tag{10}
$$

Therefore, we further write down the perturbation term for general case where $(M+1)$ molecules are there in the system without further derivation

$$
\mathscr{V}'_{0\ldots M} = \mathscr{V}_0 + \sum_{i=1}^{M}(\mathscr{V}_{0i} - \mathscr{V}_0) - \mathscr{V}_{\text{ref}}(Q_0) + \text{'}3^+\text{-body error'}.
\tag{11}
$$

Also note that the works are based on the assumption where isolated atoms are of 0 energy, which is true in semi-empirical quantum chemistry code like MOPAC, and the unrelated energy from dimensions Q_1 to Q_M are thought as constant, which cannot be true but it will not affect QVP result. Hence, equation (11) only gives right vibration frequency even at two-body approximation. It means if you just want to check the derivation here by some *ab initio* calculation, remember there can be a difference of the potential energy by a (maybe large) constant.