Intermolecular diatomic energies of a hydrogen dimer with non-Born-Oppenheimer nuclear and electron wave packets

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Abstract

We have developed an efficient theoretical framework of a non-Born-Oppenheimer (non-BO) nuclear and electron wave packet (NWP and EWP) method and applied it to intra- and inter-molecular energies of a hydrogen dimer. The energy surface functions were derived at low computational cost. In contrast with the ordinary BO nuclear quantization on a given energy surface that reduces the effective barrier, non-trivial non-BO interactions between the EWPs and NWPs resulted in increases of intermolecular rotational and translational barriers. A direct comparison demonstrated that the non-BO effect on the intermolecular energy is significant.

1. Introduction

A goal of theoretical and computational chemistry is to develop approaches to a solution of full molecular time-dependent Schrödinger equations treating both electronic and nuclear degrees of freedom as dynamical vari-

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ables. Developing methods capable of treating quantum many-body systems is a key problem of computational chemistry and physics. It is obviously too demanding at present for time-dependent ab initio quantum chemical calculations to study chemical dynamics involving both degrees of freedom in non-trivial manners. Due to exponential scaling on the number of degrees of freedom, the standard grid or basis set techniques are limited to small systems [1].

The present work has been motivated by the recent development of the semiquantum time-dependent Hartree (SQTDH) theory [2–6] that accounts for the nuclear quantum effects (NQEs) such as zero-point energy and wave packet delocalization via a Hartree product of three-dimensional Gaussian nuclear wave packets (NWPs). The semiquantum molecular dynamics (MD) simulation was actually developed to study the structure and dynamics of liquid water composed of 1024 molecules [5, 6], and reproduced major properties of other semiquantum approaches such as centroid MD (CMD) and ring polymer MD (RPMD) [7, 8] at lower computational cost.

While the SQTDH method has similarities to the other Gaussian wave packet (GWP) methods [9–16], it is distinguished by the treatment of momentum variables conjugate to the GWP widths that follow canonical equations of motion (EOM) in the conceptually extended phase space. This enabled straightforward formulations of analytical theories [2, 4] as well as the realistic MD simulations [5, 6]. The advantage of the extended Hamiltonian formalism is shared by the expectation-value approaches of moments [17–19] and cumulants [20], although their extensibility to electron wave packets (EWPs) is yet unclear. We might extend our approach in a similar manner

2

as, e.g., the multi-configurational time-dependent Hartree methods [13] by including many coupled variational parameters and basis sets, but this will limit the applicability to large systems.

As the Hartree approximation indicates, many fermion systems were out of the scope of the approaches mentioned above. The SQ WP approach was thus extended recently to an EWP method [21, 22], in which floating and breathing Gaussian EWPs are treated by the perfect-pairing (PP) valence bond (VB) theory [23, 24] that appropriately treats the Pauli exclusion energy for many-electron systems. In the present work, we attempted to extend the previous SQ WP theory further to simultaneously calculate the EWPs and NWPs in a non-Born-Oppenheimer (non-BO) manner. All the semi-quantum energy functions for the combined EWP and NWP systems were derived explicitly and non-perturbatively. It is thus distinguished from most of the previous NWP approaches in which the potential surfaces were given in advance by a separate modeling and, in many cases, expanded quadratically around the moving NWP centers [5, 6, 9–16]. The difference from the conventional VB calculations in the BO framework is also obvious.

The EWP part of the present method is more closely related to the fermion GWP MD simulations developed in plasma physics [25–27]. They compute the energy of a collection of classical point charge nuclei and Gaussian EWPs by approximating the potential energy as a sum of the electron kinetic energies, electrostatic energies, and simple Pauli exclusion interactions. The electron force field (eFF) method, recently proposed and applied to a variety of systems by Su and Goddard [28–30], introduced a spin-dependent Pauli potential that is parametrized in a way to compensate for the lack of

3

explicit antisymmetry in the Hartree product wave function. The present work differs from these works in the treatment of the fermion antisymmetry via the PP VB theory and the non-BO combination of EWPs and NWPs.

