On correlated electron-nuclear dynamics using time-dependent density functional theory

Neepa T. Maitra[a)]
Department of Physics and Astronomy, Hunter College and City University of New York, New York, New York 10021

(Received 2 May 2006; accepted 11 May 2006; published online 7 July 2006)

We discuss possibilities and challenges for describing correlated electron and nuclear dynamics within a surface-hopping framework using time-dependent density functional theory (TDDFT) for the electron dynamics. We discuss the recent surface-hopping method proposed by Craig *et al.* [Phys. Rev. Lett. **95**, 163001 (2005)] that is based on Kohn-Sham potential energy surfaces. Limitations of this approach arise due to the Kohn-Sham surfaces generally having different gradients than the true TDDFT-corrected ones. Two mechanisms of the linear response procedure cause this effect: we illustrate these with examples. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2210471]

I. INTRODUCTION

Based on the assumption of adiabatic separation of nuclear and electronic degrees of freedom, molecular dynamics is often treated within the Born-Oppenheimer approximation with nuclei moving on the ground-state electronic potential energy surface. For time-dependent problems, methods have been developed that treat nuclei with classical dynamics, coupled to some approximate quantum scheme for electron dynamics. Ubiquitous is the Ehrenfest method, a mean-field method, where the expectation value of the gradient of the Hamiltonian in the time-evolving electronic wave function contributes to the classical force on the nuclei. Although successful for many problems, it is well known that the lack of electron-nuclear correlation in such schemes renders it a poor description for phenomena where there is a branching of nuclear trajectories.[1,2] This is important in processes such as electron transfer reactions, reactions near metal surfaces, and in photochemistry. Surface-hopping methods[1–6] pioneered by Tully have been successful in capturing electron-nuclear correlation effects: the nuclear trajectories evolve on a single electronic potential energy surface, instantaneously and stochastically "hopping" between them. An ensemble of trajectories is run, with the number that begin to evolve on the electronic state i being determined by its initial occupation. Most popular is the "fewest-switches surface-hopping" algorithm, which minimizes the number of hops between surfaces.

The fewest-switches hopping algorithm works best when the electronic potential energy surfaces are the adiabatic ones, i.e., electronic eigenstates for the instantaneous nuclear configuration. Thus one needs an accurate method to calculate electronic excitations. For systems of chemical interest, an increasingly popular method for excitation energies and spectra is time-dependent density functional theory (TDDFT).[7,8] The recent surge of interest in TDDFT is driven by both its accuracy and efficiency. Its accuracy for spectra is often comparable with correlated wave function methods such as CASPT2; yet implementations can scale with size even more favorably than that of time-dependent Hartree-Fock.[9,10] This is possible due to mapping the system of N interacting electrons to a fictitious non-interacting Kohn-Sham (KS) system, which exactly reproduces the one-body density, and from which one can extract in principle all properties of the interacting system *exactly*.[7] In practice, approximations are needed for the exchange-correlation effects. Typically, errors in excitation energies fall well within 0.4 eV, but properties of excited states are given more accurately e.g., bond lengths are within 1%.[11–13]

The recent paper of Craig *et al.*[14] is the first calculation that includes electron-nuclear correlation effects in TDDFT calculations of coupled electron-nuclear dynamics. Almost all previous TDDFT calculations of coupled dynamics have treated the nuclei via classical dynamics, with Ehrenfest forces providing the "quantum back reaction." In Ref. 14 this approach was applied for the first time using the time-dependent Kohn-Sham equations to evolve the electron dynamics, coupled to classical nuclei evolving on KS potential energy curves. The time-evolving KS orbitals are expanded in a basis of KS eigenstates at the instantaneous nuclear geometry, while, between hops, the electronic force on the nuclei is provided by the gradient, with respect to the nuclear coordinate, of the KS potential energy surface. The hopping probability is determined by the expansion coefficients of the time-dependent KS wave function in the instantaneous KS eigenbasis and the nonadiabatic couplings between the KS potential energy surfaces.

