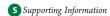# Derivation of an Electron−Proton Correlation Functional for Multicomponent Density Functional Theory within the Nuclear−Electronic Orbital Approach

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ABSTRACT: Multicomponent density functional theory enables the quantum mechanical treatment of electrons and selected hydrogen nuclei. An electron−proton correlation functional is derived from the electron−proton pair density associated with a recently proposed ansatz for the explicitly correlated nuclear−electronic wave function. This ansatz allows the retention of all terms in the pair density, and the resulting functional is expected to scale properly and to be computationally efficient. Applications to model systems illustrate that it provides accurate nuclear densities.

Conventional density functional theory (DFT) relies on the Born−Oppenheimer separation of electrons and nuclei, and typically the nuclei move classically on adiabatic electronic surfaces. Nuclear quantum effects have been shown to be important for a broad range of systems, particularly those involving hydrogen bonding and hydrogen transfer.[1−3] In some cases, such as proton-coupled electron transfer reactions, non-adiabatic effects between the electrons and transferring protons have been shown to be significant.[4−6] Multicomponent DFT is a computationally practical method for incorporating these types of nuclear quantum effects into electronic structure calculations.[7−13] In the implementation of multicomponent DFT within the framework of the nuclear−electronic orbital (NEO) approach,[11,12,14] electrons and selected hydrogen nuclei are treated quantum mechanically without the Born−Oppeneheimer approximation. This NEO-DFT approach is designed for systems in which at least two nuclei are treated classically, eliminating difficulties associated with translations and rotations. Moreover, typically only a relatively small number of hydrogen nuclei, such as those involved in hydrogen bonding or hydrogen transfer, are treated quantum mechanically.

A major challenge of this approach is the development of electron−proton density functionals that accurately describe electron−proton correlation, which is highly significant because of the attractive interaction between the electron and proton and the disparity in the masses.[15,16] Previously, we devised a strategy for the development of electron−proton density functionals using the electron−proton pair density from an explicitly correlated nuclear−electronic wave function.[11] The initial electron−proton density functional developed with this strategy required the neglect of a large number of terms in the explicitly correlated electron−proton pair density. The objective of the present work is to derive an electron−proton density functional with a different ansatz for the explicitly correlated nuclear−electronic wave function, thereby enabling us to retain all of the terms in the electron−proton pair density. The resulting electron−proton functional has a similar form to that of the previous functional but is expected to be more reliable in terms of scaling with respect to the number of

electrons and quantum protons. The application of this new functional to model systems illustrates that it provides accurate hydrogen nuclear densities. Moreover, the form of this functional is computationally practical for larger molecular systems.

We consider a multicomponent system comprised of N_e electrons and N_p protons that are treated quantum mechanically in a field of N_c fixed classical nuclei. Within the framework of multicomponent DFT, the ground state energy is the minimum of the energy functional

$$E[\rho^e, \rho^p] = \int d\mathbf{r}_1^e \; \rho^e(\mathbf{r}_1^e) \; v(\mathbf{r}_1^e) - \int d\mathbf{r}_1^p \; \rho^p(\mathbf{r}_1^p) \; v(\mathbf{r}_1^p) + F[\rho^e, \rho^p] \tag{1}$$

subject to the constraints $\int d\mathbf{r}_1^e \; \rho^e(\mathbf{r}_1^e) = N_e$ and $\int d\mathbf{r}_1^p \; \rho^p(\mathbf{r}_1^p) = N_p$. Here $\mathbf{r}^e$ and $\mathbf{r}^p$ denote the collective spatial coordinates of the electrons and quantum protons, respectively, $\rho^e(\mathbf{r}_1^e)$ and $\rho^p(\mathbf{r}_1^p)$ denote the one-particle electron and proton densities, respectively, and $v(\mathbf{r}_1)$ is the Coulomb interaction between the electron or proton and the classical nuclei, as defined in ref 12. Analogous to electronic DFT, we define a noninteracting reference system in which all quantum particles (i.e., electrons and quantum protons) do not interact with each other. The ground state nuclear−electronic wave function of this noninteracting reference system is given by the product of electronic and nuclear Slater determinants.