NQEs such as zero-point energy and WP delocalization [31] are especially important in hydrogen systems, and have actually been studied in solid hydrogen crystals using the path integral (PI) MD [32, 33], the PI Monte Carlo method [34] and the CMD [35], and in liquid hydrogen using the PI MD, CMD and RPMD [7, 8, 36–38]. These methods employ fixed force-field potential functions under the BO approximation. Some non-BO quantum chemical approaches such as the nuclear orbital plus molecular orbital methods [39–42], the non-adiabatically coupled EWP and NWP method [43–45] and a non-BO density functional calculation based upon Green function techniques [46] seem promising but are still computationally too expensive to study condensed phase dynamics. Our method needs much lower computational cost and is expected to directly simulate real-time hydrogen dynamics via both the EWP and NWP dynamics.

In this first report, the basic framework of the developed method is described in Sec. 2, and numerical applications are examined on intra- and inter-molecular potential energy surfaces of hydrogen molecules with discussions about the NQEs and the non-BO effects in Sec. 3. The summary and future work are commented in Sec. 4.

2. Theory

Our approach is based on the TDH method, and we describe the molecular wave function by a direct product of electron and nuclear parts; the former

consisting of a VB function of EWPs is independent of nuclear coordinates, while the latter is introduced by a Hartree product of NWPs. Our EWPs can float and breathe freely following the non-BO potential energies derived below. Thus, our way to introduce the non-BO effects is different from the ways of the previous non-BO studies [39–45] where the electron wave functions depend on nuclear coordinates and the derivative couplings were taken into account.

For notational simplicity, we start with a pedagogic description of two-electron (2e) and two-nucleus (2n) systems in Sec. 2.1, and then extend to 4e-4n systems in Sec. 2.2.

2.1. Two-electron and two-nucleus system: single diatomic hydrogen molecule

We start with the Heitler-London (HL) VB wave function for two electrons expressed as

$$
\begin{aligned}
\psi_{a,b}(1,2) \;=\; & \frac{1}{2^{\frac{1}{2}}(1+S_{ab}^2)^{\frac{1}{2}}}(\phi_a(\mathbf{q}_1)\phi_b(\mathbf{q}_2) + \phi_b(\mathbf{q}_1)\phi_a(\mathbf{q}_2)) \\
& \times \frac{1}{2^{\frac{1}{2}}}(\alpha(1)\beta(2) - \beta(2)\alpha(1)),
\end{aligned} \tag{1}
$$

where α and β are the spin functions. Since we restrict our numerical calculations to the stationary wave functions in this work, momentum parameters are all nullified. The spatial Gaussian EWP ϕ_e is specified by the WP center $\mathbf{r}_e$ and width ρ_e as [47]

$$
\phi_e(\mathbf{q}) \;=\; N_e \exp[A_e|\mathbf{q} - \mathbf{r}_e|^2], \tag{2}
$$

where A_e is introduced as $A_e = -1/4\rho_e^2$. In this paper, we adopt the atomic units; $\hbar = 1$, an electron charge $e = 1$ and an electron mass $m_e = 1$. $N_e =$

$(2\pi\rho_e^2)^{-3/4}$ is a normalization factor. S_{ab} is the overlap integral between ϕ_a and ϕ_b, whose explicit form is described in Appendix.

Furthermore, we take into account NQEs by introducing NWPs, and the wave function for two nuclei is expressed as a Hartree product of the two Gaussian NWPs;

$$\Psi_{A,B}(1,2) \;=\; \Phi_A(\mathbf{Q}_1)\Phi_B(\mathbf{Q}_2), \tag{3}$$

where a NWP of width ρ_n and its center position $\mathbf{R}_n$ is defined as

$$\Phi_n(\mathbf{Q}) \;=\; N_n \exp[A_n|\mathbf{Q}-\mathbf{R}_n|^2], \tag{4}$$

with $A_n = -1/4\rho_n^2$. The normalization factor is $N_n = (2\pi\rho_n^2)^{-3/4}$.

