Multicomponent Time-Dependent Density Functional Theory: Proton and Electron Excitation Energies

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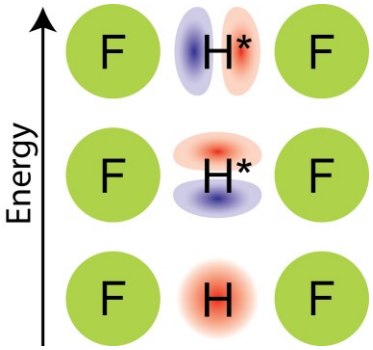
Abstract

The quantum mechanical treatment of both electrons and protons in the calculation of excited state properties is critical for describing nonadiabatic processes such as photoinduced proton-coupled electron transfer. Multicomponent density functional theory enables the consistent quantum mechanical treatment of more than one type of particle and has been implemented previously for studying ground state molecular properties within the nuclear-electronic orbital (NEO) framework, where all electrons and specified protons are treated quantum mechanically. To enable the study of excited state molecular properties, herein the linear response multicomponent time-dependent density functional theory (TDDFT) is derived and implemented within the NEO framework. Initial applications to FHF^- and HCN illustrate that NEO-TDDFT provides accurate proton and electron excitation energies within a single calculation. As its computational cost is similar to that of conventional electronic TDDFT, the NEO-TDDFT approach is promising for diverse applications, particularly nonadiabatic proton transfer reactions, which may exhibit mixed electron-proton vibronic excitations.

TOC Graphic



Multicomponent density functional theory, which treats more than one type of particle quantum mechanically, is an emerging field that has inspired several recent theoretical developments.[1–6] In contrast to conventional density functional theory (DFT) in electronic structure theory, multicomponent DFT enables the quantum mechanical treatment of specified nuclei, such as protons, on equal footing with the electrons. Therefore, it includes the delocalized proton densities and associated zero point energy during the self-consistent-field procedure, as well as during geometry optimizations and potentially the dynamics of the classical nuclei.[5,6] This treatment also provides opportunities to go beyond the Born-Oppenheimer approximation and thereby describe nonadiabatic processes, such as proton-coupled electron transfer (PCET).[7,8] Previous multicomponent DFT studies have focused mainly on the ground states of molecular systems, whereas multicomponent methods to study excited states have not been practically implemented, although the theoretical foundation has been formulated.[9–11] The description of these excited states is important for nonadiabatic processes involving excited electron-proton vibronic states, such as photoacids and photoinduced PCET.[12,13]

This Letter centers on the development of the linear-response multicomponent time-dependent density functional theory within the nuclear-electronic orbital (NEO) framework,[14] denoted NEO-TDDFT, and its application to compute proton and electron excitation energies. The NEO framework is a multicomponent approach that balances practical implementation with chemical accuracy.[4–6,15] It treats all electrons and one or more key protons quantum mechanically and requires at least two classical nuclei to avoid difficulties with translations and rotations. Previously developed explicitly correlated wavefunction-based NEO methods[16–18] were found to be computationally expensive and unable to describe proton densities accurately. Recently, the epc17-1 functional, an electron-proton correlation functional developed within the NEO-DFT

framework, was shown to be the first working functional that is able to produce accurate proton densities in molecular systems.[5] Moreover, quantitatively accurate proton affinities were obtained with a slightly reparameterized form, denoted the epc17-2 functional.[6] Despite these recent successes, excited states, which are more challenging but also of broad interest, have never been investigated within the NEO-DFT framework. Although a related multicomponent linear response theory has been formulated,[10,11] this previous formulation used the electronic one-body density and the diagonal of the nuclear *N*-body density matrix as the variables, where *N* is the number of nuclei. In contrast, the NEO-TDDFT method uses the electronic one-body and proton one-body densities as the variables within a fixed frame of the classical nuclei. Herein we derive, implement, and test linear-response NEO-TDDFT.