Reference 14 is an important step in developing surface-hopping methods using TDDFT. In the present paper, we point out an aspect of the theory in Ref. 14 that should be carefully considered when applying the proposed method to a general problem. The accuracy of the method depends on the requirement that the KS eigenstates at each nuclear configuration form the adiabatic potential energy surfaces for the nuclear dynamics. In fact, KS excitations are not those of the

[a)]Electronic mail: nmaitra@hunter.cuny.edu

 © 2006 American Institute of Physics

Downloaded 08 Aug 2006 to 146.95.156.197. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

true interacting system, and do not form the electronic adiabatic basis. Instead, true potential energy surfaces should be obtained from the TDDFT linear response procedure, whereby the KS excitations are corrected to the true ones using the exchange-correlation kernel[17,18] (see also Sec. II). The resulting forces on the nuclei can be significantly different. We give examples of this in Sec. II. If, however, the correct TDDFT surfaces are used in the surface-hopping framework, we immediately encounter a problem in defining hopping probabilities, since the true wave function is unknown in TDDFT. More precisely, although the true wave function is a functional of the time-evolving density, it is unknown what this functional is. We discuss this further in Sec. III.

II. POTENTIAL ENERGY SURFACES FROM TDDFT

There are (at least) three methods to obtain TDDFT corrections on the bare KS energy levels. The first is running a real-time TDDFT calculation with a perturbing time-dependent potential, beginning in the ground state of the system:[15,16] taking the Fourier transform reveals poles where excitations predicted by TDDFT lie. The second is directly in the frequency domain, where one solves a Dyson-like equation for the density-density response function of the true system, applying the exchange-correlation kernel to the response function of the KS system;[17] this corrects the KS excitations, lying at poles of the KS response function, to the true excitations, lying at poles of the true response function. The third transforms the Dyson-like equation into a matrix form,[18,19] and it is this that is programmed in quantum chemistry packages, such as NWCHEM, assuming an adiabatic approximation for the exchange-correlation kernel. Let $q=(i,a)$ be an index representing a single excitation: a transition from an occupied KS orbital ϕ_i to an unoccupied one ϕ_a, and let ω_q be the difference in the KS orbital energies, $\omega_q=\epsilon_a-\epsilon_i$. Then, the squares of the true transition frequencies $\Omega_I=\omega_I^2$ are the eigenvalues of the matrix,

$$\tilde{\Omega}(\omega)_{qq'} = \delta_{qq'}\omega_q^2 + 4\sqrt{\omega_q\omega_{q'}}[q|f_{\mathrm{HXC}}(\omega)|q'], \tag{1}$$

where

$$[q|f_{\mathrm{HXC}}(\omega)|q'] = \int d\mathbf{r}d\mathbf{r}'\,\phi_i^*(\mathbf{r})\phi_a(\mathbf{r})f_{\mathrm{HXC}}(\mathbf{r},\mathbf{r}',\omega) \times \phi_{i'}(\mathbf{r}')\phi_{a'}^*(\mathbf{r}'). \tag{2}$$

(The form of the equations for a spin-saturated system is written here). Here, the Hartree-exchange-correlation kernel $\overleftrightarrow{f}_{\mathrm{HXC}}(\omega)$ is the sum of the Hartree kernel and the exchange-correlation (XC) kernel: $f_{\mathrm{HXC}}[n_0](\mathbf{r},\mathbf{r}',\omega)=1/|\mathbf{r}-\mathbf{r}'| + f_{\mathrm{XC}}[n_0](\mathbf{r},\mathbf{r}',\omega)$, where $f_{\mathrm{XC}}[n_0](\mathbf{r},\mathbf{r}',t-t')=\delta v_{\mathrm{XC}}(\mathbf{r}t)/\delta n(\mathbf{r}t')|_{n_0}$, with $v_{\mathrm{XC}}(\mathbf{r}t)$ being the exchange-correlation potential. In principle, Eqs. (1) and (2) yield the exact excitations and oscillator strengths of the true interacting system; in practice, approximations are needed for the ground-state KS potential, out of which the bare KS excitations ω_q are calculated, and for the exchange-correlation kernel. This kernel is the key player in correcting the excitations of the fictitious KS system to the true ones.