The total potential energy of this case, E_{tot}, is a sum of kinetic energies of electrons and hydrogen nuclei, and three electrostatic energies of electron-electron, nucleus-nucleus, and nucleus-electron;

$$E_{\text{tot}} \;=\; E_{\text{ke,elec}} + E_{\text{ke,nuc}} + E_{\text{ee}} + E_{\text{nn}} + E_{\text{ne}}. \tag{5}$$

Since all the momentum parameters are set zero in the starting Gaussian EWP and NWP, Eqs. (1) and (4), the current total energy will be referred to the total potential energy in this letter. The momentum parameters will be revived in forthcoming dynamics studies as in the previous MD simulations [5, 6]. The terms which can be obtained only by electron integrations with $\psi_{a,b}$ are listed in Appendix. Since we introduce the NWPs in the present work, it is further necessary to integrate the remaining energy terms with the nuclear wave function $\Psi_{A,B}$. We finally obtained the expressions for kinetic energy of hydrogen nuclei, and electrostatic energies of nucleus-nucleus and

6

nucleus-electron as

$$E_{\text{ke,nuc}} = \sum_{i=1}^{N_{\text{nuc}}} \frac{3}{8 M_{\text{nuc}} \rho_{\text{H},i}^2}, \tag{6}$$

and

$$E_{\text{nn}} = \sum_{i>j}^{N_{\text{nuc}}} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \text{erf} \left(\frac{|\mathbf{R}_i - \mathbf{R}_j|}{2^{\frac{1}{2}} \left(\rho_{\text{H},i}^2 + \rho_{\text{H},j}^2 \right)^{\frac{1}{2}}} \right), \tag{7}$$

and

$$E_{\text{ne}} = \sum_{i=1}^{N_{\text{nuc}}} \frac{V_{aa,i} + V_{bb,i} + 2 S_{ab} V_{ab,i}}{1 + S_{ab}^2}, \tag{8}$$

respectively. Here, N_{nuc} is a total number of nuclei, M_{nuc} is a relative mass of a proton atom to an electron, and $\rho_{\text{H},i}$ indicates width of an ith NWP. The nuclear-electron energy term $V_{ab,i}$ after the integration by the nuclear wave function is derived as

$$V_{ab,i} = -\frac{S_{ab}}{|\mathbf{r}_{\text{p}} - \mathbf{R}_i|} \text{erf} \left[\frac{|\mathbf{r}_{\text{p}} - \mathbf{R}_i|}{\left(2\rho_{\text{H},i}^2 + (\alpha + \beta)^{-1} \right)^{1/2}} \right], \tag{9}$$

in which $\alpha \equiv 1/4\rho_a^2$ and $\beta \equiv 1/4\rho_b^2$.

Our method performed not only the electron integration with the electron wave function $\psi_{a,b}$ but also the nucleus integration with the nuclear wave function $\Psi_{A,B}$, which enables the non-BO interaction between the EWPs and NWPs. This distinguishes our method from the previous EWP methods [28–30].

2.2. Four-electron and four-nucleus system: two diatomic hydrogen molecules

The total potential energy of the PP VB wave function in which EWP pairs (a, b) and (c, d) are coupled in the singlet configuration is given by

$$E_{ab,cd} = \frac{1}{\Delta}(J_0 + J_2 + J_3 + J_4) + E_{\text{ke,nuc}} + E_{\text{nn}}, \tag{10}$$

7

where J_n represents n-electron exchange integrals listed in Appendix [23]. Δ is the normalization factor [21]. The electron pair (a, b) belongs to one hydrogen molecule, while the other electron pair (c, d) belongs to the other hydrogen molecule. The electronic Hamiltonian H is composed of kinetic energy of electrons, and two electrostatic energies of electron-electron and nucleus-electron. We derived the general form of the electron exchange integral as

