Molecular Dynamics Simulation for Infrared Spectroscopy with Intramolecular Forces from Electronic Properties of On-the-Fly Quantum Chemical Calculations

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We calculated vibrational spectra by means of a molecular dynamics simulation which utilizes intramolecular forces from *ab initio* molecular orbital calculations for instantaneous configurations of each molecule. Intermolecular interactions were determined with conventional force fields. Calculated molecular orbitals from the time-dependent, instantaneous molecular configurations were also used to evaluate dipole moment and partial charges. We examined the validity of the present approach by evaluating infrared spectra for liquid carbon dioxide and water. We could capture some important features of intramolecular vibrational spectra of molecular liquids by this method, *albeit* there is room for further improvement in the descriptions of intermolecular interactions, especially of hydrogen bond. Possible extensions for accurate intermolecular and intramolecular vibrational spectrum were discussed. © 2012 Wiley Periodicals, Inc.

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Introduction

Classical molecular dynamics (MD) simulations are powerful means to analyze experimentally obtained optical spectra,[1–4] vibrational spectra,[5] and physical quantities[6,7] of various kind of molecules, since we can monitor molecular motions and manipulate physical conditions in a variety of ways. Although this approach is convenient, it is phenomenological. Molecular interactions inherently arise from the interactions between the atoms and their surrounding electrons; however, classical MD simulations replace these interactions by empirical force fields to reproduce experimental data.[8–10] The problems associated with the force field can be avoided in *ab initio* MD (AIMD) simulation, where the forces are computed directly from first principles electronic structure calculations.[11–13] As the dipole moment and electronic polarizability can be also evaluated from the electronic states of molecules, AIMD is generally suitable for simulating optical spectra. AIMD techniques have been therefore applied to study optical properties of liquid water[14,15] as well as spectra in aqueous solutions.[16]

The accuracy of force fields and calculated electronic properties can be examined by calculating multidimensional vibrational spectra[17] from full MD simulations.[18]

Simulating multidimensional spectra such as fifth-order Raman[18–22] and third-order infrared (IR)[23,24] is, however, computationally costly, since the convergence of a signal for different sampling trajectories is slow, and we have to repeat the calculation for different time durations between the pulses. Thus, to obtain multidimensional spectrum, we have to take an accurate but computationally effective approach.

This fact motivated the present research to develop a reliable methodology to reproduce multidimensional vibrational spectra. As simulating multidimensional spectra by means of AIMD simulations is not feasible with typical computational resources, one has to adopt a strategy that maintains certain advantages of the AIMD approach. One possibility is a MD simulation which partially uses the force field constructed from on-the-fly quantum chemical calculations. Such methodology has a longer history than the AIMD approach and continues to improve the mostly common decomposition scheme introduced by Hankins et al.,[25] for example, as in the many body expansion (MBE) approach[26] and the fragmental molecular orbital MD (FMO–MD) approach.[27–29]

Although such MBE and FMO–MD approaches require less computer resources than the AIMD approach, it is still too expansive to calculate multidimensional spectra. In this article, we explore the possibility of incorporating force fields constructed from on-the-fly quantum chemical calculations for only the intramolecular interactions, while using conventional empirical force fields for intermolecular interactions. Intramolecular interactions change in complex manner depending on the instantaneous atomic configurations. In turn, the dynamics is affected by both intermolecular and intramolecular interactions. Optical responses also depend upon the electronic state of the molecules. This incorporation is therefore important to calculate the optical spectrum of liquids accurately. The present approach can be regarded as a kind of quantum mechanics/molecular mechanics (QM/MM) approach where several

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quantum mechanical intramolecular sites are embedded in molecular mechanical intermolecular regions. That is, we consider the slowly changing intermolecular regions in the MM calculations, while the high frequency intramolecular sites are treated in the QM calculations. We can apply a variety of quantum chemistry techniques for the QM descriptions. The present approach is conceptually simple and can be implemented easily, while it is applicable to a wide range of problems. To examine the validity and efficiency of the present method, we calculate the signals of vibrational spectroscopies for liquid carbon dioxide and water. Our motivation with this work is to construct a parameter-free MD scheme, which can handle a variety of systems including a mixture of molecular liquids and a system whose dynamics is governed by electronically excited states, in a same framework. Although a methodology that we tested in this article is very simple, still we could capture some important features of intramolecular vibrational spectra of CO_2 liquids. Although there is plenty of room for further improvement in the descriptions of intermolecular interactions, especially of the hydrogen bond, we think that this work provides an important first step toward this goal.