Following the Kohn−Sham procedure,[17,18] the universal functional $F[\rho^e, \rho^p]$ for the interacting system can be expressed as[11,12]

$$F[\rho^e, \rho^p] = T_s[\rho^e, \rho^p] + J_{ep}[\rho^e, \rho^p] + E_{epc}[\rho^e, \rho^p] + J_{ee}[\rho^e] + E_{exc}[\rho^e] + J_{pp}[\rho^p] + E_{pxc}[\rho^p] \tag{2}$$

where $T_s[\rho^e, \rho^p]$ is the total kinetic energy for the noninteracting system. The classical parts of the electron−proton and

electron−electron Coulomb interactions are given by

$$J_{ep}[\rho^e, \rho^p] = - \iint d\mathbf{r}_1^e \, d\mathbf{r}_1^p \frac{\rho^e(\mathbf{r}_1^e) \, \rho^p(\mathbf{r}_1^p)}{|\mathbf{r}_1^e - \mathbf{r}_1^p|} \qquad (3)$$

and

$$J_{ee}[\rho^e] = \frac{1}{2} \iint d\mathbf{r}_1^e \, d\mathbf{r}_2^e \frac{\rho^e(\mathbf{r}_1^e) \, \rho^e(\mathbf{r}_2^e)}{|\mathbf{r}_1^e - \mathbf{r}_2^e|} \qquad (4)$$

and the proton−proton Coulomb interaction $J_{pp}[\rho^p]$ is defined analogously.

The terms $E_{epc}[\rho^e, \rho^p]$, $E_{exc}[\rho^e]$, and $E_{pxc}[\rho^p]$ are the electron−proton correlation functional, the electron exchange-correlation functional, and the proton exchange-correlation functional, respectively. In this formulation,[11,12] the definition of the electron exchange-correlation functional, $E_{exc}[\rho^e]$, is consistent with that from standard electronic DFT.[17−19] Thus, the traditional, well-established electron exchange-correlation functionals can be used, although these electronic functionals have been parametrized without the inclusion of nuclear quantum effects and electron−proton correlation. Furthermore, the contribution from the proton exchange-correlation functional, $E_{pxc}[\rho^p]$, is assumed to be negligible due to the localized nature of protons in typical molecular systems with only selected hydrogen nuclei treated quantum mechanically. For systems with multiple quantum nuclei, the quantum protons may be treated with a generalized Hartree−Fock approach, in which each proton can occupy a different localized spatial orbital, and the proton exchange-correlation functional may be chosen to be the diagonal proton exchange interaction terms to eliminate the self-interaction terms.[20] The present paper focuses on the development of a suitable electron−proton correlation functional, $E_{epc}[\rho^e, \rho^p]$.

Following the strategy devised in ref 11, we define the electron−proton correlation functional in terms of the electron−proton pair density, $\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)$, as

$$E_{epc}[\rho^e, \rho^p] = - \iint d\mathbf{r}_1^e \, d\mathbf{r}_1^p \frac{\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)}{|\mathbf{r}_1^e - \mathbf{r}_1^p|} - J_{ep}[\rho^e, \rho^p] \qquad (5)$$

In ref 11, the electron−proton pair density was obtained from an explicitly correlated nuclear−electronic wave function defined as $\Psi_{gem} = (1 + G)\Phi^e\Phi^p$,[15] where Φ^e and Φ^p are electronic and nuclear Slater determinants, respectively, and

$$G(\mathbf{r}^e, \mathbf{r}^p) = \sum_{i=1}^{N_e} \sum_{i'=1}^{N_p} g(\mathbf{r}_i^e, \mathbf{r}_{i'}^p) \qquad (6)$$

$$g(\mathbf{r}_i^e, \mathbf{r}_{i'}^p) = \sum_{k=1}^{N_{gem}} b_k \, e^{-\gamma_k |\mathbf{r}_i^e - \mathbf{r}_{i'}^p|^2} \qquad (7)$$

Here, N_{gem} is the number of Gaussian type geminal functions used in the expansion, and b_k and γ_k are parameters that define these functions. Gaussian type geminal functions are used to ensure the tractable calculation of integrals over Gaussian basis functions.