$$
\begin{aligned}
(abcd|H|ijkl) \equiv\ & (T_{ai} + \sum_{n=1}^{N_{\mathrm{nuc}}} V_{ai,n})S_{bj}S_{ck}S_{dl} + S_{ai}(T_{bj} + \sum_{n=1}^{N_{\mathrm{nuc}}} V_{bj,n})S_{ck}S_{dl} \\
& + S_{ai}S_{bj}(T_{ck} + \sum_{n=1}^{N_{\mathrm{nuc}}} V_{ck,n})S_{dl} + S_{ai}S_{bj}S_{ck}(T_{dl} + \sum_{n=1}^{N_{\mathrm{nuc}}} V_{dl,n}) \\
& + (ai|bj)S_{ck}S_{dl} + (ai|ck)S_{bj}S_{dl} + (ai|dl)S_{bj}S_{ck} \\
& + (bj|ck)S_{ai}S_{dl} + (bj|dl)S_{ai}S_{ck} + (ck|dl)S_{ai}S_{bj}, \quad\quad (11)
\end{aligned}
$$

where T_{ab} is the one-electron kinetic term introduced in Appendix. We obtained all the above expressions by introducing the four Gaussian NWPs and by integrations with the nuclear wave function composed of the four hydrogen NWPs. Thus, $E_{\mathrm{ke,nuc}}$, E_{nn}, and $V_{ab,i}$ in Eqs. (6)-(9) now explicitly and non-perturbatively depend on the NWP widths of the four hydrogen nuclei, i.e. $N_{\mathrm{nuc}} = 4$. This again distinguishes our method from the previous NWP methods which needed to expand the electronic potential surfaces given in advance around the moving NWP centers [5, 6, 9–16]. The introduced NQEs actually influence intra- and inter-molecular potential energies of hydrogen molecules, as will be shown in the next section.

3. Results and discussions

In this section, intra- and inter-molecular potential energy profiles of a hydrogen dimer will be calculated by optimizing all the WP center and width parameters to find the optimal energy in eq.(10) whose components are derived analytically in Eqs. (6)-(11). The energy minimizations were carried out by the method of Brent that does not require derivatives. We note that the NWP contribution is already taken into account in the current total potential energy profiles, and therefore, these should not be confused with the conventional BO surfaces on which nuclear WPs are to be calculated subsequently. We will demonstrate that the non-BO quantum effects significantly influence both the intra- and inter-molecular hydrogen interactions, especially the latter in an unintuitive manner. A detailed analysis of the EWPs will also be given.

3.1. Intramolecular energy of H_2

First, we examine the NQE on the intramolecular potential shape. Figure 1 shows the total potential energy E_{tot} of a H_2 molecule as a function of the interatomic distance or the distance between the NWP centers. The red and green curves correspond to the energies with and without the NWPs of two hydrogen atoms, respectively. (Here, 'without NWPs' means classical particle nuclei.) The NQEs such as zero-point energy and WP delocalization introduced by the NWPs quantitatively influence the interatomic energy; the difference is larger especially around the *equilibrium* bond length. The well depths are -4.93×10^4 K with the NWPs, and -5.51×10^4 K without the NWPs; the difference as large as $\sim 5.83 \times 10^3$ K indicates that the

phase diagram in a condensed hydrogen plasma system will be significantly affected by the NQEs. The value without NWPs, -5.51×10^4 K, is closer to the value obtained by the high-level quantum chemical calculation without NQEs, -5.49×10^4 K [48], than the energy values given by the Hartree-Fock (HF) calculation, -4.33×10^4 K, and eFF, -3.37×10^4 K [29]. The bond length estimated from the well bottom is 0.744 Å with the NWPs and 0.704 Å without the NWPs. The NWPs delocalized at the both sides of a hydrogen molecule repel each other, and attract the EWPs from the both sides, resulting in the broader EWPs and the longer bond length. The bond length without the NWPs should be compared with the equilibrium bond length, 0.741 Å, from both experiment and the high-level quantum chemical calculation without NQEs [48], and that by eFF, 0.780 Å [28–30]. On the other hand, the bond length with the NWPs, 0.744 Å, is reasonably close to the *average* bond length, 0.751 Å from the experiment [49] and 0.753 Å and 0.751 Å from the more accurate quantum chemistry calculations with NQEs and non-BO nuclear and molecular orbital calculations [39–41]. Considering the overestimate of the bond length by a non-BO density functional calculation with the Green function technique, 0.778 Å [46], the accuracy of our simple WP method seems satisfactory. In the following calculations, we will use the fixed values 0.744 Å for the interatomic bond length with the NWPs and 0.704 Å without the NWPs.

