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Time-dependent density functional theory based Ehrenfest dynamics with atom-centered basis functions is developed in present work. The equation of motion for electrons is formulated in terms of first-order reduced density matrix and an additional term arises due to the time-dependence of basis functions through their dependence on nuclear coordinates. This time-dependence of basis functions together with the imaginary part of density matrix leads to an additional term for nuclear force. The effects of the two additional terms are examined by studying the dynamics of H_2 and C_2H_4, and it is concluded that the inclusion of these two terms is essential for correct electronic and nuclear dynamics. © *2011 American Institute of Physics*. [doi:10.1063/1.3615958]

I. INTRODUCTION

Born-Oppenheimer molecular dynamics (BOMD) and extended Lagrangian molecular dynamics[1–3] are extensively used to describe processes when the systems are constrained to the ground state or a certain excited state potential energy surface. However, these methods cannot be applied to non-adiabatic processes where several potential energy surfaces are involved or where a rapidly varying time-dependent external field is present. To properly describe these processes, surface hopping method[4–9] or Ehrenfest dynamics[8–21] have been developed. A detailed comparison of these two approaches can be found in the review article by Hack and Trular.[8] Furthermore, surface hopping is found to be more appropriate to describe reactions passing through close lying electronic states while ending at well-separated states such as photoisomerisation, whereas Ehrenfest dynamics is more appropriate to the statistical averages of the dynamics. However, one must calculate the energies, nuclear forces of several involved states and the non-adiabatic couplings between these states in surface hopping method, which renders the method intractable for large systems. On the other hand, in Ehrenfest dynamics, electrons follow the time-dependent Schrödinger equation and the nuclei move on an averaged potential surface that involves several electronic states. It is thus conceptually simpler and can be readily applied to larger systems.

For a many-electron system such as atoms and molecules, approximations have to be employed to solve the time-dependent Schrödinger equation. Time-dependent density functional theory (TDDFT) (Ref. 22) has shown to be a reasonably good method by mapping a time-dependent interacting many-electron system to a non-interacting system. In principle TDDFT is not applicable to the case involving nuclei motions,[23] and instead, multi-component TDDFT (Refs. 24 and 25) should be used. Nonetheless, TDDFT based Ehren-

fest dynamics still provides an attractive method to deal with non-adiabatic processes.

TDDFT-based Ehrenfest dynamics has been implemented mostly in methods employing plane wave basis set.[10–14] Whereas the electron dynamics and the nuclear forces are readily evaluated using plane wave basis set, pseudopotential has to be adopted to describe core electrons. On the other hand, the methods employing atom-centered basis functions, e.g., Gaussian functions and Slater functions, are more efficient for finite systems such as atoms or molecules. In the present work, a TDDFT-based Ehrenfest dynamics employing atom-centered Gaussian basis set is developed. Compared with previous works,[15, 19, 21] we propagate the first-order reduced single electron density matrix in time domain together with the movement of basis functions. This makes linear-scaling or order-N (O(N)) (Refs. 26–28) implementation of Ehrenfest dynamics possible. Furthermore, nuclear forces can also be formulated readily in terms of density matrix and the imaginary part of density matrix is shown to contribute to the nuclear forces due to the moving basis set. The resulting Ehrenfest dynamics is applied to simulate the dynamics of H_2 and C_2H_4.

II. METHOD

A. Basic equations

For a mixed quantum-classical system where the electrons are moving in a mean field, such as that of Hartree-Fock (HF) approximation or density-functional theory (DFT),[29, 30] the Lagrangian can be written as[21]

$$L = \sum_A \frac{1}{2} M_A \dot{\vec{R}}_A^2 - U_N + \sum_i \langle \varphi_i | i \frac{\partial}{\partial t} | \varphi_i \rangle - E_{elec}, \quad (1)$$

where M_A and $\vec{R}_A$ are the mass and position of nucleus A, U_N is the potential energy of nuclei including nucleus-nucleus repulsion energy and the external potential, φ_i is the ith occupied molecular orbital and E_{elec} is the electronic energy. With

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the nuclear coordinates $\{\vec{R}_A\}$ and the molecular orbital wavefunctions $\{\varphi_i\}$ as the basic variables, we have the following equations of motion for nuclei and electrons:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\varphi}_i} = \frac{\partial L}{\partial \varphi_i} \Rightarrow i\frac{\partial \varphi_i}{\partial t} = h_{elec}\varphi_i, \qquad (2)$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\vec{R}}_A} = \frac{\partial L}{\partial \vec{R}_A} \Rightarrow M_A\ddot{\vec{R}}_A = -\frac{\partial U_N}{\partial \vec{R}_A} - \frac{\partial E_{elec}}{\partial \vec{R}_A}, \qquad (3)$$

where h_{elec} in Eq. (2) is the effective one-electron Hamiltonian determined by the form of E_{elec}. It can be seen that Eq. (2) is just the time-dependent Hartree-Fock (TDHF) or Kohn-Sham (TDKS) equation for electronic part. Using the fact that h_{elec} is Hermitian, the orthonormality condition for molecular orbitals $\{\varphi_i\}$ can be satisfied automatically at any time if they are orthonormal at the initial time. As in most quantum chemistry calculations, the molecular orbitals are expanded with atom-centered basis functions such as Gaussian functions or Slater functions:

$$\varphi_i(\vec{r}, t) = \sum_\mu c_{\mu\,i}(t)\chi_\mu(\vec{r} - \vec{R}_{A_\mu}(t)), \qquad (4)$$

where $\{c_{\mu i}\}$ are the molecular orbital coefficients and χ_μ is the atomic orbital. Using the nuclear coordinates $\{\vec{R}_A\}$ and the molecular orbital coefficients $\{c_{\mu i}\}$ as the basic variables, we can have the following equations:[15]