Among the various linear response theories used in quantum chemistry,[19–23] the widely used density-density response theory describes the response of the density matrix to a small perturbative potential. The NEO framework requires two key density-density response functions — one for electrons and one for protons, as indicated by "*e*" and "*p*" superscripts, respectively. In the orbital basis, these response functions can be expressed as

$$\chi^{e}_{pq,rs}(\omega) = \sum_n \left(\frac{\langle 0|a_q^\dagger a_p|n\rangle\langle n|a_r^\dagger a_s|0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle 0|a_r^\dagger a_s|n\rangle\langle n|a_q^\dagger a_p|0\rangle}{\omega+(E_n-E_0)+i\eta}\right), \quad (1)$$

$$\chi^{p}_{PQ,RS}(\omega) = \sum_n \left(\frac{\langle 0|b_Q^\dagger b_P|n\rangle\langle n|b_R^\dagger b_S|0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle 0|b_R^\dagger b_S|n\rangle\langle n|b_Q^\dagger b_P|0\rangle}{\omega+(E_n-E_0)+i\eta}\right), \quad (2)$$

where 0 denotes the ground state, n denotes the nth excited state, E_n is the energy for the state n, and η is an infinitesimal positive real number. Here $a^\dagger(a)$ denote creation (annihilation) operators for electrons, and $b^\dagger(b)$ denote the corresponding operators for protons, where lower (upper) case indices indicate electron (proton) orbitals. We adopt the convention that subscripts i,j,k,l denote occupied orbitals, a,b,c,d denote virtual orbitals, and p,q,r,s denote general

orbitals.

In the Kohn-Sham NEO-DFT framework, the multicomponent noninteracting system is the product of an electronic and a nuclear determinant. The electron and proton response functions, χ_s^e and χ_s^p, associated with this noninteracting system can be calculated from Eqs. 1 and 2. The corresponding response equations are

$$\delta P_{ia}^e(\omega) = (\chi_s^e)_{ia,ia}(\omega)\delta v_{ia}^e(\omega) = -\frac{\delta v_{ia}^e(\omega)}{\omega+(\varepsilon_a-\varepsilon_i)+i\eta} \tag{3}$$

$$\delta P_{ai}^e(\omega) = (\chi_s^e)_{ai,ai}(\omega)\delta v_{ai}^e(\omega) = \frac{\delta v_{ai}^e(\omega)}{\omega-(\varepsilon_a-\varepsilon_i)+i\eta} \tag{4}$$

$$\delta P_{IA}^p(\omega) = (\chi_s^p)_{IA,IA}(\omega)\delta v_{IA}^p(\omega) = -\frac{\delta v_{IA}^p(\omega)}{\omega+(\varepsilon_A-\varepsilon_I)+i\eta} \tag{5}$$

$$\delta P_{AI}^p(\omega) = (\chi_s^p)_{AI,AI}(\omega)\delta v_{AI}^p(\omega) = \frac{\delta v_{AI}^p(\omega)}{\omega-(\varepsilon_A-\varepsilon_I)+i\eta} \tag{6}$$

where δP denotes the change in the density matrix, δv denotes the change in the potential, and ε denotes the orbital energies for the noninteracting system. The two components of the change in the potential are the change in the external applied potential δv_{ext}, which is not influenced by the changes in the density matrices, and the change in the internal potential δv_{in}, which is influenced by those changes. In multicomponent theory, the change in the internal potential further consists of two parts: the same-particle-induced potential and the different-particle-induced potential, each including a Coulomb term and an exchange-correlation term, where exchange is only relevant for same-particle interactions.