In the present paper, we determine the electron−proton pair density from the alternative explicitly correlated nuclear−electronic

wave function defined as[21]

$$\Psi_{gem} = \sqrt{1 + G}\Phi^e\Phi^p \qquad (8)$$

The significant advantage of this alternative nuclear−electronic wave function ansatz over the previous ansatz is that all terms quadratic in the geminal functions are eliminated from the electron−proton pair density. Note that this alternative ansatz retains the important characteristics of a mixed nuclear−electronic wave function: it is antisymmetric with respect to the exchange of electrons or quantum protons, approaches the Hartree−Fock wave function at large electron−proton distances, and has the numerical flexibility to describe the correct linear behavior at small electron−proton distances. As a result of this alternative ansatz, in conjunction with a physically reasonable approximation for the two-particle electron and proton densities, all terms in the electron−proton pair density can be retained in the present treatment, compared to the neglect of 24 out of 26 terms in the electron−proton pair density in the previous treatment.[11,22] The remainder of this Letter presents the derivation of the new electron−proton density functional and an initial application to a model system.

Prior to the derivation, we define the geminal reduced densities, which are associated with the geminal wave function, and the auxiliary reduced densities, which are associated with the Slater determinants. The geminal one-particle and two-particle electron densities are defined as

$$\rho_1^e(\mathbf{r}_1^e) = \frac{N_e}{\langle \Psi_{gem} | \Psi_{gem} \rangle} \langle \Psi_{gem} | \Psi_{gem} \rangle_{-e_1} \qquad (9)$$

$$\rho_2^e(\mathbf{r}_1^e, \mathbf{r}_2^e) = \frac{N_e(N_e - 1)}{2\langle \Psi_{gem} | \Psi_{gem} \rangle} \langle \Psi_{gem} | \Psi_{gem} \rangle_{-e_1 e_2} \qquad (10)$$

and the one-particle and two-particle proton densities are defined analogously. The geminal electron−proton pair density is defined as

$$\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p) = \frac{N_e N_p}{\langle \Psi_{gem} | \Psi_{gem} \rangle} \langle \Psi_{gem} | \Psi_{gem} \rangle_{-e_1 p_1} \qquad (11)$$

In these expressions and those that follow, angular brackets without subscripts indicate integration over all coordinates, angular brackets with subscripts indicate the spatial coordinates of integration (i.e., $\langle \cdots \rangle_{e1}$ indicates integration over $\mathbf{r}_1^e$), and angular brackets with subscripts preceded by a minus sign denote integration over all coordinates except the specified spatial coordinate(s) (i.e., $\langle \cdots \rangle_{-e1}$ indicates integration over all coordinates except $\mathbf{r}_1^e$). The auxiliary one-particle and two-particle electron densities, $\tilde{\rho}_1^e(\mathbf{r}_1^e)$ and $\tilde{\rho}_2^e(\mathbf{r}_1^e, \mathbf{r}_2^e)$, are defined by substituting Φ^e for Ψ_{gem} in eqs 9 and 10, and the auxiliary proton densities are defined analogously with Φ^p. Note that the Slater determinants, Φ^e and Φ^p, are normalized because they are constructed with orthonormal spin orbitals, but the geminal wave function, Ψ_{gem}, is not normalized due to the geminal factor in eq 8.

The geminal electron−proton pair density corresponding to the ansatz given in eq 8 can be expressed in terms of the auxiliary densities as follows:

$$\begin{aligned}
\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p) = \frac{1}{1 + \langle \tilde{\rho}_1^e(\mathbf{r}_1^e) \, \tilde{\rho}_1^p(\mathbf{r}_1^p) \, g(\mathbf{r}_1^e, \mathbf{r}_1^p) \rangle_{e_1 p_1}} \big[& \tilde{\rho}_1^e(\mathbf{r}_1^e) \, \tilde{\rho}_1^p(\mathbf{r}_1^p) \\
\times \{1 + g(\mathbf{r}_1^e, \mathbf{r}_1^p)\} + 2\tilde{\rho}_1^p(\mathbf{r}_1^p) & \langle \tilde{\rho}_2^e(\mathbf{r}_1^e, \mathbf{r}_2^e) \, g(\mathbf{r}_2^e, \mathbf{r}_1^p) \rangle_{e_2} \\
+ 2\tilde{\rho}_1^e(\mathbf{r}_1^e) \langle \tilde{\rho}_2^p(\mathbf{r}_1^p, \mathbf{r}_2^p) & \, g(\mathbf{r}_1^e, \mathbf{r}_2^p) \rangle_{p_2} \\
+ 4\langle \tilde{\rho}_2^e(\mathbf{r}_1^e, \mathbf{r}_2^e) \, \tilde{\rho}_2^p(\mathbf{r}_1^p, \mathbf{r}_2^p) & \, g(\mathbf{r}_2^e, \mathbf{r}_2^p) \rangle_{e_2 p_2} \big] \qquad (12)
\end{aligned}$$