$$iS\dot{C}_{AO} + iBC_{AO} = F_{AO}C_{AO}, \qquad (5)$$

$$M_A\ddot{\vec{R}}_A = -\frac{\partial U_N}{\partial \vec{R}_A} - Tr\left(\frac{\partial h}{\partial \vec{R}_A} + \frac{1}{2}\frac{\partial G}{\partial \vec{R}_A}\right)P_{AO}$$
$$- \frac{\partial E_{XC}}{\partial \vec{R}_A} + Tr(S^{-1}F_{AO}P_{AO}B_A^+ + P_{AO}F_{AO}S^{-1}B_A)$$
$$+ iTr\,P_{AO}(C_A^+ - C_A + B^+S^{-1}B_A - B_A^+S^{-1}B), \qquad (6)$$

where C_{AO} is the molecular orbital coefficient matrix in atomic orbital, F_{AO} is the Fock matrix in atomic orbital, S is the overlap matrix, h is the one-electron part of the Fock matrix, G is the Coulomb matrix, E_{xc} is the exchange-correlation (XC) energy in DFT, P_{AO} is the density matrix in atomic orbital representation. Note that adiabatic approximation[31] is already adopted for the XC energy in Eqs. (5) and (6). The B, B_A, and C_A matrices are defined as follows:

$$(B_A)_{\mu\nu} = \left\langle\chi_\mu \left| \frac{\partial \chi_\nu}{\partial \vec{R}_A}\right.\right\rangle, \quad B_{\mu\nu} = \left\langle\chi_\mu \left| \frac{\partial \chi_\nu}{\partial t}\right.\right\rangle$$
$$= \sum_A (B_A)_{\mu\nu} \cdot \vec{v}_A,$$

$$(C_A)_{\mu\nu} = \left\langle\frac{\partial \chi_\mu}{\partial t} \left| \frac{\partial \chi_\nu}{\partial \vec{R}_A}\right.\right\rangle = \sum_B \left\langle\frac{\partial \chi_\mu}{\partial \vec{R}_B} \left| \frac{\partial \chi_\nu}{\partial \vec{R}_A}\right.\right\rangle \cdot \vec{v}_B, \quad (7)$$

where $\vec{v}_A$ is the velocity of nucleus A. Equation (5) is just the TDKS equation in matrix form with an additional contribution due to the moving basis set. The RHS of Eq. (6) is the expression for forces acting on nuclei, where the fourth term

is due to the dependence of basis functions on nuclear coordinates, and the last term stems from the imaginary part of the density matrix as well as the moving basis functions. For ground state density matrix, which is real, the last term on the RHS of Eq. (6) vanishes. In addition, the ground state density matrix satisfies $F_{AO}P_{AO}S = SP_{AO}F_{AO}$ and the nuclear force in Eq. (6) becomes

$$\vec{F}_A = -\frac{\partial U_N}{\partial \vec{R}_A} - Tr\left(\frac{\partial h}{\partial \vec{R}_A} + \frac{1}{2}\frac{\partial G}{\partial \vec{R}_A}\right)P_{AO}$$
$$- \frac{\partial E_{XC}}{\partial \vec{R}_A} + Tr\left(S^{-1}F_{AO}P_{AO}\frac{\partial S}{\partial \vec{R}_A}\right). \qquad (8)$$

This is just the expression for the ground state nuclear force in DFT used in BOMD. Unlike the formulation for the nuclear force used in some previous extended Lagrangian molecular dynamics[3] or Ehrenfest dynamics,[19] the nuclear force from the present formulation is invariant with respect to unitary transformation of basis functions. This is because that for the extended Lagrangian molecular dynamics proposed in Ref. 3, the density matrix in orthogonal basis functions is chosen as basic variables and the results of the dynamics and the nuclear force would thus depend on how the basis functions are orthogonalized. For the Ehrenfest dynamics proposed in Ref. 19, the basic equations are not derived from the Lagrangian and the derivative of the density matrix in orthogonal basis functions with respect to nuclear coordinate are not included in the derivation of nuclear forces. On the other hand, the molecular orbitals are chosen as basic variables and the results of the dynamics as well as the nuclear forces will not depend on unitary transformation of basis functions with the present formalism.

The equation of motion (EOM) for electrons can be readily expressed through the first-order density matrix. For fixed basis functions, the EOM for electrons can be written as

$$i\dot{P}_{OR} = [F_{OR}, P_{OR}], \qquad (9)$$

where P_{OR} and F_{OR} are the corresponding density matrix and Fock matrix in orthonormal basis set, respectively. Using the following relations for P_{OR} and the overlap matrix S together with Eq. (5),

$$S = (S^{1/2})^+ S^{1/2}, \quad P_{OR} = S^{1/2}P_{AO}(S^{1/2})^+$$
$$= S^{1/2}C_{AO}nC_{AO}^+(S^{1/2})^+, \quad (10)$$

the EOM for electrons based on P_{OR} takes the following form:

$$i\dot{P}_{OR} = (F_{OR} + iD)P_{OR} - P_{OR}(F_{OR} - iD^+),$$
$$D = \dot{S}^{1/2}S^{-1/2} - (S^{-1/2})^+ BS^{-1/2}. \qquad (11)$$