In the NEO framework, the change in the potential can be expressed as

$$\delta v^e = \delta v_{ext}^e + \delta v_{in}^e = \delta v_{ext}^e + (\delta v_{eeJ}^e + \delta v_{exc}^e) + (\delta v_{epJ}^e + \delta v_{epc}^e), \tag{7}$$

$$\delta v^p = \delta v_{ext}^p + \delta v_{in}^p = \delta v_{ext}^p + (\delta v_{ppJ}^p + \delta v_{pxc}^p) + (\delta v_{epJ}^p + \delta v_{epc}^p), \tag{8}$$

where eeJ (ppJ) denotes the electron-electron (proton-proton) Coulomb interaction, exc (pxc)

denotes the electron (proton) exchange-correlation, epJ denotes the electron-proton Coulomb interaction, and epc denotes the electron-proton correlation. Note that the e (p) superscripts indicate the change in the potential experienced by the electron (proton), respectively. The influence of the density matrices on the potential can be described with the frequency-dependent exchange-correlation kernels $K(\omega)$:

$$\delta v_{in}^{e}(\omega) = K^{ee}(\omega)\delta P^{e}(\omega) + K^{ep}(\omega)\delta P^{p}(\omega), \tag{9}$$

$$\delta v_{in}^{p}(\omega) = K^{pe}(\omega)\delta P^{e}(\omega) + K^{pp}(\omega)\delta P^{p}(\omega). \tag{10}$$

These kernels can be expressed as follows, where the frequency dependence is omitted for notational simplicity:

$$K_{rs,pq}^{ee} = \frac{(\delta v_{eeJ}^{e})_{rs}}{\delta P_{pq}^{e}} + \frac{(\delta v_{exc}^{e})_{rs}}{\delta P_{pq}^{e}} + \frac{(\delta v_{epc}^{e})_{rs}}{\delta P_{pq}^{e}}, \tag{11}$$

$$K_{RS,PQ}^{pp} = \frac{(\delta v_{ppJ}^{p})_{RS}}{\delta P_{PQ}^{p}} + \frac{(\delta v_{pxc}^{p})_{RS}}{\delta P_{PQ}^{p}} + \frac{(\delta v_{epc}^{p})_{RS}}{\delta P_{PQ}^{p}}, \tag{12}$$

$$K_{rs,PQ}^{ep} = \frac{(\delta v_{epJ}^{e})_{rs}}{\delta P_{PQ}^{p}} + \frac{(\delta v_{epc}^{e})_{rs}}{\delta P_{PQ}^{p}}, \tag{13}$$

$$K_{RS,pq}^{pe} = \frac{(\delta v_{epJ}^{p})_{RS}}{\delta P_{pq}^{e}} + \frac{(\delta v_{epc}^{p})_{RS}}{\delta P_{pq}^{e}}. \tag{14}$$

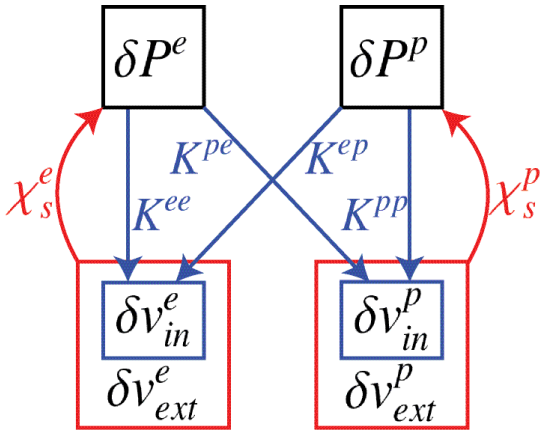


Figure 1: Summary of the relationships among the changes in density matrices (δP), changes in potentials (δv), exchange-correlation kernels (K), and response functions (χ_s) for the multicomponent Kohn-Sham reference system. The changes in total potentials influence the

density matrices, as indicated in red (Eqs. 3-6), and the changes in the density matrices impact the changes in the internal potentials, as indicated in blue (Eqs. 9-10).