3.2. Intermolecular energy of H_2 dimer

Second, we calculate intermolecular energy profiles between two hydrogen molecules. The intermolecular energies $E_{ab,cd}$ along the molecular distance for the two representative configurations are displayed in Figure 2 [50].

10

Throughout this paper, the intermolecular distance R refers to that between the molecular centers. All the energies shown here include the nuclear quantum contributions from the four hydrogen NWPs. The upper panel shows that the configurations I and II exhibit energy wells whose depths are -41.3 and -16.8 K at 3.61 and 3.87 Å, respectively. The energy wells were also obtained by the previous CCSD(T) calculations [50–53] where the I and II well depths are ~ -55 and -40 K at both 3.4 Å, respectively. Our result is also comparable to the result obtained by the configuration interaction calculation which gave the energy well of -34.3 K at 3.57 Å [54]. The present results of the I and II energies can well be fitted by the LJ intermolecular energy function of the form

$$V_{\text{inter}}(R) \;=\; 4\epsilon \left\{ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right\}. \tag{12}$$

The fitted parameters σ in Å and ϵ in K are displayed in the panel. Our EWP method can describe the long-range intermolecular dispersion interaction of $1/R^6$ dependence, which is impossible by the HF and difficult by the density functional method. On the other hand, the total potential energies for the configurations III and IV are simply repulsive. The former seems in accordance with the well-known 2s+2s symmetry-forbidden reaction. However, the CCSD(T) calculations [50–53] have shown small wells of ~ -20 K for III and ~ -10 K for IV. Although these shallower wells are expected to be minor in condensed phase structure and dynamics that will be dominated by the main configurations I and II, this issue should be carefully examined in future investigations. We incidentally note that, in order to describe a nonadiabatic avoided-crossing around a tetra-radical state along the configuration III, we need to relax the PP restriction, which is, however, out of the

scope of the present study.

The lower panel compares contributions of 4-body and 3-body electron exchange integrals, J_3 and J_4 shown in Appendix, to the total potential energies in the configurations I and II. It demonstrates importance of the 4-body and 3-body contributions in the repulsive energies. As the blue and yellow lines show, neglecting both the 4-body and 3-body contributions results in the absence of the repulsive force and would cause an anomalously dense hydrogen configuration. Lack of the repulsive forces becomes severe especially when the hydrogen molecules approach beyond the stable intermolecular distance and their EWPs start to overlap. Even removing the 4-body contribution makes the energy wells shallower, and the stable intermolecular distances change both in the configurations I and II. (see the green and sky-blue lines) These findings are in accord with the previous report that exchange energy is indispensable for intermolecular interaction between hydrogen molecules. [55] All our results shown hereafter were calculated using the full contributions, i.e. including the 4-body electron exchange integrals.

3.3. Rotational and translational barriers of H_2 dimer

Third, we demonstrate calculations of intermolecular multidimensional potential energy surfaces. Two representative configurations of the H_2 dimer to be examined is shown in Figure 3, in which the geometrical parameters θ and R_1 are defined. Symbol θ represents the angle between the x-axis and the molecular axis of the right-hand-side H_2 molecule on the xy plane. R_1 denotes the distance between the x-axis and the center of the right H_2 molecule whose molecular axis is parallel to the y-axis.

Figures 4 display the 2D energy surfaces as functions of (R, θ) and (R, R_1).

12

The left panels show the full potential energy surfaces including the NQEs, and the right panels show the difference between the energies with and without the NQEs. The energy well corresponding to the configuration I in Figure 2 is seen at $\theta = 0°$ in the upper (R, θ) plot. The 2D figure clearly shows how the well along R disappears as θ increases. The well almost disappears beyond $\theta = 50°$. The shallow wells appearing in the (R, R_1) plot at around the both edges of R_1 are related to the configuration II in Figure 2.