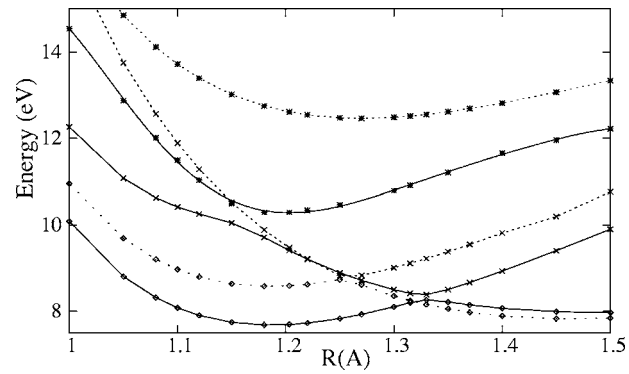

FIG. 1. Potential energy curves for the three lowest excited states of $^1A_1$ symmetry in formaldehyde as a function of C–O bond distance: TDDFT (solid) and bare KS (dotted).

One may think of the differences between the bare KS eigenvalues and their TDDFT-corrected values as arising from two mechanisms: the diagonal correction $[q|f_{\mathrm{HXC}}(\omega)|q]$ that shifts each KS single excitation, and the mixing of the different single excitations in diagonalizing the matrix (1). Examples where each mechanism creates a new dependence on the nuclear coordinate will now be given.

Consider first the diagonal correction. In cases where the KS single excitations are well separated so that there is little mixing, the diagonal correction is a good approximation to solving the full TDDFT matrix and can be significant. The question then is the degree to which this correction is independent of coordinate: if it is independent, then forces calculated from the gradients of KS curves will be the true forces. This is, however, not generally the case. An example of strong dependence of the diagonal kernel matrix element on nuclear coordinate is provided by the case of long-range charge transfer.[20,21] The case of a molecule composed of two open-shell fragments was considered in Ref. 20. An explicit expression for the diagonal kernel matrix elements relevant to the lowest charge transfer states in the limit of large separation R was demonstrated to contain the crucial $-1/R$ fall off of the charge transfer states. The Kohn-Sham surfaces, on the other hand, are essentially flat at large separations, depending on the nuclear separation only in an exponentially small way. So, even neglecting coupling between KS levels, the KS potential energy surfaces may vary with nuclear coordinates in quite a different way than those obtained using TDDFT.

We now turn to the second mechanism, the mixing of the KS single excitations with each other. As an illustration of this, consider the CO-stretch cross section of the $^1A_1$ manifold of formaldehyde. This was extensively studied by Casida *et al.* in Ref. 22 where it was shown that TDDFT can capture strong valence-Rydberg configuration mixing that underlies the prominent avoided crossings in the potential energy curve. In Fig. 1, we have plotted the curves for the lowest three states of $^1A_1$ symmetry, obtained using TDDFT (solid) and compared to the bare KS (dotted) eigenvalues. An asymptotically corrected ground-state functional was used in order for the Rydberg states to be properly captured: in the present work, we used the B3LYP functional with the CS00

Downloaded 08 Aug 2006 to 146.95.156.197. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

asymptotic correction method,[25,24] with the shift being determined by the Hirata-Zhan-Nichols-Apra-Windus-Dixon scheme,[26] using the NWCHEM code.[23] The kernel was approximated using the adiabatic B3LYP, and calculations were performed in the aug-cc-pVDZ basis. It is evident from the graphs that, while there are regions where corresponding surfaces are parallel to each other, the gradients of the KS potential energy surfaces are generally quite different from those of the TDDFT-corrected ones. If used in a surface-hopping method, the effective forces on the nuclei would be quite different if using the KS curves rather than the TDDFT ones; sometimes even in the opposite direction. The TDDFT linear response procedure significantly mixes the KS single excitations, especially strongly at the avoided crossing of the lowest two excited curves at around 1.33 Å, incorrectly captured by the bare KS curves.