The relations in Eqs. (3-12) are summarized in Fig. 1 and can be cast into a matrix form. Regardless of the perturbative external potential, the internal resonance gives rise to excitation energies when the following relation is satisfied:

$$\begin{bmatrix} \mathbf{A}^e & \mathbf{B}^e & \mathbf{C} & \mathbf{C} \\ \mathbf{B}^e & \mathbf{A}^e & \mathbf{C} & \mathbf{C} \\ \mathbf{C}^T & \mathbf{C}^T & \mathbf{A}^p & \mathbf{B}^p \\ \mathbf{C}^T & \mathbf{C}^T & \mathbf{B}^p & \mathbf{A}^p \end{bmatrix} \begin{bmatrix} \mathbf{X}^e \\ \mathbf{Y}^e \\ \mathbf{X}^p \\ \mathbf{Y}^p \end{bmatrix} = \omega \begin{bmatrix} \mathbf{I} & 0 & 0 & 0 \\ 0 & -\mathbf{I} & 0 & 0 \\ 0 & 0 & \mathbf{I} & 0 \\ 0 & 0 & 0 & -\mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{X}^e \\ \mathbf{Y}^e \\ \mathbf{X}^p \\ \mathbf{Y}^p \end{bmatrix}, \tag{15}$$

where the matrix elements are given by

$$A^e_{ia,jb}(\omega) = K^{ee}_{ia,jb}(\omega) + (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij}, \tag{16}$$

$$B^e_{ia,jb}(\omega) = K^{ee}_{ia,bj}(\omega), \tag{17}$$

$$A^p_{IA,JB}(\omega) = K^{pp}_{IA,JB}(\omega) + (\varepsilon_A - \varepsilon_I)\delta_{AB}\delta_{IJ}, \tag{18}$$

$$B^p_{IA,JB}(\omega) = K^{pp}_{IA,BJ}(\omega), \tag{19}$$

$$C_{ia,JB}(\omega) = K^{ep}_{ia,JB}(\omega). \tag{20}$$

Note that the kernel depends on the frequency in these expressions. For practical calculations, however, we invoke the adiabatic approximation, in which the kernel K is assumed to be independent of frequency and is evaluated with the second derivatives of the ground state functional. Here we also adopt the convention of replacing the changes in density matrices δP with $\mathbf{X}$ for the occupied-virtual elements (Eqs. 3 and 5) and with $\mathbf{Y}$ for the virtual-occupied elements (Eqs. 4 and 6). The orthonormalization condition[19] for any two eigenvectors denoted by m and n is

$$\langle \mathbf{X}^e_m | \mathbf{X}^e_n \rangle - \langle \mathbf{Y}^e_m | \mathbf{Y}^e_n \rangle + \langle \mathbf{X}^p_m | \mathbf{X}^p_n \rangle - \langle \mathbf{Y}^p_m | \mathbf{Y}^p_n \rangle = \pm\delta_{mn}. \tag{21}$$

Similar to TDDFT, the excitation energies arise in pairs with opposite signs (i.e., excitations

and de-excitations). In principle, maintaining the frequency-dependent kernel[19,24] would enable the description of single, double, and higher-order excitations, which could involve electron, proton, and mixed electron-proton excitations. However, because we invoked the adiabatic approximation, where the kernel is assumed to be frequency-independent, only single excitations can be captured. In general, these single excitations could be pure electron, pure proton, or mixed electron-proton character. Such excitations could be described as a linear combination of products of electron and proton determinants in which only one determinant is singly excited in each term. For electronically adiabatic systems, where the electron density responds instantaneously to changes in the proton density, the proton and electron excitations are separable, as depicted in Figure 2. Note that this usage of the word "adiabatic" is different from the adiabatic approximation related to the frequency-independent kernel. By electronically adiabatic, we are referring to the regime in which the non-Born-Oppenheimer effects between the electrons and proton(s) are negligible. In this limit, each proton and electron excitation can be identified by examining the corresponding eigenvector: proton excitations are dominated by $\mathbf{X}^p$, while electron excitations are dominated by $\mathbf{X}^e$. Due to coupling between the electrons and protons, these are not rigorously pure proton vibrational excitations and electronic excitations, although they will be closely associated with such pure excitations in the electronically adiabatic limit. For systems with significant nonadiabatic or non-Born-Oppenheimer effects between the electrons and the proton(s), the eigenvectors are expected to exhibit non-negligible contributions from both the electron and proton elements (i.e., both $\mathbf{X}^e$ and $\mathbf{X}^p$), corresponding to a combination of electron and proton excitation character. The oscillator strengths and transition densities can be obtained in an analogous manner as in electronic TDDFT.[20]