The right panels in Figure 4 show that the NQEs introduced by the NWPs systematically change the potential energy surfaces. As seen in the plots, the magnitudes of the differences are significant: at $R = 3.8$ Å passing the well bottom, the NQEs deepen the energy well by ~ 5 K at $\theta = 0$, and increase the barrier height by ~ 10 K along both θ and R_1, indicating that the intermolecular motions along these geometrical parameters are hindered by the NQEs. These features are not only quantitative but also unintuitive, i.e., contrasting with the conventional picture from nuclear quantization on a given BO potential energy surface that normally lifts the well bottom and reduces the effective barrier by the zero-point and tunneling effects. The present results arise from a non-trivial interplay between the EWP and NWP degrees of freedom. The well is deepened primarily because the bond length of H_2 monomer is elongated with the NWPs, which reduces the repulsive interaction between the NWPs and enhance the attraction between EWPs of one H_2 molecule with the NWPs of the other molecule. The increase in the barriers is also related to the elongation of the monomer bond length: the NWPs delocalized on each side of a molecule attract and broaden the EWPs, which leads to the higher potential energy barriers. A related analysis of the

13

EWPs and NWPs is given in Supplementary Material.

We will now analyze physical relationships between structures of EWPs and the 2D potential energy profiles discussed above. Figure 5 shows the x-positions of the two EWPs in the left hydrogen molecule. As they have different widths, around 0.67 Åand 0.36 Å, we define the first and second EWPs in the descending order of the width. We found that the x-positions of EWPs are systematically correlated to the energy profiles in such a way that when the potential energy well appears, the EWPs are attracted to the right hydrogen molecule. In the (R, θ) plot where the potential energy well is deeper, both the two EWPs move toward the right hydrogen molecule. The displacement of the first (broader) EWP is much larger, as the figure scales show. In the (R, R_1) case, the movement of the EWPs is smaller, reflecting the shallower potential energy well. It should be noted that the GWP width contribution is relatively minor; see discussion in Figures S3 and S4 of Supplementary Material.

3.4. Non-Born-Oppenheimer effects

Finally, we investigate the non-BO effects on the intermolecular potential energy surface in the major configuration I. Figure 6 compares the intermolecular potential energies obtained by the full non-BO calculation and the BO calculations with and without the NWPs. The red line corresponds to the section at $\theta = 0°$ of the upper-left panel in Figure 4. The BO calculation with the NWPs (green line) was performed by first optimizing the EWP structure with the point nuclei and then the resultant BO surface is used for the subsequent calculation of the NWPs. The intermolecular potential energy from the BO approximation with the NWPs (green line) exhibits the

14

shallower potential energy well than the non-BO case (red line). The difference clearly demonstrates the non-BO effects at 0 K. The configurations II, III, and IV show similar non-BO effects, as displayed in Supplementary Material, while little difference is seen in the intramolecular potential energy. The BO approximation gives the shorter monomer bond length as discussed in Figure 1, and the non-BO effects emerge mainly through the difference in such intramolecular structure. As the green and blue lines in Figure 6 show, the former energy profile is always higher than the latter, indicating a weakened intermolecular interaction by the NQEs. This is normally expected for the bound potential and in accordance with the previous BO approaches with the NQEs [5–8, 34, 36–38]. Comparison between the red and blue lines shows that the intermolecular potential energy by the non-BO with NWPs is more stable in the whole attractive part up to the long-range region, while the potential energy without the NWPs are more stable in the short range repulsive part. The shift of the potential energy profile toward the longer intermolecular distance appears similar between the non-BO and the BO with NWP, but the physical origin is obviously different and as non-trivial as the results discussed in Sec. 3.3.

The actual transport properties of condensed hydrogen systems such as viscosity and diffusion coefficients will be determined by the balance between this structural shift along R and the hindered motions along the geometrical parameters θ and R_1, as well as by effects of the collective many-body dynamics [5–8]. The higher potential energy barrier along θ caused by the NQEs and discussed in Figure 4 seems closely related to the rotational ordering in the solid hydrogen crystal predicted by the PIMD calculation [32]. On the

other hand, the increase in the barrier along R_1 could increase the shear viscosity of liquid hydrogen; in order for hydrogen molecules to generate shear motions, the molecules should be aligned parallel because the aligned hydrogen configuration lets hydrogen molecules most easily pass by one another. This is in contrast with the CMD predictions that the NQEs will suppress liquid-hydrogen crystallization [7, 8]. This different picture originates from the spherical and symmetric particle model used in the CMD simulation–the hydrogen molecule of our model can change its bond length which plays an important role in determining the overall potential energy shape. Further details on bond flexibility and the related EWP and NWP structures are discussed in Supplementary Material.