It is also worth noting that the usual TDDFT approximations (including the one utilized above) cannot capture states with a significant component of a double excitation: for such states, a strongly frequency-dependent exchange-correlation kernel is required.[27,28] This can lead to qualitative differences in the global potential energy surfaces using the usual TDDFT approximations compared with what would be obtained if the exact TDDFT kernel were known (or, at least, a good approximation that captures multiple excitations).

It is the TDDFT curves which form the true adiabatic basis, and these should provide the correct nuclear forces in the fewest-switches surface-hopping scheme. The method of Ref. 14 in a sense involves an *additional* approximation on top of the approximations already inherent in surface-hopping techniques: that is, the KS energy levels approximate the interacting eigenlevels, or, at least, are shifted by an amount independent of the nuclear coordinates. This is not true even if the exact functionals were known. If the KS and true surfaces happen to have similar gradients, they may lead to similar nuclear dynamics, at least in between hops: perhaps this is behind the good agreement with experiment found in the examples of Ref. 14.

A criterion of surface-hopping methods is that if the electrons begin in an eigenstate at the initial nuclear configuration, and the dynamics is adiabatic such that no electronic transitions occur, then the method must reduce to Born-Oppenheimer molecular dynamics: That is, the nuclear dynamics occur on the potential energy surface of that electronic eigenstate. The method proposed in Ref. 14 does not satisfy this because the excited KS electronic potential curves are not those of the true system.

We point out here that the ground-state surface is a special case, because the interacting energy E_0 may be extracted directly from the ground-state KS system [e.g., Eq. (1) of Ref. 14].

III. DISCUSSION AND OUTLOOK

The fact that the KS energy curves are not the adiabatic curves of the interacting system presents a difficulty for surface-hopping methods using TDDFT: Although the correct adiabatic potential energy surfaces can be obtained from TDDFT linear response, the trajectory hopping probabilities depend on coefficients of the evolving wave function expanded in these, and these coefficients are not accessible from the usual TDDFT procedures. The interacting wave function is deliberately not known in TDDFT (this is behind why density functional methods scale so well with system size). The time-dependent KS wave function, even if expanded in the true eigenstates, would not give physical hopping probabilities. The KS wave function, a Slater determinant of noninteracting orbitals, is that of a fictitious noninteracting system, designed to produce the true time-dependent density. Quantities directly related to the density are immediately obtained. Although in principle the true wave function and hopping probabilities are functionals of the time-evolving density and initial state[7] it is not known what these functionals are. (We note that although it would be inconsistent to use KS hopping coefficients while using the TDDFT surfaces, it is at least consistent to use them if the KS surfaces are used, as is done in the approximate method of Ref. 14.)

The hopping probabilities also depend on the nonadiabatic couplings between the electronic potential energy surfaces. We first note that the nonadiabatic couplings in Ref. 14 are nonzero only between KS determinants that differ in a single orbital: these couplings lack the correlated excitations characteristic of true eigenstates. Although ground-to-excited nonadiabatic couplings between the true interacting states can be obtained from residues of the TDDFT matrix,[29,30] couplings between excited states are not directly accessible from linear response TDDFT. Sometimes[29,30] it is the former that are the most important, but in the general case, this poses a problem for surface-hopping approaches using TDDFT. One could go to higher-order response in TDDFT, but this is much messier.