From the relation: $\dot{S}^{1/2}S^{-1/2} + S^{1/2}\dot{S}^{-1/2} = 0$, D matrix is shown to be anti-symmetric. Equation (11) can thus be written as

$$i\dot{P}_{OR} = [F_{OR} + iD, P_{OR}]. \qquad (12)$$

As $F_{OR} + iD$ is Hermitian, the idempotency condition for P_{OR} can be preserved as long as the initial density matrix is idempotent. Depending on the way of orthogonalization of

atomic orbitals, $\dot{S}^{1/2}$ can be calculated differently. In the case of Löwdin orthonormalization, we have[2,19]

$$\dot{S}^{1/2} = \sum_A \frac{dS^{1/2}}{d\vec{R}_A} \cdot \vec{v}_A$$

$$= \sum_A \sum_{ij} s_i \frac{1}{\sigma_i^{1/2} + \sigma_i^{1/2}} \left(s_i^T \frac{dS}{d\vec{R}_A} s_j \right) s_j^T \cdot \vec{v}_A, \quad (13)$$

where s_i and σ_i are the ith eigenvector and eigenvalue of the overlap matrix S, respectively. In the case of Cholesky transformation, $\dot{S}^{1/2}$ and $S^{-1/2}$ are both upper triangular matrices and hence $\dot{S}^{1/2}S^{-1/2}$ is also upper triangular matrix. D matrix is an anti-symmetric matrix and can thus be determined by

$$D_{ij} = \begin{cases} [-(S^{-1/2})^+ B S^{-1/2}]_{ij} & i > j, \\ -D_{ji} & i < j. \end{cases} \quad (14)$$

It is worth noting that the results of Eq. (12) may be different with Löwdin orthonormalization or Cholesky transformation. This difference only arises from numerical errors in solving Eq. (12) since it is equivalent to Eq. (5), whose accurate solution does not depend on how the basis functions are orthogonalized. In our implementation, Cholesky transformation is adopted and Eq. (14) is used to calculate the D matrix.

B. Numerical solution

For the electronic part, any numerical method designed for Eq. (9) can also be applied to Eq. (12). In the present work, we adopt the exponential midpoint method (EMM) (Ref. 32) to solve Eq. (12). In EMM, the density matrix is calculated as

$$P_{OR}(t + \Delta t) = e^{-i(F_{OR}(t+\Delta t/2)+iD(t+\Delta t/2))\Delta t}$$
$$\times P_{OR}(t)e^{i(F_{OR}(t+\Delta t/2)+iD(t+\Delta t/2))\Delta t}, \quad (15)$$

To calculate the Fock matrix at time $t + \Delta t/2$, one can either use extrapolation or evaluate the density matrix at time $t + \Delta t/2$. Based on our experience, a higher accuracy can be achieved by first calculating the density matrix at time $t + \Delta t/2$ by applying the following equation:

$$P_{OR}(t + \Delta t/2) = e^{-i(F_{OR}(t)+iD(t))\Delta t/2}$$
$$\times P_{OR}(t)e^{-i(F_{OR}(t)+iD(t))\Delta t/2}, \quad (16)$$

and $P_{OR}(t + \Delta t/2)$ is in turn used to evaluate the Fock matrix $F_{OR}(t + \Delta t/2)$. Furthermore, higher order methods such as Magnus method[32] could also be used to solve Eq. (12). The exponential of $F_{OR} + iD$ is calculated by diagonalizing $F_{OR} + iD$. The dimension of this matrix is not large since the atomic orbital is used as basis set. Otherwise, alternative methods such as Lancoz method[32] have to be used.

One of the most popular methods for nuclear motion in molecular dynamics is the velocity Verlet method:[33]

$$\vec{v}_A(t) = \vec{v}_A(t - \Delta t) + \frac{1}{2M_A}[\vec{F}_A(t) + \vec{F}_A(t - \Delta t)]\Delta t, \quad (17)$$
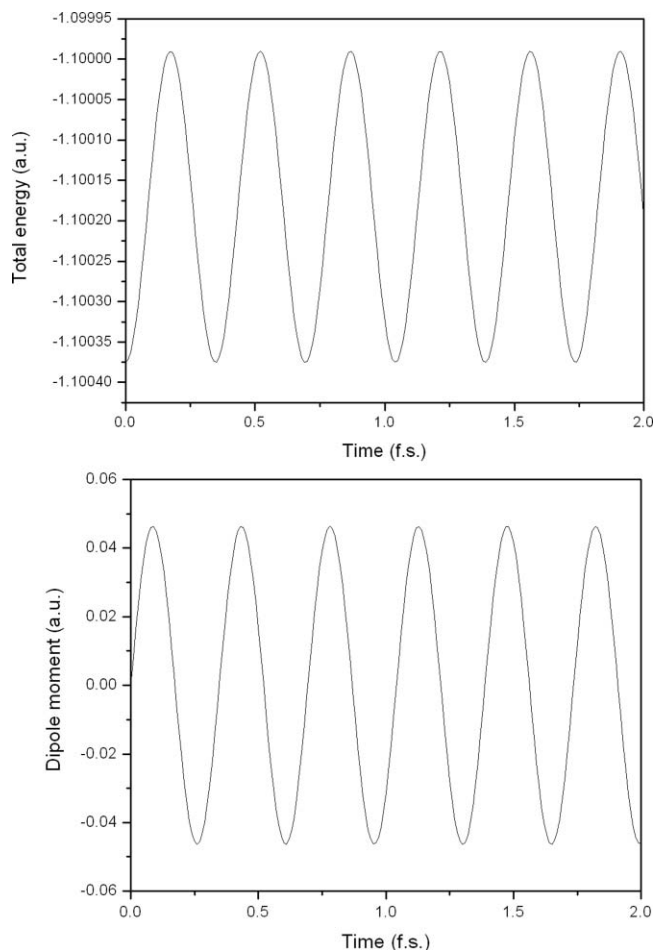

FIG. 1. The total energy and dipole moment of a translational H_2 molecule.

$$\vec{R}_A(t + \Delta t) = \vec{R}_A(t) + \vec{v}_A(t)\Delta t + \frac{1}{2}\frac{\vec{F}_A(t)}{M_A}(\Delta t)^2. \quad (18)$$

From Eq. (17) it can be seen that the nuclear velocity at time t depends on nuclei forces at the same time, while nuclei forces at time t depend in turn on nuclear velocity at time t according to Eqs. (6) and (7). In our implementation, we use the following form of nuclear velocity to evaluate matrices B and C_A in Eqs. (6) and (7) at time t:

$$\vec{v}_A'(t) = \vec{v}_A(t - \Delta t) + \frac{\vec{F}_A(t - \Delta t)}{M_A}\Delta t. \quad (19)$$

The error should be negligible since this additional force term is relatively small. Furthermore, typical time step for nuclear movement is ~0.5 fs, while it is ~0.01 fs for electrons. To achieve high efficiency, the same strategy as in Ref. 19 is used. Three time steps are adopted in the propagation of nuclear and electron motions: t_N, t_e, and t_{Ne}, which are the time step for nuclear movement, the time step for electron propagation, and the time step within which positions of the nuclei are fixed, respectively. Specifically, t_N is the time step used in Eqs. (17) and (18), t_e is the time step used in Eqs. (15) and (16). The change of nuclear coordinates during the propagation of electron movement within time step t_N is
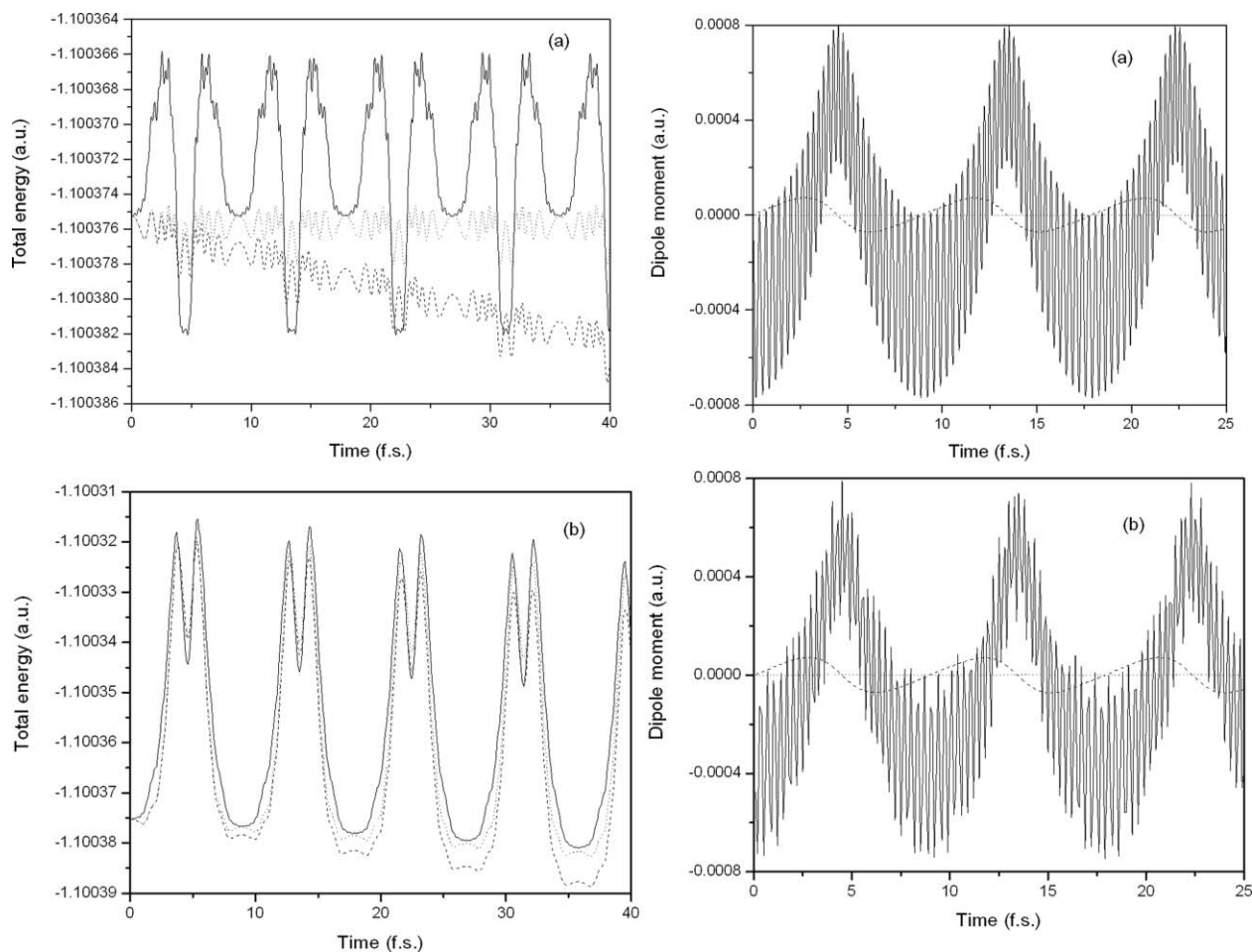
FIG. 2. The total energy and dipole moment of a vibrating H_2 (a: Results with small time step, b: results with large time step, dot line: including both the D term and the additional force term, dash line: including only the D term, solid line: neglect both the D term and the additional force term).

taken into account at a time step of t_{Ne} to reduce the number of calculations of all the related matrices and integrals, especially the two-electron integrals. In the propagation of the electron motion from t to $t + \Delta t_N$, the nuclear velocities at intermediate time are required to evaluate the D matrix (see Eq. (14)). In our implementation, the velocities within t_{Ne} are held as constants and calculated with a formula similar to Eq. (19) at the midpoint of the time step t_{Ne}.

III. RESULTS AND DISCUSSION

Eqs. (6), (7) and (12) are solved and implemented based on methods described in previous section in our in-house LODESTAR software package.[34] In previous Ehrenfest dynamics implementations with atom-centered basis functions,[19] the D term in Eq. (12) and the last term on the RHS of Eq. (6) are neglected. However, the computational effort for these two terms is relatively small compared to that for two-electron integrals, since only evaluation of the overlap matrix and its derivatives as well as matrix multiplications are involved. To demonstrate the effect of the two terms, we study the translational and vibrational motion of a H_2 molecule. In the following calculations, 6-31G basis set is used, and local density approximation (LDA) (Refs. 35 and 36) is adopted for the XC energy. The ground state density matrix is set as the

initial density matrix which commutes with the initial ground state Fock matrix. However, if the initial velocities of the nuclei are nonzero, the D term becomes nonzero and the time derivatives of the density matrix at the initial time are thus nonzero as well. When the D matrix is neglected, the time derivative of the density matrix at the initial time will be zero. To demonstrate this, we simulate the translational motion of H_2. The inter-nuclear distance is fixed at 1.1 Å and the initial kinetic energy of nuclei is set as 0.2178 a.u., and the nuclei are moving in the same direction as the molecular axis. The total energy and dipole moment along the molecular axis are calculated and plotted in Fig. 1. It can be seen that the total energy is not conserved and the dipole moment is nonzero when the D term is included. One would expect the total energy to be conserved from the derivation of the basic equations. However, it should be noted that the inter-nuclear distance is fixed in this simulation in order to investigate the effect of translational motion alone. The total energy is thus not conserved in this simulation. If the inter-nuclear distance is allowed to change due to the nonzero nuclear force, the total energy is then conserved. On the other hand, with the D term in Eq. (12) being neglected, the total energy is conserved and the dipole moment is always zero. The result shown in Fig. 1 demonstrates that the translational movement would cause the change of the electron states in the present formulation. This
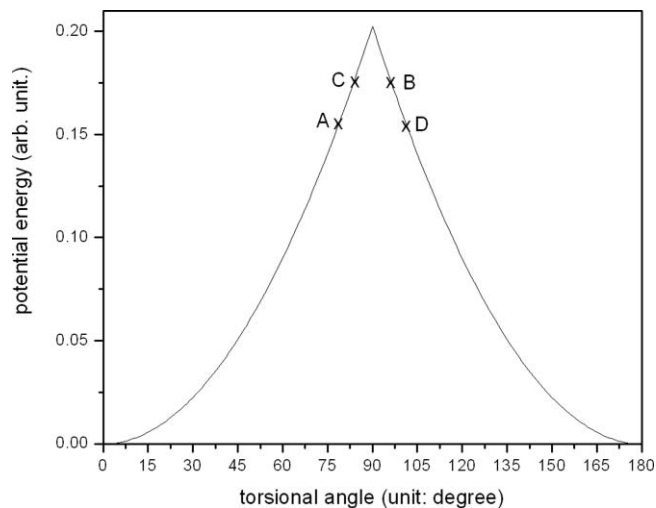
FIG. 3. The potential energy surface with respect to the torsional angle. This figure is only used to indicate why the total energy is not conserved in BOMD.

FIG. 4. The total energy and torsional angle (solid line: results of Ehrenfest dynamics, dash line: results of BOMD).

unphysical result arises from the initial density matrix used in the calculation. When the system is in a translational motion, the ground state density matrix should commute with $F_{OR} + iD$ instead of the Fock matrix alone! The time derivative of the molecular orbital on the LHS in Eq. (2) leads to an explicit dependence of molecular orbital on the moving nuclear coordinates. This shows that the D term is critical in Ehrenfest dynamics with atom-centered basis functions. We study further the vibrational motion of H_2 with initial bond length at 1.1 Å and zero initial nuclear velocity. To investigate the effect of D term and the last term of Eq. (6), we performed the following calculations. A: Both terms are included, B: only the D term is included; and C: both terms are neglected. Two sets of time step are employed for all three cases: $\{t_N = 0.01\,\text{fs}, t_{Ne} = 0.002\,\text{fs}, t_e = 0.001\,\text{fs}\}$ and $\{t_N = 0.1\,\text{fs}, t_{Ne} = 0.01\,\text{fs}, t_e = 0.001\,\text{fs}\}$. The calculated total energy and total dipole moment with respect to time are plotted in Fig. 2. For small time step, the total energy is conserved for case A where both D term and the last term of Eq. (6) are kept, while energy is not conserved for both cases B and C. In particular, energy drifts for case B in which only D term is kept. For large time step, the performances for cases A and C are similar in terms of total energy, while energy drifts again for case B. As for the dipole moment, since the centro-symmetry is kept during the vibrational motion of H_2, the total dipole moment should remain zero during the time propagation. However, the calculated dipole moment is zero only in the case of A. All these show the importance of D term in Eq. (12) and the last term in Eq. (6).

To demonstrate the different behavior of Ehrenfest dynamics and BOMD, we also simulate the rotation of CH_2 fragments around the C = C bond in C_2H_4. Very small time steps are adopted here, $\{t_N = 0.02\,\text{fs}, t_{Ne} = 0.001\,\text{fs}, \text{and } t_e = 0.0001\,\text{fs}\}$, to reduce the numerical error. The initial velocities of carbon atoms are set as zero and the initial speeds for the four hydrogen atoms are set equal and along the direction perpendicular to the molecular plane. When the initial kinetic energy is not large enough for
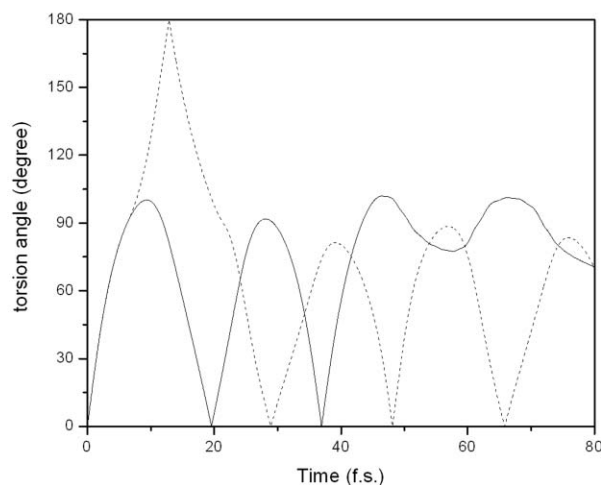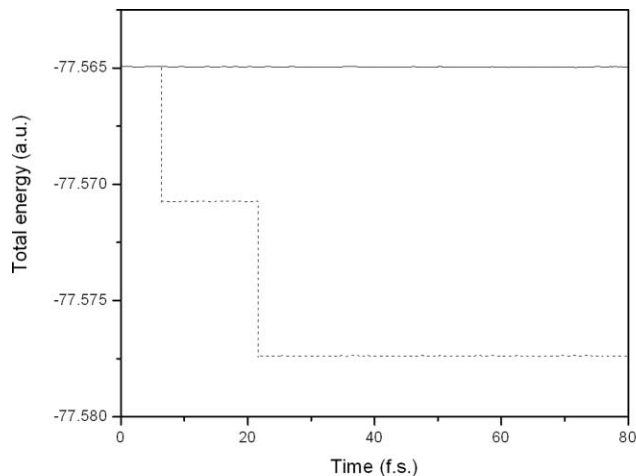
the torsional angle ϕ around the C = C bond to exceed $\pi/2$, the trajectories due to Ehrenfest dynamics and the BOMD are almost the same. However, when the initial kinetic energy is large enough, significant difference arises. This is easy to understand since when ϕ equals to $\pi/2$, the ground state and excited state are actually degenerate and Born-Oppenheim dynamics is thus no longer applicable. Furthermore, the self-consistent field (SCF) calculation in BOMD is difficult to converge when ϕ is very close to $\pi/2$. Even with converged results, the potential energy surface is not smooth at the point $\phi = \pi/2$ using spin restricted DFT or HF method[37] so that there is no well-defined nuclear force at this point. In the simulation it is rare that the torsional angle ϕ is exactly equal to $\pi/2$ at a certain time step and the total energy is, however, not conserved when the torsional angle ϕ goes across $\pi/2$. This can be understood from Fig. 3 and Eq. (17). When the system goes from point A to point B, the change of the velocity is almost zero since the forces on point A and point B are in opposite direction. However, the potential energy increases so that the total energy will increase. On the other hand, when the system goes from point C to point D, the total energy will decrease for the same reason. This could be alleviated by using smaller time step. However, when the time step is
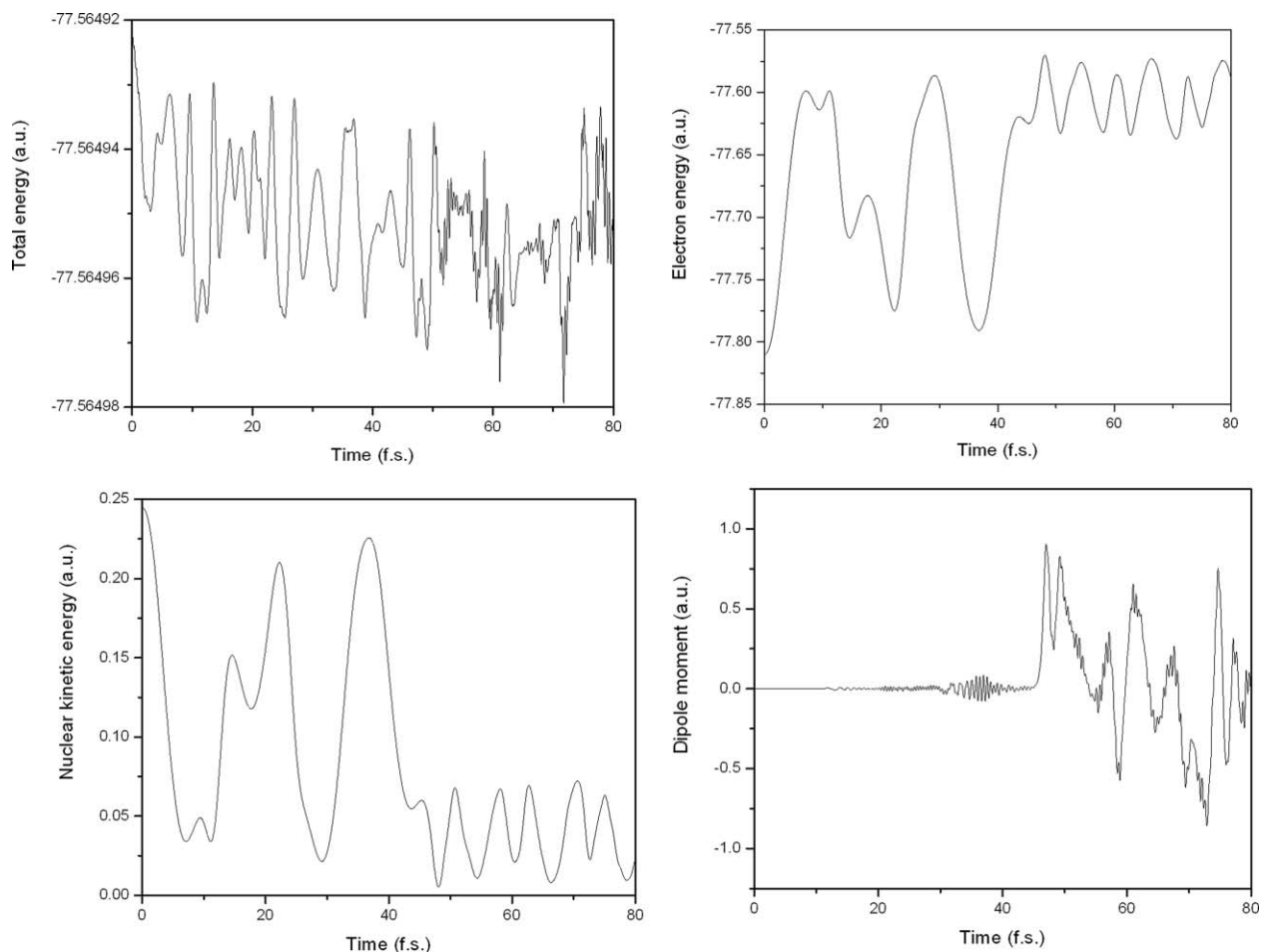
FIG. 5. The total energy, the electronic energy, the nuclear kinetic energy, and the total dipole moment of C_2H_4.

too small so that the torsional angle comes too close to $\pi/2$ at certain time steps, the SCF convergence problem in BOMD would show up. With Ehrenfest dynamics, such scenario does not occur. The total energy and the torsional angle ϕ calculated with BOMD and Ehrenfest dynamics are plotted in Fig. 4 with an initial kinetic energy of 0.245 a.u. It can be seen that the total energy of BOMD changes significantly when ϕ goes across $\pi/2$, while the total energy is conserved in the case of Ehrenfest dynamics. The torsional angle ϕ in the BOMD simulations changes from 0 to π as long as ϕ goes across $\pi/2$. However, with Ehrenfest dynamics, the system rotates back once it crosses $\pi/2$ and the torsion angle never reaches π. In another word, the CH_2 fragment could not be fully turned over in C_2H_4 in the Ehrenfest dynamics simulations. This is probably due to that the excited state has minimum at $\phi = \pi/2$ and when ϕ goes across $\pi/2$, the excited state has significant contribution in the electron state so that the system could not be fully turned over. The total energy, the electronic energy and nuclear kinetic energy as well as the dipole moment along the C–C direction are plotted in Fig. 5. It can be seen clearly that energy transfers from nuclei to electrons at around 50 fs. As for the dipole moment, although the system has a centro-symmetry center, small oscillation of the dipole moment can be observed before 50 fs. A large change in dipole moment happens when the energy is transferred from nuclei to electrons.

IV. CONCLUSION

In the present work, the TDDFT based Ehrenfest dynamics with atom-centered basis set is developed. The EOM for electron is formulated in terms of the first-order density matrix in orthonormal basis functions. Time-dependence of the basis functions due to its dependence on the nuclear coordinates is taken into account which results in a D term in the EOM for electrons and an addition contribution to the nuclear forces. This additional force term arises from the imaginary part of the density matrix and the moving basis set. These two additional terms can be easily implemented since they only involve the derivatives of the overlap matrix with respect to nuclear coordinate and simple matrix multiplication. To solve the EOM numerically, the EMM approach is adopted for electron dynamics, and the velocity Verlet is applied for the motions of nuclei. The idempotency condition for the density matrix can be kept with the EMM method. The same strategy as in Ref. 19 is adopted for time steps of nuclei and electron dynamics to achieve high efficiency.

The effects of the D term and the additional force term are studied by investigating translational and vibrational motions of H_2. The results indicates that it is critical to remove translational motion using Ehrenfest dynamics with atom-centered basis functions and simulations including these two terms provides much better conserved total energy and reasonable

dipole moment for vibrational motion of H_2. The rotation of CH_2 fragments along the C=C bond in C_2H_4 is studied to demonstrate the difference between Ehrenfest dynamics and BOMD. Significant difference arises if the initial kinetic energy is large enough for the torsional angle of rotation to exceed $\pi/2$. A jump in total energy happens each time when the torsional angle of rotation goes across $\pi/2$ in BOMD simulations, while total energy is conserved in Ehrenfest dynamics simulations. Furthermore, CH_2 fragment cannot be fully turned over in C_2H_4 in Ehrenfest dynamics and energy transfers from nuclei to electron. Small oscillation in the dipole moment for this centro-symmetric system is observed before the energy transfer and significant change in dipole moment arises at the time of energy transfer.

One important advantage of our Ehrenfest dynamics formalism is the usage of first-order density matrix. Our earlier work shows that O(N) calculation is possible for the time evolution of the first-order density matrix.[38] The O(N) algorithm has been implemented at semiempirical[39] and DFT levels.[40] As both the electronic and nuclear dynamics are integrated in time domain, it may thus be straightforward to develop O(N) Ehrenfest dynamics method. The result O(N) Ehrenfest dynamics method can be possibly applied to complex systems, for instance, charge transfer process in biological molecules. As the molecular systems of our interests are ever complex, the energy separations of the ground and excited states could be much less compared to the thermal energy at room temperature, the exact energy of a particular electronic state is no longer important. Rather, we are interested in the statistical average and fluctuation of energy or other physical properties. Ehrenfest dynamics is ideal to account for the statistical nature of electronic and nuclear motions. Therefore, O(N) Ehrenfest dynamics is expected to be a potentially very useful tool to evaluate the statistics properties of complex systems. Work along this direction is in progress.

ACKNOWLEDGMENTS

[1] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[2] H. B. Schlegel, J. M. Millam, S. S. Iyengar, G. A. Voth, A. D. Daniels, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **114**, 9758 (2001).

[3] J. M. Herbert and M. Head-Gordon, J. Chem. Phys. **121**, 11542 (2004).

[4] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

[5] N. L. Doltsinis and D. Marx, Phys. Rev. Lett. **88**, 166402 (2002)

[6] C. F. Craig, W. R. Duncan, and O. V. Prezhdo, Phys. Rev. Lett. **95**, 163001 (2005).

[7] E. Tapavicza, I. Tavernelli, and U. Rothlisberger, Phys. Rev. Lett. **98**, 023001 (2007).

[8] M. D. Hack and D. G. Trular, J. Phys. Chem. A **104**, 7917 (2000)

[9] A. W. Jasper, S. Nangia, C. Zhu, and D. G. Trular, Acc. Chem. Res. **39**, 101 (2006).

[10] W. R. Duncan and O. V. Prezhdo, J. Phys. Chem. B **109**, 17998 (2005).

[11] A. Castro, M. A. L. Marques, J. A. Alonso, G. F. Bertsch, and A. Rubio, Eur. Phys. J. D **28**, 211 (2004).

[12] I. Tavernelli, U. F. Röhrig, and U. Rothlisberger, Mol. Phys. **103**, 963 (2005).

[13] Y. Tateyama, N. Oyama, T. Ohno, and Y. Miyamoto, J. Chem. Phys. **124**, 124507 (2006).

[14] Y. Miyamoto, A. Rubio, and D. Tománek, Phys. Rev. Lett. **97**, 126104 (2006).

[15] T. Kunert and R. Schmidt, Eur. Phys. J. D **25**, 15 (2003).

[16] T. Kunert, F. Crossmann, and R. Schmidt, Phys. Rev. A 023422 (2005).

[17] J. Handt, T. Kunert, and R. Schmidt, Chem. Phys. Lett. **428**, 220 (2006).

[18] Y. Zhao, S. Yokojima, and G. Chen, J. Chem. Phys. **113**, 4016 (2000).

[19] X. Li, J. C. Tully, H. B. Schlegel, and M. J. Frisch, J. Chem. Phys. **123**, 084106 (2005).

[20] C. M. Isborn, X. Li, and J. C. Tully, J. Chem. Phys. **126**, 134307 (2007).

[21] T. A. Niehaus, D. Heringer, B. Torralva, and T. Frauenheim, Eur. J. Phys. D, **35**, 467 (2005).

[22] E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).

[23] A. K. Dhara and S. K. Ghosh, Phys. Rev. A **35**, 442 (1987).

[24] T. Kreibich and E. K.U. Gross, Phys. Rev. Lett. **86**, 2984 (2001).

[25] O. Butriy, P. L. de Boeij, R. van Leeuwen, and E. K. U. Gross, Phys. Rev. A **76**, 052514 (2007).

[26] W. Yang and J. M. Pérez-Jordá, in *Encyclopedia of Computational Chemistry*, edited by P. Schleyer (Wiley, New York, 1998), pp. 1496–1513.

[27] G. E. Scuseria, J. Phys. Chem. A **103**, 4782 (1999).

[28] S. Goedeck, Rev. Mod. Phys. **71**, 1085 (1999).

[29] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[30] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[31] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, J. Chem. Phys. **120**, 5932 (2004).

[32] A. Castro, M. A. L. Marques, and A. Rubio, J. Chem. Phys. **121**, 3425 (2004).

[33] L. Verlet, Phys. Rev. **159**, 98 (1967).

[34] G. H. Chen, C. Y. Yam, S. Yokojima, W. Z. Liang, X. J. Wang, F. Wang, and X. Zheng, LODESTAR v1.0, download via http://yangtze.hku.hk/new/software.php.

[35] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[36] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[37] Y. Shao, M. Head-Gordon, and A. Krylov, J. Chem. Phys. **118**, 4807 (2003).

[38] S. Yokojima and G. H. Chen, Chem. Phys. Lett. **292**, 379 (1998); S. Yokojima and G. H. Chen, **59**, 7259 (1999); W. Z. Liang, S. Yokojima, M. F. Ng, G. H. Chen, and G. He, J. Am. Chem. Soc. **123**, 9830 (2001); W. Z. Liang, S. Yokojima, D. H. Zhou, and G. H. Chen, J. Phys. Chem. A **104**, 2445 (2000); W. Z. Liang, S. Yokojima, and G. H. Chen, J. Chem. Phys. **110**, 1844 (1999).

[39] F. Wang, C. Y. Yam, and G. H. Chen, J. Chem. Phys. **126**, 134104(2007); X. Zheng, G. H. Chen, Z. B. Li, S. Z. Deng, and N. S. Xu, Phys. Rev. Lett. **92**, 106803 (2004); F. Wang, C. Y. Yam, G. H. Chen, X. J. Wang, K. N. Fan, T. A. Niehaus, and T. Frauenheim, Phys. Rev. B **76**, 045114 (2007).

[40] C. Y. Yam, S. Yokojima, and G. H. Chen, Phys. Rev. B **68**, 153105 (2003); C. Y. Yam, S. Yokojima, and G. H. Chen, J. Chem. Phys. **119**, 8794 (2003).