4. Concluding remarks

A theoretical framework of non-BO combination of EWPs and NWPs was developed and applied to calculations of intra- and inter-molecular potential energies of a hydrogen dimer. The NWPs yielded a sound description of significant NQEs in the intramolecular potential energy. Non-trivial interactions between the EWPs and NWPs in the non-BO framework resulted in the unintuitive intermolecular potential energy profiles. These features are notable and cannot be neglected even at 0 K, where the NWP widths are much smaller than the EWP widths. Such effects are expected to become more significant in finite-temperature dynamic simulations where the NWPs can be more delocalized dynamically. Their consequence on the quantum phase diagram including transitions and hydrodynamic properties in condensed hydrogen systems is an intriguing open problem. Our method is expected to

16

derive equations of motion with an extended Hamiltonian including auxiliary coordinates and momenta representing EWP and NWP widths, and directly simulate real-time hydrogen dynamics via both the EWP and NWP dynamics with insignificant (i.e., off the bottleneck) addition of computational cost, being suitable for studying condensed hydrogen systems. On the other hand, the current method is not suitable for describing the excited states because it assumes a simple Gaussian WP to describe an electron or a nucleus. Introduction of multi-Gaussian WPs to express a more complicated excited-state wave function is one of the possible future extensions. In addition, inclusion of quantum phase dynamics by introducing the time-dependent phase parameter and evaluating the action integral is another target of our challenge.

Acknowledgments

Appendix: Theoretical Definitions

S_{ab} in eq.(1) is the overlap integral between ϕ_a and ϕ_b;

$$
\begin{aligned}
S_{ab} &= \int \mathrm{d}\mathbf{q}_1 \phi_a^*(\mathbf{q}_1)\phi_b(\mathbf{q}_1) \tag{13} \\
&= \left(\frac{2\rho_a\rho_b}{\rho_a^2 + \rho_b^2}\right)^{\frac{3}{2}} \exp\left[-\frac{|\mathbf{r}_a - \mathbf{r}_b|^2}{4(\rho_a^2 + \rho_b^2)}\right]. \tag{14}
\end{aligned}
$$

The electron kinetic energy and the electron-electron electrostatic energy are obtained as

$$
E_{\mathrm{ke,elec}} = \frac{T_{aa} + T_{bb} + 2S_{ab}T_{ab}}{1 + S_{ab}^2}, \tag{15}
$$

17

and

$$E_{\text{ee}} = \frac{(aa|bb) + (ab|ba)}{1 + S_{ab}^2}, \tag{16}$$

respectively [21]. Here, the one-electron kinetic term is

$$T_{ab} = \frac{1}{4(\rho_a^2 + \rho_b^2)} \left(3 - \frac{|\mathbf{r}_a - \mathbf{r}_b|^2}{2(\rho_a^2 + \rho_b^2)} \right) S_{ab}, \tag{17}$$

and $(ab|cd)$ is the two-electron integral

$$
\begin{aligned}
(ab|cd) &= \int\int d\mathbf{q}_1 d\mathbf{q}_2 \phi_a^*(\mathbf{q}_1)\phi_b(\mathbf{q}_1)\frac{1}{|\mathbf{q}_1 - \mathbf{q}_2|}\phi_c^*(\mathbf{q}_2)\phi_d(\mathbf{q}_2) &(18)\\
&= \pi^3 N_a N_b N_c N_d \left(\alpha + \beta\right)^{-3/2} \left(\gamma + \delta\right)^{-3/2} |\mathbf{r}_{\text{p}} - \mathbf{r}_{\text{q}}|^{-1} \\
&\quad \times \exp[-\alpha\beta(\alpha + \beta)^{-1}|\mathbf{r}_a - \mathbf{r}_b|^2 - \gamma\delta(\gamma + \delta)^{-1}|\mathbf{r}_c - \mathbf{r}_d|^2] \\
&\quad \times \text{erf}[(\alpha + \beta)^{1/2}(\gamma + \delta)^{1/2}(\alpha + \beta + \gamma + \delta)^{-1/2}|\mathbf{r}_{\text{p}} - \mathbf{r}_{\text{q}}|] &(19)
\end{aligned}
$$