Note that TDDFT within Ehrenfest dynamics does not have such a problem. Classical forces on nuclei are obtained from the gradient of the expectation value of the Hamiltonian in the time-evolving electronic wave function $\Psi(t)$, added to forces from other nuclei, $\nabla_R V_{\mathrm{nn}}$:

$$M\ddot{R}(t) = -\langle \Psi(t)|\nabla_R H_{\mathrm{el}}|\Psi(t)\rangle - \nabla_R V_{\mathrm{nn}}, \tag{3}$$

where V_{nn} is the classical nuclear-nuclear potential. H_{el} consists of the electronic kinetic energy, electron interaction, and electron-nuclear attraction V_{en}^R; the gradient acts only on the latter. The first term on the right of Eq. (3) becomes $-\langle \Psi(t)|\nabla_R V_{\mathrm{en}}^R|\Psi(t)\rangle = -\int d^3 r n(\mathbf{r}t)\nabla_R V_{\mathrm{en}}^R$. The dependence solely on the time-evolving electron density means that Ehrenfest forces can be obtained directly from the KS system. Coupled electron-ion dynamics done in this way scales well with system size, and has been successful in many cases. While including electron correlation, the method, however, lacks all quantum behavior of nuclei, and fails where electron-nuclear correlation is important, as mentioned in the introduction.

Finally, we mention that an eventual aim would be to go beyond a classical description for the nuclei. For example, nuclear quantum interference and tunneling effects cannot be captured in the surface-hopping scheme. This would be of particular importance for lighter nuclei. A *complete* quantum description for coupled electrons and nuclei has been formu-

Downloaded 08 Aug 2006 to 146.95.156.197. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

lated within density functional theory.[31] A theory that includes nuclear quantum effects by building on a classical framework is the semiclassical dynamics, originated by van Vleck in the 1920's,[32] and developed intensively by Miller,[33] Heller,[34] and others.[35–44] These semiclassical methods are rigorous in that they give the correct classical limit. They can describe quantum interference, zero-point effects, and can be extended to describe classically forbidden processes such as tunneling.[45] The majority of semiclassical propagations of nuclei have taken place on one potential energy surface, and so they do not describe electron-nuclear correlation. Herman has developed a semiclassical surface-hopping scheme to capture this:[46–48] the idea is for the method to capture the coupled quantum dynamics of electrons, the leading-order quantum behavior of the nuclei, and also electron-nuclear correlation. As TDDFT is rapidly becoming the method of choice for electronic excited states, it would be desirable to utilize TDDFT within this kind of scheme. However, the fundamental problem of defining the hopping probabilities between TDDFT surfaces will need to be surmounted first. Similar issues are encountered if one attempts to utilize TDDFT within the multiple-spawning method of Ben-Nun and co-workers,[49,50] which solves the nuclear Schrödinger equation.

ACKNOWLEDGMENTS

Conversations with Oleg Prezhdo and Karsten Krogh-Jespersen are gratefully acknowledged. This work is financially supported by grants from the American Chemical Society's Petroleum Research Fund and National Science Foundation Career Program, CHE-0547913.