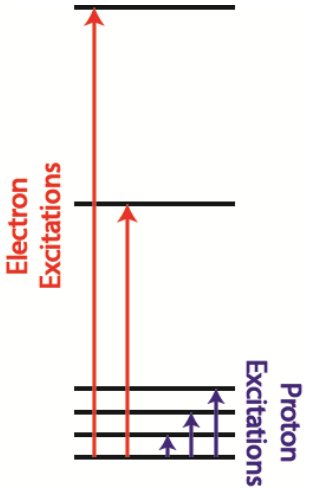


Figure 2: Schematic depiction of the electron and proton excitations that can be computed with NEO-TDDFT in a single calculation. In the case shown, the electronic excitation energies are significantly greater than the proton vibrational excitation energies, leading to the separation depicted. For systems in which these excitation energies are similar (i.e., significant nonadiabatic or non-Born-Oppenheimer effects between the electrons and proton(s)), this separation would no longer be valid, and the single excitations would represent electron-proton vibronic excitations.

The Tamm-Dancoff approximation (NEO-TDDFT-TDA)[25] is obtained by eliminating all rows and columns involving $\mathbf{B}^e$ and $\mathbf{B}^p$, leading to the following simplified matrix equation:

$$\begin{bmatrix} \mathbf{A}^e & \mathbf{C} \\ \mathbf{C}^T & \mathbf{A}^p \end{bmatrix} \begin{bmatrix} \mathbf{X}^e \\ \mathbf{X}^p \end{bmatrix} = \omega \begin{bmatrix} \mathbf{X}^e \\ \mathbf{X}^p \end{bmatrix}. \tag{22}$$

The NEO-TDDFT equation in Eq. 15 is a generalized eigenvalue problem. It can be simplified using similar tricks as developed for conventional electronic TDDFT and thereby transformed to an eigenvalue problem with an identity metric. The spin adapted formulation can also be carried out.[19] The NEO-TDDFT and NEO-TDDFT-TDA equations can be solved by direct diagonalization with overall $O(N^6)$ scaling. However, it is straightforward to implement the iterative Davidson method and thereby reduce the formal cost to $O(N^4)$ for a single root.[26,27]

We implemented NEO-TDDFT and NEO-TDDFT-TDA in GAMESS[28] with direct diagonalization and investigated their performances on both proton and electron excitations. We

used the molecules FHF^- and HCN as test systems because they have been characterized in previous NEO ground state studies.[5,6,18,29] The geometries were optimized at the conventional electronic DFT/B3LYP[30,31] level (i.e., all nuclei were treated as point charges) with the def2-QZVP electronic basis set. For the NEO-TDDFT calculations, the heavy nuclei were fixed to these geometries, and the hydrogen nucleus was treated quantum mechanically with the associated electronic and nuclear basis sets centered at the optimized hydrogen position. We performed electronic basis set convergence tests with the NEO-TDDFT method, as provided in the SI. Utilizing these results, we employed the cc-pVDZ electronic basis set for the heavy atoms and the cc-pV5Z electronic basis set for the quantum hydrogen atom. Note that a relatively large electronic basis set on the quantum hydrogen is necessary to obtain accurate proton vibrational excitation energies. An even-tempered 8*s*8*p*8*d* proton basis set with exponents spanning the range from $2\sqrt{2}$ to 32 was used for all calculations.[5] The electronic exchange-correlation energy was approximated by either the B3LYP or the PBE[32] functional, while the exchange-correlation of the proton was computed as the Hartree-Fock exchange. The electron-proton correlation energy was treated at three different levels: using the epc17-1[5] or the epc17-2[6] functional, or alternatively at the no-epc level, which neglects all electron-proton correlation.