In the next section, we will discuss the theoretical descriptions briefly. The calculated results for liquid carbon dioxide and water are given in "Calculations and Discussions" section. The final "Summary and Outlook" section summarizes the present results and discusses several important issues to improve the methodology.

Theory

Intramolecular and intermolecular forces

We use a quantum chemically calculated on-the-fly potential for intramolecular interactions, while classical force fields are used for intermolecular interactions. For a pure molecular liquid, we divide the whole potential into intramolecular and intermolecular interactions, that is,

$$V^{\mathrm{tot}} = \sum_{\alpha=1}^{n} \sum_{\beta=1}^{\alpha>\beta} V^{\mathrm{inter}}(\alpha,\beta) + \sum_{\alpha=1}^{n} V^{\mathrm{intra}}(\alpha), \tag{1}$$

where n is the number of molecules. The intramolecular potential for the α molecule $V^{\mathrm{intra}}(\alpha)$ is evaluated from *ab initio* molecular orbital calculations for an isolated molecule of the instantaneous configuration. For simplicity, we use the Hartree–Fock approximation in this particular work. The analytic energy gradient method is used for the forces. Dipole moment required for IR spectra is also calculated from the electronic structure calculation of each of the monomers. Electrostatic potential (ESP) derived atomic point charges are calculated for intramolecular interactions.

Although intramolecular interactions of each molecule are evaluated from on-the-fly quantum chemistry calculations, we use conventional MD force fields for intermolecular interactions. This is because on-the-fly quantum chemical evaluations of intermolecular interactions are numerically too expensive to simulate vibrational spectra of our present interest. Fortunately, the precision of intermolecular interactions is much less important than that of intramolecular interactions for the spectra. Optical properties such as polarizability and dipole moments are also less sensitive to the electronic state of surrounding molecules. In conventional classical MD simulations, the intermolecular interaction between the molecule α and β is expressed in terms of Coulomb interaction and repulsion force as

$$V^{\mathrm{inter}}(\alpha,\beta) = V^{\mathrm{Coulomb}}(\alpha,\beta) + V^{\mathrm{Repulsion}}(\alpha,\beta). \tag{2}$$

The ESP charges from the direct electronic structure calculations are used for $V^{\mathrm{Coulomb}}(\alpha,\beta)$. In this study, we consider liquid carbon-dioxide and liquid water.

In the case of carbon-dioxide, we used a model developed by S. Bock group.[30] It consists of three sites for the Coulomb interactions and five sites for repulsion interactions expressed as

$$V^{\mathrm{inter}}(\alpha,\beta) = \sum_{k,l=\mathrm{O,C,B}}^{k\in\alpha,l\in\beta} \Bigg[a_1 \exp(-a_2 r_{kl}) + D(r_{kl}) \left(\frac{q_k q_l}{4\pi\epsilon_0 r_{kl}} + \frac{a_3}{r_{kl}^6} + \frac{a_4}{r_{kl}^8} + \frac{a_5}{r_{kl}^{10}} + \frac{a_6}{r_{kl}^{12}} \right) \Bigg] \tag{3}$$

where

$$D(r_{kl}) = \left\{ 1 + \exp\left[2\left(\frac{r_{kl}}{a_0} - 2 \right) \right] \right\}^{-15} \tag{4}$$

is a damping factor, and B is a label that indicates the center of a C—O bond. On the B sites, only LJ-like interactions are applied, so $\alpha_0,\alpha_1 = 0$ and $q_B = 0$.

In the case of water, we used the TIP4P 2005 potential[31] expressed as

$$V^{\mathrm{inter}}(\alpha,\beta) = 4\left[\left(\frac{\sigma}{r_{\alpha_O\beta_O}} \right)^{12} - \left(\frac{\sigma}{r_{\alpha_O\beta_O}} \right)^{6} \right] + \sum_{k,l=\mathrm{H1,H2,M}}^{k\in\alpha,l\in\beta} \frac{q_k q_l}{4\pi\epsilon_0 r_{kl}}, \tag{5}$$

where $r_{\alpha,\beta}$, is the distance between atoms i and j in molecule α and β respectively, and H1, H2 mean hydrogen atoms, and M is the mass center of molecule. The charges on the M site equals to that of the oxygen atom.

IR spectrum

We calculate physical observables defined by the auto-correlation function as

$$\begin{aligned} C(t) &= \langle \mathbf{A}(0)\cdot\mathbf{A}(t) \rangle \\ &= \int \cdots \int \mathrm{d}p\mathrm{d}q [\mathbf{A}(p,q;0)\cdot\mathbf{A}(p,q;t)] f(p,q), \end{aligned} \tag{6}$$

where $\mathbf{A}(t) = \mathbf{A}(p,q;t)$ is a vector, and $f(p,q)$ is the equilibrium phase space distribution function, $f(p,q) = \exp(-\beta E(p,q))$. IR signal was calculated from the above expression in terms of the dipole moments of the monomers. For a time-discretized and finite NVE MD simulation, the IR response function is expressed as

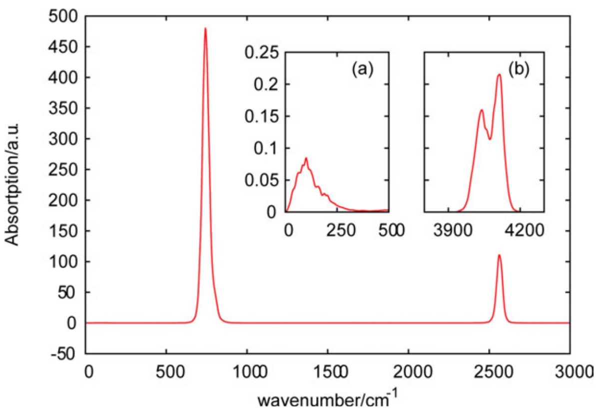

Figure 1. Calculated IR signal of liquid carbon dioxide. The insets (a) and (b) illustrate low frequency (0–500 cm^{-1}) and high frequency (3800–4300 cm^{-1}) vibrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$C^{\text{dipole}}(t) = \sum_{i}^{Q} \vec{\mu}(i)\cdot\vec{\mu}(i+t)/Q \tag{7}$$

where Q is the number of sample determined by the length of MD simulation and t for $C(t)$. The equilibrium distribution functions are not included in the expressions, because the sampling in the equilibrium state is automatically taken into account by an NVE simulation.

We need to introduce correction functions to reproduce experimentally observed spectra from our classical simulation with a small box size. IR spectra are then calculated from Ref. [32]

$$I_{\text{IR}}(\omega) = \frac{\beta\hbar\omega}{1-e^{\beta\hbar\omega}}\,\frac{\omega(1-e^{\beta\hbar\omega})}{6\hbar\epsilon_0 c n(\omega) V}\int_{-\infty}^{\infty} C_{\mu}(t)e^{-\frac{i\omega t}{\hbar}}w(t), \tag{8}$$

where $n(\omega)$ is refractive index, which is set to be a constant in this work. We choose the window function as $w(t) = \exp(-t^2/T^2)$ to reduce numerical noise, where T is the width of the Gaussian window function and we set $T = 1000$ fs. The factors in the IR signal included the correction that arises from the density of photon energy. The factor $\beta\hbar\omega/1-e^{\beta\hbar\omega}$ is quantum correction which is exact in a harmonic case.

Calculations and Discussions

In both the carbon-dioxide and water cases, we performed MD simulations for 42 molecules with the NVE ensemble with a periodic boundary condition. The number densities are 1.00 and 0.70 g/cm^3 for water and carbon oxide, respectively, to fit the real experimental conditions. In the vicinity of boundaries, we applied a switching function to intermolecular interactions to maintain continuous energies. We used the Ewald summation for the Coulomb interaction. The cc-pVDZ basis set was used to calculate the intramolecular energy, force, and partial charges (electric static potential) for each atomic configuration. The quantum chemistry part of calculations were performed with the GELLAN program suite.[33] We used the second-order symplectic integration algorithm with a time step of 0.1 and 0.5 fs for nuclear motions of water and carbon dioxide.[34] To ensure an initial equilibrium distribution, we ran NVT MD simulations using the Nose–Hoover thermostat to maintain the temperature around 300 K Distribution functions calculated from MD trajectories converged to 1.0 after fluctuations, which indicate each system was liquid-like. Then, we performed NVE MD simulations up to 10 ps and evaluated the dipole moments μ from the calculated molecular orbitals. Using Eq. (8) with Eq. (7), we then obtained the IR spectra.

Carbon dioxide

The calculated IR spectrum of liquid carbon-dioxide is shown in Figure 1. The O—C—O bending mode (ν_1) peak and the C—O antisymmetric stretching mode (ν_3) peak were observed at 800 and 2410 cm^{-1}, respectively. A very weak signal appeared around 1500 cm^{-1}, and was regarded as the symmetric stretching mode (ν_2). As illustrated in the inset (a) in Figure 1, intermolecular modes are observed as a weak bumpy broadened peak in 50–200 cm^{-1}.

Twin peaks at 4000 and 4100 cm^{-1} in the inset (b) in Figure 1 are the combination tones of the modes around 1500 cm^{-1} ($2\nu_1$,ν_2) and ν_3, which become IR active when they combined with the ν_3 mode, although the intensities are very weak.

In Figures 2 and 3, we compare our results with the experimentally obtained IR spectrum in the gas[35] and supercritical liquid phases,[36] respectively. Note that because of instrumental limitations, the signals in the range of 0–500 cm^{-1} were not observed and the height of peaks at around 750, 2300, and 3750 cm^{-1} were truncated in the experimental results in Figure 3. First we should notice that, while the intramolecular potentials are evaluated in quantum mechanically, our calculations for nuclear motions are classical. Thus, the calculated peaks shift to blue especially for high-frequency intramolecular modes due to the lack of quantum effects arise from the anharmonicity of potentials.[37]

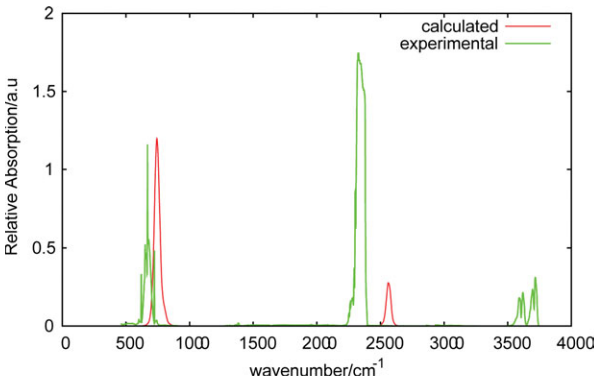

Figure 2. Comparison of IR spectra with the gas phase experiment[35] (green line) and the present result (red line) for carbon dioxide. The experiment condition is 200 mmHg of diluted CO_2 to a total pressure of 600 mmHg with N_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Note that the blue shift and under estimation of combination tones and overtones may also arise from the lack of

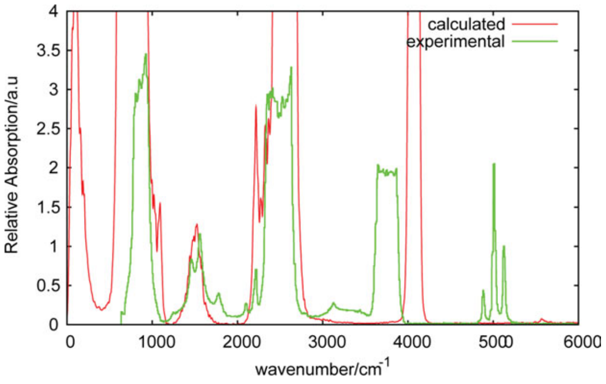

Figure 3. Comparison of IR spectra with the supercritical phase experiment [36] (green line) and the present result (red line) for carbon dioxide. Experiment conditions are 50 °C, 174.0 atm, 0.749 g/cm^3 and 5.9 mm path length. Because of instrumental limitations, the signals in the range of 0–500 cm^{-1} were not observed and the height of peaks at around 750, 2300, and 3750 cm^{-1} are truncated in the experimental results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electron correlation effects. This will be checked by dropping the Hatree–Fock approximation.

In Figure 2, the peak strength at around 0–500 and 3000–4000 cm^{-1} are much weaker than those in the gas phase. This is because while the normal mode description of each molecule is well maintained in the gas phase, the symmetry of normal modes is broken due to the intermolecular interactions in the liquid phase.

Compared with the experimental spectrum in the supercritical liquid phase in Figure 3, our results predict the peak positions in the range 500–4000 cm^{-1} besides the blue shifts. The experimentally observed peaks around 5000 cm^{-1} are the combination tone of $2\nu_3$ and ν_2. The corresponding peak appears at 5500 cm^{-1} in our calculation, while the peaks intensities are noticeably small.

This might be due to the underestimation of the nonlinear coupling strength between the ν_3 and ν_2 modes that arises from the electron correlation effects.

Even with the present straightforward implementation of QM calculations, we still could capture some important features of CO_2 liquids. Intramolecular interactions dramatically changed the signal strength, width and positions were from the QM result for an isolated molecule. The calculated spectrum is closer to that of the liquids than the gas.

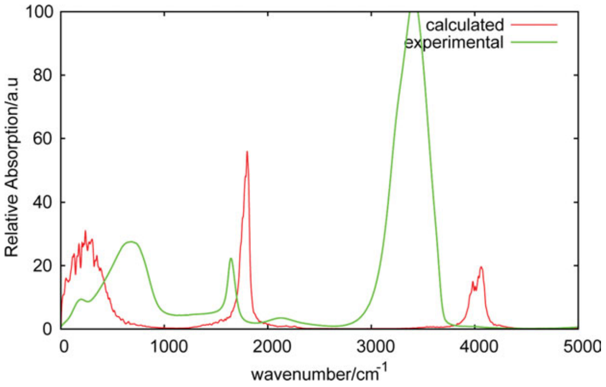

Figure 4. Comparison of experimentally obtained IR signal for liquid water[38] (green line) and the present work (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

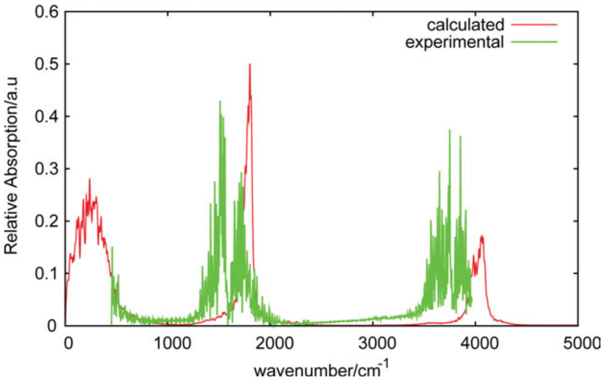

Figure 5. Comparison of experimentally obtained IR signal for vapor water[35] (green line) and the present work (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water

The calculated IR spectrum of liquid water is compared with the experimentally obtained spectrum in the liquid[38] and vapor phases[35] in Figures 4 and 5, respectively. First of all, our calculated spectrum is closer to the vapor case rather than the liquid case, indicating that our treatment of intermolecular interactions based on TIP4P potentials was insufficient to include the effects of intermolecular interactions on the intramolecular modes. In this calculation, the effect of the electric fields that arises from surrounding molecules were neglected in the MO calculations. As polarization of water molecule is important to reproduce vibrational spectra,[39–41] we needed to include induced field effects to perform MO calculations.

Although the experimentally obtained spectrum in the liquid phase exhibits the stretching modes as one broadened band at 3400 cm^{-1}, the present result depicts them as weak and separated peaks at around 4000 cm^{-1}. The peak intensity of calculated bending mode at 1800 cm^{-1} is also stronger and sharper than that of experimental one at 1600 cm^{-1}. In our IR spectra, unlike other calculated and experimental results,[35,38,41] two intramolecular peaks at 1808 and 4050 cm^{-1} show long tails on both sides. This is due to the underestimation of hydrogen bond interactions that were described from the TIP4P potential. This causes the structural fluctuations of the hydrogen bonds network, as well as the vibrational dephasing of intramolecular modes to become small. Thus, the peak width becomes narrower. There are also intermolecular peaks at around 378 cm^{-1}, which are much higher frequency than experimentally obtained signal (around 100 cm^{-1} area) in the liquid phase.[42] The source of these discrepancies will be discussed in the last section. Although the accuracy to describe the peak profiles is rather limited at this stage, we can reasonably predict the peak positions of intramolecular modes except for the overestimate of the blue shift of the peaks by ca. 10%. As in the case of CO_2, this shift is partially due to the limitation of the classical treatment of the highly anharmonic vibrations,[37] or the nature of Hartree–Fock method. In the water case, electron correlation that could not be taken into account in this work might cause an additional shift. This contribution can be eliminated by improving the quantum mechanical descriptions.

Summary and Outlook

In this article, we examined a methodology of MD simulation for IR spectroscopy. Although intermolecular interactions were determined with conventional force fields, intramolecular forces are evaluated from direct molecular orbital calculations for instantaneous configurations of each molecule. Optical observables with time dependence were also evaluated from the obtained molecular orbitals. Calculated spectra for liquid carbon dioxide and water indicated that the present scheme can reproduce optically active intramolecular modes and convention bands reasonably well especially for carbon dioxide case, *albeit* the descriptions of peak width and strength were limited. In the water case, however, due to the limitation to describe intermolecular interactions especially for hydrogen bond interaction, the peak strength and width for the stretching and bending mode were not accurate.

Although MD with phenomenological potentials[41,43] or with mapped potentials[44,45] can reproduce IR signals very well, it is not so flexible to apply them to a complex system such as a mixtures of liquids molecules or a system whose spectrum or dynamics are governed by electronically excited states. At this stage, our approach is computationally costly and is also not satisfactory to describe IR spectrum of water. Our ultimate goal with this work is to calculate the spectrum of a system that cannot be accessed by conventional approaches. The present article is a first small step toward that goal.

Many of the present results are preliminary and a lot of room for improvement in various ways. From classical MD point of view, (i) we need to tune the force field parameters. In the water case, a choice of the classical potential strongly effects on spectrum.[46] The inclusion of quadrupole interactions may also be important.[41] From MO point of view, (ii) we should take into account the effects of external fields that arise from the surrounding molecules to have accurate intermolecular interactions. For water, (iii) we need to use quantum chemical calculations beyond the Hartree–Fock level to have the right peak positions for the intramolecular modes.

If we properly treat excited states for intramolecular quantum calculations, we may be able to study problems involving visible light through to X-ray radiation.

Although, it may be computationally very expense, (iv) we need to evaluate pair intermolecular interaction directly from MO calculations to have a better description of intermolecular interactions. This has been demonstrated by MBE calculations[26] and FMO–MD calculations.[27–29] Even with all of these improvements, dynamics of the nuclei are still classical and are not suitable to evaluate high frequency anharmonic modes.[37] Thus, (v) we need to treat the high-frequency intramolecular modes quantum mechanically.[15,40,47–51]

A motivation of the present research is to calculate reliable multidimensional vibrational spectra. Because of such spectroscopies are sensitive to the choice of force field parameters and optical properties determined from the electronic state of molecules, we have to have a very accurate description of the MD as well as the molecular electronic state.

The calculation of multidimensional spectra from accurate simulations are computationally costly due to the slow convergence of signal for sampled trajectories and that we have to calculate the signal by changing two or three different time durations between the pulse sequences. Thus, to calculate multidimensional spectra, we have to take an accurate but computationally economical approach. The present approach utilizes MO calculations from only the important parts of molecule to compute right spectrum. Although, the present approach requires 1000 times as much computational cost as the regular MD simulations without parallelization, it is still much cheaper than the first principle MD simulation especially for a large system. The inclusion of the electronically excited states of molecules, which is important to study electronic resonant spectroscopies, is also straightforward. If we evaluate pair intermolecular interactions, the calculation will become parameter free, and we can handle a mixture of molecular liquids and a solute–solvation system. Massive parallelization is easy to perform, since each MO calculation can be performed independently even if we include MO calculations for intermolecular pair interactions. The inclusion of the external force mentioned as (ii) is under way and will be reported in a future paper.

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