For comparison, the electron−proton pair density corresponding to the previous wave function ansatz, with the geminal factor of $(1+G)$ rather than $(1+G)^{1/2}$, was comprised of 26 terms, as given by eq 32 in ref 22. Thus, the present electron−proton pair density is much simpler. In the previous derivation,[11] the geminal electron−proton pair density was truncated in a manner that eliminated all terms of order g^2 and all terms that included densities other than one-particle densities. As a result, the electron−proton pair density included only the first two terms, $\tilde{\rho}_1^e \tilde{\rho}_1^p (1+g)$, in eq 12. This truncation required the renormalization of the electron−proton pair density so that $\langle \rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p) \rangle_{e_1 p_1} = N_e N_p$, leading to an additional factor of $(N_e N_p)^{-1}$ in the second term of the denominator. In the present approach, the electron−proton pair density in eq 12 is already normalized properly because no terms have been eliminated. Note that the wave function ansatz with the geminal factor of $(1+G)^{1/2}$ does not lead to any terms of order g^2 in the electron−proton pair density, and the terms including two-particle densities have been retained in eq 12.

To develop an effective electron−proton density functional, the electron−proton pair density given in eq 12 should depend on only one-particle densities. For this purpose, we assume that the auxiliary two-particle electron density can be approximated as

$$\tilde{\rho}_2^e(\mathbf{r}_1^e,\mathbf{r}_2^e) \approx \frac{1}{2}\frac{N_e-1}{N_e}\tilde{\rho}_1^e(\mathbf{r}_1^e)\,\tilde{\rho}_1^e(\mathbf{r}_2^e) \tag{13}$$

This independent particle approximation is based on the assumption that the direct electron−electron exchange contributions included in the electron exchange-correlation functional, as defined in eq 2, are significantly greater than the indirect electron−electron exchange contributions in the electron−proton correlation functional. As a result, the indirect electron−electron exchange effects arising from the dependence of the electron−proton pair density on the two-particle electron density are neglected. We invoke the analogous approximation for the auxiliary two-particle proton density. These two-particle density terms were completely neglected in the previous treatment.[11]

Substituting these approximate auxiliary two-particle electron and proton densities into eq 12 leads to

$$\rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p) = \frac{\tilde{\rho}^e \tilde{\rho}^p}{1+\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}}\left[1+g+\frac{N_e-1}{N_e}\langle\tilde{\rho}^e g\rangle_e \right.$$
$$\left. +\frac{N_p-1}{N_p}\langle\tilde{\rho}^p g\rangle_p + \frac{(N_e-1)(N_p-1)}{N_e N_p}\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}\right] \tag{14}$$

For notational convenience, we have dropped the dependence of the reduced densities on the coordinates, defined $g \equiv g(\mathbf{r}_1^e,\mathbf{r}_1^p)$, dropped the subscript on the one-particle densities, and simplified the subscripts on the brackets to denote the electron and/or proton spatial coordinates in the integrand. The analogous procedure for the geminal one-particle electron and proton densities leads to

$$\rho^e(\mathbf{r}_1^e) = \frac{\tilde{\rho}^e}{1+\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}}\left[1+\langle\tilde{\rho}^p g\rangle_p + \frac{N_e-1}{N_e}\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}\right] \tag{15}$$

$$\rho^p(\mathbf{r}_1^p) = \frac{\tilde{\rho}^p}{1+\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}}\left[1+\langle\tilde{\rho}^e g\rangle_e + \frac{N_p-1}{N_p}\langle\tilde{\rho}^e\tilde{\rho}^p g\rangle_{ep}\right] \tag{16}$$

Note that these densities satisfy the sum rules, $\rho^e(\mathbf{r}_1^e) = N_p^{-1}\langle\rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p)\rangle_p$ and $\rho^p(\mathbf{r}_1^p) = N_e^{-1}\langle\rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p)\rangle_e$.