The proton vibrational excitation energies are compared to those obtained with a grid-based method that is numerically exact for electronically adiabatic systems. In this approach, the total electronic energy was calculated at the DFT/B3LYP level for the hydrogen nucleus positioned at each grid point on a three-dimensional grid spanning the relevant region for the proton density, and the three-dimensional Schrödinger equation was solved numerically for the proton using the Fourier grid Hamiltonian method.[33,34] Note that the NEO-TDDFT method is designed to capture non-Born-Oppenheimer effects and therefore will be applicable to electronically nonadiabatic

systems, but our initial benchmarking focuses on electronically adiabatic systems to allow direct comparison to numerically exact results. The electronic excitation energies are compared to the corresponding conventional TDDFT results. These comparisons are based on the assumption of weak coupling between the electronic and proton vibrational excitations, a valid assumption in the electronically adiabatic limit. For the two molecules investigated herein, we found that the magnitudes of the electronic elements are extremely small for those eigenvectors corresponding to proton excitations, and vice versa, suggesting that the electronic excitations and proton vibrational excitations are predominantly separable. This observation is consistent with the known electronic adiabaticity of these systems. However, it is possible that in other systems, such as photoacids[12] or photoinduced PCET systems,[7,8,13] which exhibit electronically nonadiabatic or non-Born-Oppenheimer effects, mixing between the two types of excitations might be observed.

Table 1 presents the proton excitation energies for FHF^- and HCN computed with the B3LYP electronic exchange-correlation functional and the epc17-2 electron-proton correlation functional, as well as with no electron-proton correlation (no-epc). The analogous results with the PBE electronic functional and the epc17-1 electron-proton correlation functional are provided in Tables S1 and S2 of the SI. The choice of electronic exchange-correlation functional has negligible impact on the proton excitation energies, with the B3LYP and PBE electronic excitation energies differing by less than 200 cm^{-1}.

The impact of electron-proton correlation on the proton vibrational excitation energies is somewhat unexpected. Although the NEO-DFT/no-epc method does not provide even qualitatively accurate proton densities[5] for the ground state, the corresponding NEO-TDDFT/no-epc method provides accurate proton vibrational excitation energies with average errors of only ~200 cm^{-1}. In contrast, the epc17-1 functional does not perform as well as neglecting electron-

proton correlation altogether, even though it provides much more accurate ground state proton densities. The epc17-2 functional, which has been shown to provide quantitatively accurate proton affinities,[6] performs equally well or slightly better than the no-epc case for computing proton vibrational excitation energies. Thus, the relation between the ground state proton density and excitation energies is not clear.

The electron-proton correlation functionals epc17-1 and epc17-2 were parameterized to reproduce ground state proton densities or energies in previous work[5,6] and were not further parameterized in the present work. Moreover, as indicated from the basis set convergence study presented in the SI, the results are sensitive to the basis sets, particularly on the quantum hydrogen. Further parameterization of the electron-proton functionals, as well as larger electronic and nuclear basis sets, could improve the quantitative accuracy of the proton vibrational excitation energies. In addition, the grid-based method used as a reference assumes electronic adiabaticity, and in principle NEO-TDDFT might include non-Born-Oppenheimer effects that are not accurately reflected in this grid-based method. An exact benchmark that includes all of these nonadiabatic effects would be a grid-based method that includes the first-order and second-order nonadiabatic couplings.[35]

Although it violates the sum rules, the Tamm-Dancoff approximation often gives comparable excitation energies as the underlying full linear-response treatment in conventional electronic structure theory methods.[25,36,37] However, this trend is not observed for proton excitations within the NEO framework, as indicated by the results in Table 1. The NEO-TDDFT-TDA method overestimates the proton excitation energies by ~2000 cm^{-1} compared to the corresponding NEO-TDDFT method. The reason for this disparity is not yet fully clear, although it might arise from the small vibrational excitation energies, which could reduce the validity of the Tamm-Dancoff

approximation.[38] We will further investigate this phenomenon in future studies.