with $\gamma \equiv 1/4\rho_c^2$, $\delta \equiv 1/4\rho_d^2$, and

$$\mathbf{r}_{\text{p}} \equiv \frac{\alpha\mathbf{r}_a + \beta\mathbf{r}_b}{\alpha + \beta}, \quad \mathbf{r}_{\text{q}} \equiv \frac{\gamma\mathbf{r}_c + \delta\mathbf{r}_d}{\gamma + \delta}. \tag{20}$$

The n-electron exchange integrals are defined as

$$J_0 = (abcd|H|abcd), \tag{21}$$

and

$$
\begin{aligned}
J_2 &= (abcd|H|bacd) + (abcd|H|abdc) \\
&\quad - \frac{1}{2}\{(abcd|H|cbad) + (abcd|H|dbca) + (abcd|H|acbd) + (abcd|H|adcb)\},
\end{aligned}
\tag{22}
$$

and

$$
\begin{aligned}
J_3 &= -\frac{1}{2}\{(abcd|H|cabd) + (abcd|H|bdca) + (abcd|H|dbac) + (abcd|H|acdb) \\
&\quad + (abcd|H|bcad) + (abcd|H|dacb) + (abcd|H|cbda) + (abcd|H|adbc))\},
\end{aligned}
\tag{23}
$$

18

and

$$J_4 = (abcd|H|badc) + (abcd|H|cdab) + (abcd|H|dcba) + (abcd|H|cdba) + (abcd|H|dcab)$$
$$- \frac{1}{2}\{(abcd|H|bcda) + (abcd|H|bdac) + (abcd|H|cadb) + (abcd|H|dabc)\}. \tag{24}$$

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Figure Captions

Figure 1: Total potential energy of H_2 molecule as a function of internuclear distance. The potential energy with NWPs (red line) and the potential energy without the NWPs (i.e., classical particle nuclei, green line) exhibit energy difference larger than 5.83×10^3 K around the potential energy wells. The bond length is 0.744 Å with the NWPs and 0.704 Å without the NWPs. The former is close to the corresponding experimental bond length, 0.751 Å.

Figure 2: (top) Four representative configurations of two interacting hydrogen molecules. (upper panel) Intermolecular potential energy as a function of intermolecular distance between the molecular centers R. The configurations I and II exhibit energy wells, while the configurations III and IV show simple repulsive potential energies. The former two potential energies can be well fitted by the long-range LJ intermolecular energy functions. (lower panel) Contributions of 4-body and 3-body electrons to the total potential energies in the configurations I and II. Lack of the 4-body and 3-body contributions results in the absence of the repulsive force. Removal of the 4-body contribution makes the potential energy wells shallower.

Figure 3: Two representative configurations for the multidimensional intermolecular potential energy surfaces of two diatomic hydrogens. The geometrical parameters θ and R_1 are graphically defined with the intermolecular distance between the molecular centers R.

Figure 4: (left panels) 2D potential energy surfaces along the geometrical parameters and the intermolecular distance between the molecular centers R. Full potential energy surfaces include the NQEs introduced by the NWPs. The upper panel shows how the deep well disappears as the geometrical parameter θ increases. (right panels) Difference between the full potential energies and the corresponding energies without the NQEs. The difference is shown as three sections at the displayed intermolecular distances.

Figure 5: X-positions of two EWPs in the left hydrogen molecule in Figure 3. The x-positions are systematically correlated to the corresponding energy wells shown in Figure 4.

Figure 6: Non-BO effects on the intermolecular potential energy as a function of the intermolecular distance R. Introducing the NWPs with the BO approximation leads to the potential energy well shallower than that based on the non-BO calculation. The full energy profile with the NWPs exhibits the intermolecular coupling along R weaker than that without the NWPs.