The next step is to express the electron−proton pair density in eq 14 in terms of the one-particle densities given in eqs 15 and 16 by eliminating the auxiliary densities. To achieve this goal, expressions for the auxiliary one-particle densities in terms of the geminal one-particle densities must be determined. In principle, eqs 15 and 16 could be inverted to determine these expressions, but the exact analytical solution is not known. Instead, we follow the approximate procedure of ref 11 and replace $\tilde{\rho}^e(\mathbf{r}_1^e)$ with $\rho^e(\mathbf{r}_1^e)$ and $\tilde{\rho}^p(\mathbf{r}_1^p)$ with $\rho^p(\mathbf{r}_1^p)$ whenever they are multiplied by the geminal factor g in eqs 14, 15, and 16. These substitutions lead to the following expressions for the approximate geminal densities:

$$\rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p) = \frac{1}{1+\langle\rho^e\rho^p g\rangle_{ep}}\left[\tilde{\rho}^e\tilde{\rho}^p + \rho^e\rho^p g \right.$$
$$+\frac{N_e-1}{N_e}\rho^e\rho^p\langle\rho^e g\rangle_e + \frac{N_p-1}{N_p}\rho^e\rho^p\langle\rho^p g\rangle_p$$
$$\left. +\frac{(N_e-1)(N_p-1)}{N_e N_p}\rho^e\rho^p\langle\rho^e\rho^p g\rangle_{ep}\right] \tag{17}$$

$$\rho^e(\mathbf{r}_1^e) = \frac{1}{1+\langle\rho^e\rho^p g\rangle_{ep}}\left[\tilde{\rho}^e + \rho^e\langle\rho^p g\rangle_p + \frac{N_e-1}{N_e}\rho^e\langle\rho^e\rho^p g\rangle_{ep}\right] \tag{18}$$

$$\rho^p(\mathbf{r}_1^p) = \frac{1}{1+\langle\rho^e\rho^p g\rangle_{ep}}\left[\tilde{\rho}^p + \rho^p\langle\rho^e g\rangle_e + \frac{N_p-1}{N_p}\rho^p\langle\rho^e\rho^p g\rangle_{ep}\right] \tag{19}$$

Note that these reduced densities still satisfy the sum rules given above and retain the property that $\lim_{r_{ep}\to\infty}\rho^{ep} = \tilde{\rho}^e\tilde{\rho}^p = \rho^e\rho^p$.

Substituting the expressions for the auxiliary one-particle electron and proton densities obtained from eqs 18 and 19 into the electron−proton pair density given in eq 17 leads to the final expression for the approximate pair density in terms of the one-particle densities:

$$\rho^{ep}(\mathbf{r}_1^e,\mathbf{r}_1^p) = \rho^e\rho^p\left[1+\langle N_e^{-1}N_p^{-1}\rho^e\rho^p g\rangle_{ep}\right.$$
$$\left. -\langle N_e^{-1}\rho^e g\rangle_e - \langle N_p^{-1}\rho^p g\rangle_p + \frac{g+\langle\rho^e g\rangle_e\langle\rho^p g\rangle_p}{1+\langle\rho^e\rho^p g\rangle_{ep}}\right] \tag{20}$$

Equation 20 represents an approximate pair density derived from the explicitly correlated nuclear−electronic wave function given in eq 8 and defines an electron−proton correlation functional when substituted into eq 5. This expression is identical to the previous expression[11] derived from a different explicitly correlated nuclear−electronic wave function, except the last term, which differs by a factor of $N_e N_p$ in the second term of both the numerator and denominator. These differences arise from the truncation of the electron−proton pair density and the subsequent renormalization in the previous treatment. Since the

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present derivation includes all terms of the electron—proton pair density, whereas the previous derivation neglected a large number of terms, we expect the present functional to be more reliable in terms of scaling with respect to the number of electrons and protons. The computational cost is identical for the two functionals.

We applied the NEO-DFT approach with this electron—proton density functional to the model system, $[He-H-He]^+$, and the isotopomers $[He-D-He]^+$ and $[He-T-He]^+$. The two helium nuclei were treated classically at a fixed distance, and the central nucleus and four electrons were treated quantum mechanically. We studied these systems with the cc-pVDZ and cc-pVTZ electronic basis sets,[23,24] where the electronic basis functions corresponding to the central nucleus were placed at the midpoint between the two helium nuclei. The nuclear basis set was comprised of a single 1s nuclear basis function placed at the midpoint between the two helium nuclei, and the exponent was optimized variationally during the NEO-DFT calculation. Two Gaussian type geminal functions were used with geminal parameters obtained variationally with the wave function ansatz in eq 8 for a one-electron/one-proton model system.[21] To account for differences between the NEO-DFT and variational wave function approach, the geminal functions were scaled by a single constant factor to reproduce the hydrogen vibrational stretching frequency of $[He-H-He]^+$ with the cc-pVDZ electronic basis set. For all other systems and basis sets, these geminal parameters were fixed during the NEO-DFT calculations. Moreover, in this Letter, the electron exchange-correlation functional was chosen to be the Hartree—Fock exchange. Future studies will examine the effects of combining this electron—proton correlation functional with various electron exchange-correlation functionals. All calculations were performed with a modified version of the GAMESS program.[25]

The objective of this application is to provide evidence that this electron—proton functional can provide accurate hydrogen nuclear densities. The hydrogen vibrational stretching frequencies were determined from a Gaussian fit of the nuclear density along the He—He axis. These frequencies are compared to the corresponding splitting for the three-dimensional hydrogen vibrational states calculated with the Fourier grid Hamiltonian (FGH) method.[26] Since the nuclear basis set contains only a single 1s nuclear basis function, it is incapable of reproducing both the stretching and bending hydrogen vibrational frequencies. For these calculations, we determined the He—He distances at which the stretching and bending frequencies calculated with the FGH method are qualitatively similar. The resulting He—He distances for the cc-pVDZ and cc-pVTZ electronic basis sets were determined to be 1.955 and 1.945 Å, respectively. Future work will focus on studies with larger electronic and nuclear basis sets that will enable the calculation of bending as well as stretching frequencies.

The results of these calculations are provided in Table 1. The NEO-HF (Hartree—Fock) frequencies are much higher than the NEO-DFT frequencies, which are in qualitative agreement with the FGH frequencies. These values illustrate the importance of electron—proton correlation. In addition, these results indicate that the geminal parameters are reasonably transferable to larger electronic basis sets and to other isotopes of hydrogen for this model system. From a physical perspective, the geminal parameters are expected to be transferable because these terms are significant only at small electron—proton distances and should be relatively independent of the external chemical environment.

Table 1. Vibrational Frequencies in cm^{-1} Corresponding to the Hydrogen Vibrational Stretching Motion Calculated with the NEO-HF, NEO-DFT, and FGH Methods for the $[He-X-He]^+$ Systems with X = H, D, or T^a

	cc-pVDZ			cc-pVTZ		
isotope	NEO-HF	NEO-DFT	FGH	NEO-HF	NEO-DFT	FGH
H	3098	1191	1191	3122	1103	1111
D	2284	820	801	2330	782	740
T	1903	660	633	1954	646	581

^{a} The cc-pVDZ or cc-pVTZ electronic basis set was used as indicated. The NEO-HF and NEO-DFT calculations were performed using a single 1s nuclear basis function with a variationally optimized exponent, and the NEO-DFT calculations were performed using two geminals with parameters $(b_1, \gamma_1) = (0.3969, 0.34)$ and $(b_2, \gamma_2) = (0.8912, 2.47)$ for the electron—proton functional presented in this paper. Values of γ_k given in bohr^{-2}.

Future work will focus on optimizing the geminal parameters for applications to a wide range of chemical systems.

Qualitatively similar results are obtained for this model system with the previously derived electron—proton functional[11] using different geminal parameters, as given in the Supporting Information. Note that this previous functional may be derived from the ansatz given in eq 8 if the two-particle densities are neglected. The two electron—proton functionals will exhibit different scaling behaviors with respect to the number of electrons and protons, however, and the present functional is expected to be more reliable because fewer approximations were invoked in the derivation. Investigation of these scaling properties will require the study of systems with a larger number of quantum particles and is a direction for future research.

In this Letter, we derived an electron—proton density functional for use in multicomponent DFT calculations, where electrons and selected hydrogen nuclei are treated quantum mechanically. This functional was derived directly from the electron—proton pair density associated with a recently proposed ansatz for the explicitly correlated nuclear—electronic wave function. The advantage of this functional over the previously derived functional is that the new wave function ansatz, combined with the independent particle approximation for the auxiliary two-particle electron and proton densities, enabled us to retain all of the terms in the electron—proton pair density, whereas the previous derivation neglected a large number of terms. Thus, the present functional is based on a more rigorous derivation and therefore may be more robust, although further studies are required to assess both functionals. In particular, future work will focus on the further development of these types of electron—proton functionals with larger electronic and nuclear basis sets in conjunction with standard electron exchange-correlation functionals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Analog to Table 1 for the previously derived electron—proton functional. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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