In addition to the proton excitation energies, NEO-TDDFT also provides electron excitation energies, as depicted in Figure 2. Table 2 presents the excitation energies for the lowest two singlet and triplet single-electron excitations for FHF^-, with the analogous results for HCN provided in Table S4. These results illustrate that NEO-TDDFT and conventional electronic TDDFT lead to almost exactly the same electronic excitation energies, regardless of how the electron-proton correlation is treated. The NEO-TDDFT-TDA method also leads to very similar results as the corresponding electronic TDDFT-TDA method, indicating that the Tamm-Dancoff approximation is better justified for pure electronic excitations than for proton vibrational excitation energies.

In summary, we derived and implemented the linear response NEO-TDDFT method and showed that it can accurately predict both proton and electron excitation energies with a single calculation. The proton excitation energies are not sensitive to the choice of electron exchange-correlation functional but are more sensitive to the choice of electron-proton correlation functional, with epc17-2 providing the best results, corresponding to errors of ~200 cm^{-1} with no reparameterization of the functionals. Neglecting electron-proton correlation altogether also leads to reasonable proton excitation energies for the molecules studied herein, although electron-proton correlation may be more important for other systems, such as proton transfer systems. The NEO-TDDFT-TDA method does not provide even qualitatively reasonable proton excitation energies, with errors of ~2000 cm^{-1} for the systems studied. Both NEO-TDDFT and NEO-TDA provide accurate electron excitation energies with all electron-proton correlation functionals studied.

We emphasize that the objective of this Letter is to present a proof of concept that the NEO-TDDFT method is able to predict accurate proton and electron excitation energies. A more

comprehensive investigation of the effects of the adiabatic approximation (i.e., the frequency-independent kernel) and the roles of electron exchange-correlation and electron-proton correlation functionals will be the focus of future work. In addition, the significance of the individual block-matrix contributions in the NEO-TDDFT working equations will be investigated to understand why TDA does not perform well for proton excitation energies. Such understanding will be critical for harnessing this method in future applications to systems such as photoacids and photoinduced PCET processes, which may exhibit mixed electron-proton vibronic excitations.

Table 1. Proton Excitation Energies for FHF^- and HCN (in cm^{-1})[a]

		NEO-TDDFT-TDA		NEO-TDDFT		Grid Ref
		no-epc	epc17-2	no-epc	epc17-2	
FHF^-	Off-axis	3351	3628	1408	1401	1278
	On-axis	3636	4005	1889	1828	1647
HCN	Off-axis	3796	3983	980	920	667
	On-axis	4875	5296	3136	3217	3195

[a] The B3LYP electronic exchange-correlation functional was used to compute all numbers in this table. Results with the PBE electronic functional and epc17-1 electron-proton correlation functional are provided in Tables S1 and S2.

Table 2. Electron Excitation Energies for FHF^- (in eV)[a]

	NEO-TDDFT-TDA		TDDFT-TDA	NEO-TDDFT		TDDFT
	no-epc	epc17-2		no-epc	epc17-2	
T1	6.84	6.84	6.86	6.83	6.84	6.85
T2	6.92	6.92	6.91	6.91	6.91	6.90
S1	7.02	7.02	7.04	7.01	7.02	7.03
S2	7.15	7.16	7.15	7.14	7.14	7.13

[a] The B3LYP electronic exchange-correlation functional was used to compute all numbers in this table. Results with the PBE electronic functional and epc17-1 electron-proton correlation functional are provided in Tables S3 and S4.

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Supporting Information

See Supporting Information for the complete derivation of the NEO-TDDFT equations and the equation for the corresponding oscillator strength, method performance with different functionals, and basis set convergence tests.

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