Supporting Information for “Molecular Structure Optimization based on Electrons-Nuclei Quantum Dynamics Computation”

Hirotoshi Hirai,* † Takahiro Horiba, † Soichi Shirai, † Keita Kanno, † Keita Omiya, †
Yuya O. Nakagawa, † and Sho Koh †

†Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan
‡QunaSys Inc., Aqua Hakusan Building 9F, 1-13-7 Hakusan, Bunkyo, Tokyo 113-0001, Japan

E-mail: hirotoshih@mosk.tytlabs.co.jp

1 Computational details for 2D H₂⁺ molecule

In numerical demonstrations in Sec. 3.1 of the main text, the 2D space was represented by an evenly spaced isotropic grid of 2⁵ × 2⁵ = 32 × 32. The step sizes of dx and dy were set to 0.075 bohr, and the ranges of the x-axis and y-axis for R and rₖ were (-1.1625: 1.1625) bohr. The wave function of the system is given by two variables of ψ(R, rₖ); therefore, the number of elements of the wave function is (2⁵)² × (2⁵)² = 2²⁰. There are singular points where the Coulomb interaction term diverges to ±∞, and we replace the value ±∞ by a finite value ±1/√(dx²+dy²). The initial state of the wave function is set to a Gaussian function centered on
the origin,
\[
\psi(\vec{R}, \vec{r}_c, \tau = 0) = \frac{1}{(\alpha \pi)^2} e^{-\frac{\vec{R}_c^2 + \vec{r}_c^2 + \vec{r}_d^2 + \vec{r}_u^2}{2\alpha^2}},
\]
where \( \alpha = 0.5 \) was used. The second-order Suzuki-Trotter decomposition method was used to calculate the quantum dynamics of the system in the imaginary time, and the time step \( \tau \) of the imaginary time evolution was set to 0.075 a.u. (1.814 attoseconds). The mass of the proton is set to 1863.15 a.u., and when calculating the deuterium ion molecule \( \text{D}_2^+ \) and the triton ion molecule \( \text{T}_2^+ \) to confirm the isotope effect, twice or three times that mass was used. The mass of an electron is 1 in the atomic unit. In this study, it is assumed that the overlap of wave functions between nuclei is almost zero, and there is no exchange interaction between them.

1.1 Calculation for point charge particles (classical particles)

For comparison, the 2D \( \text{H}_2^+ \) molecule was first calculated for the case where the protons were treated as point charges (classical particles). As a point charge, the electronic state does not change, even if the mass of the proton is changed. Place two protons at \( \vec{R}_1 = (-R/2, 0) \) and \( \vec{R}_2 = (R/2, 0) \), and parameterize the internuclear distance \( R \). The electronic state of the ground state was obtained by the imaginary time evolution method. The potential energy surface acting on the electron is visualized in FIG. S1 in the case of \( R = 0.37 \) bohr. The

Figure S1: Potential energy surface for the \( \text{H}_2^+ \) molecule.
total energies were calculated with the optimized wave functions while changing $R$ and the potential energy surface was obtained, as shown in FIG. S2. From FIG. S2, the equilibrium internuclear distance when the protons are treated as classical particles is 0.37 bohr.

![Graph showing bond lengths and energies for the H$_2^+$ molecule.](image)

Figure S2: Bond lengths and energies for the H$_2^+$ molecule.

It should be noted that the contribution of kinetic energy term (wavefunction spreads out spatially) is smaller than the ordinal three-dimensional system and the system can reach deep into the well of Coulomb potential. This dimensional difference results in the huge discrepancy in energy.

The electron probability distribution at this time is shown in FIG. S3. Here, the positions of the protons are indicated by blue dots, and the electron probability distribution has a maximum value between the two protons.

2 Computational details for H-C-N system with Lennard-Jones potential

In Sec. 3.2, the following expression of the Lennard-Jones potential is used in this study,

$$V_{ij}(r) = 4\epsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6),$$

(2)
Figure S3: Electron probability distribution for the \( \text{H}_2^+ \) molecule.

where \( r \) is the distance between atom \( i \) and \( j \), \( \epsilon_{ij} \) is the depth of the potential well. The \( r_{eq}^{ij} \) at the minimum of the potential (equilibrium bond length) can be obtained from the following equation,

\[
r_{eq}^{ij} = 2^{1/6} \sigma_{ij},
\]

(3)

where

\[
V_{ij}(r_{eq}^{ij}) = -\epsilon_{ij}
\]

(4)

corresponds to the binding energy. The parameters for the HCN system were determined based on the two-body binding energy and equilibrium bond length between each atom using the above equations. The binding energies and equilibrium bond lengths used in this study are summarized in Table S1.

Table S1: The binding energies and equilibrium bond lengths for H-C, H-N and C-N.

| Atomic pairs | Binding energy [kJ/mol] | Bond length [Å] |
|--------------|-------------------------|-----------------|
| H-C          | 413                     | 1.10            |
| H-N          | 386                     | 1.00            |
| C-N          | 890                     | 1.16            |

The determined parameters of the Lennard-Jones potential are shown in Table S2.

The step sizes for the coordinate, \( dr \), was set to 0.118 bohr, and the range of the coordinate
Table S2: The parameters of the Lennard-Jones potential for H-C-N system.

| Atomic pairs | $\epsilon$ [hartree] | $\sigma$ [bohr] |
|--------------|----------------------|-----------------|
| H-C          | 0.157                | 1.852           |
| H-N          | 0.147                | 1.684           |
| C-N          | 0.339                | 1.953           |

was $0 \sim 15.118$ bohr. Like the Coulomb interaction, the Lennard-Jones potential $V^{LJ}(R)$ also diverges at $R = 0$. To avoid divergence, we set the potential energy to $1/dr$ when the value of the potential energy exceeds $1/dr$. The initial state of the wave function is set to flat (constant in the simulation region). The second-order Suzuki-Trotter decomposition method was used to calculate the quantum dynamics of the system in the imaginary time, and the time step $\tau$ of the imaginary time evolution was set to 0.1 a.u. (2.419 attoseconds). The masses of the H, C, N atoms are set to 1840, 22080, 25760 a.u., respectively.

3 Application to larger molecules and the effect of zero-point vibrations

As the size of the molecule increases and the number of degrees of freedom increases, the number of vibrational modes also increases. As a result, some modes with large fluctuations (e.g., breathing mode) appear, and the fluctuation width of the zero-point vibration also increases, which may affect the number of measurements for the molecular structure optimization by our method. To estimate how the fluctuation width of the zero-point vibration changes with the molecular size, we consider the one-dimensional model system with $N$ mass points connected by springs. Both ends of the chain of the mass points are assumed to be free. The masses of all the mass points and the spring constants are assumed to be $m$ and $k$, respectively. The solution of this model can be obtained analytically, and the frequencies of the $n$-th normal modes are given by

$$\omega^{(n)} = 2\sqrt{\frac{k}{m}} \sin \frac{n\pi}{N}. \quad (5)$$
Here, \( n = 1, 2, \cdots, N - 1 \). We are only interested in the low frequency modes with large fluctuation widths, so we assume that \( n \ll N \). Then the above equation can be simplified to

\[
\omega^{(n)} \simeq 2\sqrt{\frac{k}{m} \frac{n\pi}{N}}.
\]  

(6)

The standard deviation of the zero-point fluctuation for the harmonic oscillator with the frequency \( \omega \) can be written as \( \sigma = \sqrt{\frac{1}{2m\omega}} \), so the standard deviation of the zero-point fluctuation for the lowest frequency mode (\( n = 1 \)) can be estimated as

\[
\sigma^{(n=1)} = \sqrt{\frac{1}{2m\omega^{(n=1)}}} \simeq \sqrt{\frac{N}{m\omega_0\pi}},
\]  

(7)

where \( \omega_0 = \sqrt{\frac{k}{m}} \) is the frequency of the single string system. Equation (7) means that the standard deviation of the zero-point fluctuation increases approximately in proportion to \( \sqrt{N} \).