[1] J. C. Tully, in *Dynamics on Molecular Collisions* edited by W. H. Miller (Plenum, New York, 1976). Pt. B.
[2] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[3] R. K. Preston and J. C. Tully, J. Chem. Phys. **54**, 4297 (1971).
[4] S. Hammes-Schiffer and J. C. Tully, J. Chem. Phys. **101**, 4657 (1994).
[5] O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 825 (1997).
[6] P. V. Parahdekar and J. C. Tully, J. Chem. Phys. **122**, 094102 (2005).
[7] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[8] *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, F. Nogueira, A. Rubio, K. Burke, C. A. Ullrich, and E. K. U. Gross (Springer, Berlin, 2006).
[9] R. J. Cave, K. Burke, and E. W. Castner, Jr., J. Phys. Chem. A **106**, 9294 (2002).
[10] J. Finley, P. A. Malmqvist, B. O. Roos, and L. Serrano-Andrés, Chem. Phys. Lett. **288**, 299 (1998).
[11] M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
[12] N. T. Maitra, K. Burke, H. Appel, E. K. U. Gross, and R. van Leeuwen, in *Reviews in Modern Quantum Chemistry: A Celebration of the Contributions of R. G. Parr*, edited by K. D. Sen, (World Scientific, Singapore, 2002).
[13] F. Furche and D. Rappaport, in *Computational Photochemistry*, edited by M. Olivucci (Elsevier, Amsterdam, 2005).
[14] C. F. Craig, W. R. Duncan, and O. V. Prezhdo, Phys. Rev. Lett. **95**, 163001 (2005).
[15] K. Yabana and G. F. Bertsch, Phys. Rev. B **54**, 4484 (1996).
[16] M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comput. Phys. Commun. **151**, 60 (2003).
[17] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
[18] M. E. Casida, in *Recent Developments and Applications in Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).
[19] R. Bauernschmidt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).
[20] N. T. Maitra, J. Chem. Phys. **122**, 234104 (2005).
[21] O. Gritsenko and E. J. Baerends, J. Chem. Phys. **121**, 655 (2004).
[22] M. E. Casida, K. Casida, and D. R. Salahub, Int. J. Quantum Chem. **70**, 933 (1998).
[23] E. Aprá, T. L. Windus, T. P. Straatsma *et al.*, NWCHEM, A Computational Chemistry Package for Parallel Computers, Version 4.7, Pacific Northwest National Laboratory, Richland, Washington 2005; R. A. Kendall, E. Apra, D. E. Bernholdt *et al.*, Comput. Phys. Commun. **128**, 260 (2000).
[24] M. E. Casida and D. R. Salahub, J. Chem. Phys. **113**, 8918 (2000).
[25] M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. **108**, 4439 (1998).
[26] S. Hirata, C.-G. Zhan, E. Apràs, T. Windus and D. A. Dixon, J. Phys. Chem. A **107**, 10154 (2003); C-G. Zhan, J. A. Nichols, and D. A. Dixon, J. Phys. Chem. A **107**, 4184 (2003).
[27] N. T. Maitra, F. Zhang, R. J. Cave and K. Burke, J. Chem. Phys. **120**, 5932 (2004).
[28] R. J. Cave, F. Zhang, N. T. Maitra, and K. Burke, Chem. Phys. Lett. **389**, 39 (2004).
[29] R. Baer, Chem. Phys. Lett. **364**, 75 (2002).
[30] V. Chernyak and S. Mukamel, J. Chem. Phys. **112**, 3572 (2000).
[31] T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. **86**, 2984 (2001).
[32] J. H. van Vleck, Proc. Natl. Acad. Sci. U.S.A. **14**, 178 (1928).
[33] W. H. Miller, J. Phys. Chem. A **105**, 2942 (2001), and references therein.
[34] W. H. Miller, Adv. Chem. Phys. **25**, 69–177 (1974).
[35] E. J. Heller, J. Chem. Phys. **34**, 321 (1975).
[36] E. J. Heller, J. Chem. Phys. **94**, 2723 (1991).
[37] M. A. SepA§lveda and E. J. Heller, J. Chem. Phys. **101**, 8016 (1994).
[38] M. Thoss and H. Wang, Annu. Rev. Phys. Chem. **55**, 299 (2004), and references therein.
[39] E. J. Heller, Prog. Theor. Phys. Suppl. **45**, 116 (1994).
[40] W. H. Miller, Faraday Discuss. Chem. Soc. **110**, 1 (1998).
[41] W. H. Miller, J. Chem. Phys. **53**, 3578 (1970).
[42] M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984).
[43] K. Kay, J. Chem. Phys. **100**, 4377 (1994).
[44] A. R. Walton and D. E. Manolopoulous, Mol. Phys. **87**, 961 (1996).
[45] N. T. Maitra and E. J. Heller, Phys. Rev. Lett. **78**, 3035 (1997).
[46] M. F. Herman, J. Chem. Phys. **103**, 8081 (1995).
[47] M. F. Herman, J. Chem. Phys. **76**, 2949 (1982).
[48] G. Yang and M. F. Herman, J. Phys. Chem. B **105**, 6562 (2001).
[49] M. Ben-Nun, J. Quenneville, and T. J. Martinez, J. Phys. Chem. A **104**, 5161 (2000).
[50] M. Ben-Nun and T. J. Martinez, Adv. Chem. Phys. **121**, 439 (2002).

Downloaded 08 Aug 2006 to 146.95.156.197. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp