Development of Electron-Proton Density Functionals for Multicomponent Density Functional Theory

Arindam Chakraborty, Michael V. Pak, and Sharon Hammes-Schiffer*

Department of Chemistry, 104 Chemistry Building, Pennsylvania State University, University Park, Pennsylvania 16802, USA

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We present a strategy for the development of electron-proton density functionals in multicomponent density functional theory, treating electrons and selected nuclei quantum mechanically without the Born-Oppenheimer approximation. An electron-proton functional is derived using an explicitly correlated electron-proton pair density. This functional provides accurate hydrogen nuclear densities, thereby enabling reliable calculations of molecular properties. This approach is potentially applicable to relatively large molecular systems with key hydrogen nuclei treated quantum mechanically.

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Density functional theory (DFT) is a powerful tool for electronic structure calculations of molecules, materials, and biological systems [1]. Conventional DFT is based on the Born-Oppenheimer separation of electrons and nuclei, and typically the nuclei are treated classically. Nuclear quantum effects play an important role in a wide range of processes, particularly for hydrogen bonding and hydrogen transfer. A multicomponent DFT for electrons and nuclei, which treats both electrons and nuclei quantum mechanically without the Born-Oppenheimer approximation, has been proposed [2–4]. Although the existence of ground-state density functionals in terms of the one-particle electronic and nuclear densities has been proven [2,5], the development of such electronic-nuclear functionals is challenging. Reparametrizing existing electronic functionals for use as electron-proton functionals [6] is not physically meaningful due to the fundamental differences between electron-electron and electron-proton interactions. Approximate electronic-nuclear functionals in terms of the one-particle electron density and the N_n particle nuclear density matrix have been proposed for systems in which all N_n nuclei are treated quantum mechanically, but this approach has not been extended beyond $H_2{}^+$ [4].

Previously we developed the nuclear-electronic orbital (NEO) approach [7], in which only selected nuclei are treated quantum mechanically on the same level as the electrons, while the remaining nuclei are treated classically. This approach is designed for systems in which at least two nuclei are treated classically, thereby eliminating the difficulties associated with translations and rotations. Inadequate treatment of electron-proton correlation has been shown to result in nonphysical extreme localization of the nuclear wave functions, leading to severe overestimation of hydrogen vibrational frequencies with errors that are often on the same order as the frequencies themselves [4,8]. The overlocalization of the nuclear wave function also significantly affects other physical properties, such as geometries, isotope effects, and tunneling splittings. Electron-proton dynamical correlation has a greater qualitative impact on the wave function than electron-electron or proton-proton dynamical correlation because of the attractive interaction between the electron and proton and the disparity in the masses. To address this problem, we developed an explicitly correlated method for the inclusion of electron-proton correlation [8,9]. An alternative route is the development of electron-proton density functionals within the context of multicomponent DFT. The advantage of this route is that it enables the consistent treatment of electron-electron and electron-proton correlation and has the potential to be computationally practical for relatively large molecules. In this Letter, we propose a general strategy for designing electron-proton density functionals in terms of the one-particle electronic and nuclear densities. The existence of such an electron-proton functional within the framework of a formally exact multicomponent DFT has been proven [2,5]. Our objective is to develop electron-proton functionals that provide accurate ground-state hydrogen nuclear densities in molecular systems.

We develop an electron-proton functional for a system with N_e electrons, N_p quantum protons, and N_c classical point charges. For this system, the Hamiltonian is

$$\hat{H} = -\sum_{i=1}^{N_e}\left(\frac{1}{2}\nabla_{ie}^2\right) - \sum_{i=1}^{N_p}\left(\frac{1}{2m_p}\nabla_{ip}^2\right) + \sum_{i=1}^{N_e} v(\mathbf{r}_i^e) - \sum_{i=1}^{N_p} v(\mathbf{r}_i^p) - \sum_{i=1}^{N_e}\sum_{j=1}^{N_p}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^p|} + \sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|} + \sum_{i=1}^{N_p}\sum_{j>i}^{N_p}\frac{1}{|\mathbf{r}_i^p - \mathbf{r}_j^p|}, \tag{1}$$

where $v(\mathbf{r}_1)$ is the interaction between the electron or proton and the classical nuclei, and $\mathbf{r}_i^e$ and $\mathbf{r}_i^p$ denote spatial coordinates of the electrons and protons, respectively.

As in conventional DFT, the ground-state energy is the minimum of the energy functional

$$E[\rho^e, \rho^p] = \int d\mathbf{r}_1^e \rho^e(\mathbf{r}_1^e) v(\mathbf{r}_1^e) - \int d\mathbf{r}_1^p \rho^p(\mathbf{r}_1^p) v(\mathbf{r}_1^p) + F[\rho^e, \rho^p], \tag{2}$$

where $F[\rho^e, \rho^p] = \min_{\Psi\to\rho^e,\rho^p}\langle\Psi|H'|\Psi\rangle$ and H' is the

Hamiltonian operator in Eq. (1) without the terms corresponding to interactions with the classical nuclei. The ground-state electron and proton densities, as well as the ground-state energy, are obtained by minimizing $E[\rho^e, \rho^p]$ subject to the constraints $\int d\mathbf{r}_1^e \rho^e(\mathbf{r}_1^e) = N_e$ and $\int d\mathbf{r}_1^p \rho^p(\mathbf{r}_1^p) = N_p$. Analogous to electronic DFT, we invoke a corresponding noninteracting reference system, in which all quantum particles (i.e., electrons and quantum protons) do not interact with each other. For this system, the ground-state electron-proton wave function can be represented by the product of electronic and nuclear Slater determinants, $\Psi_s(\mathbf{x}^e, \mathbf{x}^p) = \Phi_s^e(\mathbf{x}^e)\Phi_s^p(\mathbf{x}^p)$, where the electronic and nuclear spatial orbitals are determined by the corresponding one-particle Hamiltonians.

Following the Kohn-Sham procedure [10], we express $F[\rho^e, \rho^p]$ for the interacting system as

$$F[\rho^e, \rho^p] = T_s[\rho^e, \rho^p] + J_{ep}[\rho^e, \rho^p] + E_{epc}[\rho^e, \rho^p] + J_{ee}[\rho^e] + E_{exc}[\rho^e] + J_{pp}[\rho^p] + E_{pxc}[\rho^p], \tag{3}$$

$$E_{epc}[\rho^e, \rho^p] = V_{ep}[\rho^e, \rho^p] - J_{ep}[\rho^e, \rho^p], \tag{4}$$

$$E_{exc}[\rho^e] = T_{ee}[\rho^e] - T_s^e[\rho^e] + V_{ee}[\rho^e] - J_{ee}[\rho^e], \tag{5}$$

$$E_{pxc}[\rho^p] = T_{pp}[\rho^p] - T_s^p[\rho^p] + V_{pp}[\rho^p] - J_{pp}[\rho^p]. \tag{6}$$

The classical parts of the electron-proton and electron-electron Coulomb interactions are

$$\begin{aligned} J_{ep}[\rho^e, \rho^p] &= -\iint d\mathbf{r}_1^e d\mathbf{r}_1^p \frac{\rho^e(\mathbf{r}_1^e)\rho^p(\mathbf{r}_1^p)}{|\mathbf{r}_1^e - \mathbf{r}_1^p|}, \\ J_{ee}[\rho^e] &= \frac{1}{2}\iint d\mathbf{r}_1^e d\mathbf{r}_2^e \frac{\rho^e(\mathbf{r}_1^e)\rho^e(\mathbf{r}_2^e)}{|\mathbf{r}_1^e - \mathbf{r}_2^e|}, \end{aligned} \tag{7}$$

and the proton-proton classical Coulomb interaction $J_{pp}[\rho^p]$ is defined analogously. $T_s^e[\rho^e]$ is the electronic kinetic energy for the noninteracting system, and $T_{ee}[\rho^e]$ and $V_{ee}[\rho^e]$ are the electronic kinetic energy and the electron-electron interaction energy, respectively, including electron-electron correlation effects depending on only ρ^e. $T_s^p[\rho^p]$, $T_{pp}[\rho^p]$, and $V_{pp}[\rho^p]$ are defined analogously for protons. $V_{ep}[\rho^e, \rho^p]$ is the electron-proton interaction energy including electron-proton correlation effects. These quantities are defined in this manner for consistency with standard electronic functionals. Based on these definitions, the exact form of Eq. (4) may include additional terms (i.e., residual electron-electron and proton-proton correlation effects that depend on both ρ^e and ρ^p and electron-proton correlation effects that impact the kinetic energies), but these terms are expected to be smaller than the electron-proton interaction terms and are neglected for simplicity.

The electron-proton Kohn-Sham equations are

$$\begin{aligned} \left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^e(\mathbf{r}_1^e)\right)\psi_i^e &= \varepsilon_i^e \psi_i^e \\ \left(-\frac{1}{2m_p}\nabla^2 + v_{\text{eff}}^p(\mathbf{r}_1^p)\right)\psi_i^p &= \varepsilon_i^p \psi_i^p, \end{aligned} \tag{8}$$

$$v_{\text{eff}}^e(\mathbf{r}_1^e) = v(\mathbf{r}_1^e) - \int \frac{\rho^p(\mathbf{r}_1^p)}{|\mathbf{r}_1^p - \mathbf{r}_1^e|} d\mathbf{r}_1^p + \frac{\delta E_{epc}[\rho^e, \rho^p]}{\delta \rho^e(\mathbf{r}_1^e)} + \int \frac{\rho^e(\mathbf{r}_2^e)}{|\mathbf{r}_2^e - \mathbf{r}_1^e|} d\mathbf{r}_2^e + \frac{\delta E_{exc}[\rho^e]}{\delta \rho^e(\mathbf{r}_1^e)},$$

$$v_{\text{eff}}^p(\mathbf{r}_1^p) = -v(\mathbf{r}_1^p) - \int \frac{\rho^e(\mathbf{r}_1^e)}{|\mathbf{r}_1^e - \mathbf{r}_1^p|} d\mathbf{r}_1^e + \frac{\delta E_{epc}[\rho^e, \rho^p]}{\delta \rho^p(\mathbf{r}_1^p)} + \int \frac{\rho^p(\mathbf{r}_2^p)}{|\mathbf{r}_2^p - \mathbf{r}_1^p|} d\mathbf{r}_2^p + \frac{\delta E_{pxc}[\rho^p]}{\delta \rho^p(\mathbf{r}_1^p)},$$

where $\rho^e(\mathbf{r}_1^e) = \sum_{i=1}^{N_e} |\psi_i^e(\mathbf{r}_1^e)|^2$, and $\rho^p(\mathbf{r}_1^p) = \sum_{i=1}^{N_p} |\psi_i^p(\mathbf{r}_1^p)|^2$. These equations can be solved iteratively to self-consistency.

The objective of this Letter is to derive an electron-proton correlation functional by analyzing the relationship between the electron-proton pair density and the one-particle electron and proton densities associated with an explicitly correlated wave function constructed with Gaussian-type geminals. The electron-proton correlation functional is defined using Eq. (4) as

$$E_{epc}[\rho^e, \rho^p] = \iint d\mathbf{r}_1^e d\mathbf{r}_1^p \rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)/|\mathbf{r}_1^e - \mathbf{r}_1^p| - J_{ep}[\rho^e, \rho^p], \tag{9}$$

and the functional dependence of the electron-proton pair density ρ^{ep} on the one-particle densities ρ^e and ρ^p is determined from the analysis of the explicitly correlated wave function. Similar strategies based on explicitly correlated electronic wave functions were used previously to develop electronic density functionals [11]. The present work differs from this previous work in terms of the multicomponent nature of the system, the form of the geminal ansatz of the wave function, the approximations invoked, and the analytical properties of the functional.

This Letter focuses on the development of an electron-proton correlation functional. Because of the definition of $E_{exc}[\rho^e]$ in Eq. (5), the standard electronic functionals can be used in this formulation to include electron-electron exchange and correlation effects. We have implemented a NEO-DFT(ee) method that includes only electron-electron correlation in this manner [12]. Note that the standard electronic functionals are parametrized without the inclusion of nuclear quantum effects and electron-proton correlation. In principle, this formalism could also include proton-proton exchange and correlation if suitable nuclear functionals were available. For typical molecular systems with only selected hydrogen nuclei treated quantum mechanically in a suitable manner, however, the proton-

proton exchange and dynamical correlation effects are significantly smaller than the electron-electron and electron-proton counterparts because the proton densities are much more localized and spatially separated than the electron densities. In practice, the quantum protons may be treated with a generalized Hartree-Fock (HF) approach in which each proton can occupy a different spatial orbital, and Hartree-Fock exchange for protons may be included to alleviate potential difficulties with self-interaction.

Our ansatz for the form of the explicitly correlated nuclear-electronic wave function is

$$\Psi_{\mathrm{gem}}(\mathbf{x}^e, \mathbf{x}^p) = \Phi^e(\mathbf{x}^e)\Phi^p(\mathbf{x}^p)[1 + G(\mathbf{r}^e, \mathbf{r}^p)], \tag{10}$$

where the Gaussian-type geminal expansion is defined as

$$\begin{aligned} G(\mathbf{r}^e, \mathbf{r}^p) &= \frac{1}{2}\sum_{i=1}^{N_e}\sum_{j=1}^{N_p}\sum_{k=1}^{N_{gem}} b_k \exp[-\gamma_k|\mathbf{r}_i^e - \mathbf{r}_j^p|^2] \\ &= \frac{1}{2}\sum_{i=1}^{N_e}\sum_{j=1}^{N_p} g(\mathbf{r}_i^e, \mathbf{r}_j^p). \end{aligned} \tag{11}$$

Previously we developed an explicitly correlated HF method, NEO-XCHF, which includes explicit electron-proton correlation directly into the NEO self-consistent-field procedure using this ansatz with the variational method [8,9]. Note that the definition of g in Eq. (11) differs by a factor of 2 compared to this previous work to simplify the subsequent equations. Unfortunately, the NEO-XCHF approach becomes expensive for large, many-electron systems, but it can be used as the basis for the development of electron-proton density functionals.

The electron-proton pair density $\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)$ is obtained from the geminal wave function in Eq. (10) by integrating over the appropriate electronic and proton coordinates, retaining only first-order terms, and normalizing so that $\langle\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)\rangle_{ep} = N_e N_p$. The one-particle densities $\rho^e(\mathbf{r}_1^e)$ and $\rho^p(\mathbf{r}_1^p)$ are obtained from $\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)$ by imposing the sum-rule conditions $\rho^e(\mathbf{r}_1^e) = N_p^{-1}\langle\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)\rangle_p$ and $\rho^p(\mathbf{r}_1^p) = N_e^{-1}\langle\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)\rangle_e$. The resulting densities are

$$\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p) = \frac{\tilde{\rho}^e\tilde{\rho}^p(1 + g)}{1 + \langle\tilde{\rho}^e\tilde{\rho}^p g N_e^{-1} N_p^{-1}\rangle_{ep}}, \tag{12}$$

$$\rho^e(\mathbf{r}_1^e) = \frac{\tilde{\rho}^e(1 + \langle\tilde{\rho}^p g N_p^{-1}\rangle_p)}{1 + \langle\tilde{\rho}^e\tilde{\rho}^p g N_e^{-1} N_p^{-1}\rangle_{ep}}, \tag{13}$$

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

Here the densities associated with the electronic and nuclear Slater determinants in the geminal wave function are denoted as $\tilde{\rho}^e(\mathbf{r}_1^e)$ and $\tilde{\rho}^p(\mathbf{r}_1^p)$, respectively, and are referred to as auxiliary densities. These auxiliary densities are distinct from the geminal densities $\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)$, $\rho^e(\mathbf{r}_1^e)$, and $\rho^p(\mathbf{r}_1^p)$ obtained from the complete geminal wave function. The subscripts on the angular brackets indicate if the integration is carried over the electron coordinate, the proton coordinate, or both coordinates. We neglect the contributions of the higher-order auxiliary density terms $O(\tilde{\rho}_2^e, \tilde{\rho}_2^p, g^2)$. Both the auxiliary and geminal densities are normalized to the number of particles when integrated over all space. The geminal one-particle densities depend on both the electron and proton auxiliary densities, and the geminal electron-proton pair density depends on the geminal one-particle densities through the auxiliary densities.

In principle, Eqs. (13) and (14) can be inverted to obtain expressions for the auxiliary densities in terms of the geminal one-particle densities, which in turn can be substituted into the expression for the geminal electron-proton pair density in Eq. (12) to obtain a functional relationship between the geminal electron-proton pair density and the geminal one-particle densities. However, the analytical solution of these coupled equations is not known and may not exist for all geminal densities, so we obtain an approximate solution. Retaining the property that $\lim_{r_{ep}\to\infty}\rho^{ep} = \tilde{\rho}^e\tilde{\rho}^p = \rho^e\rho^p$, we replace $\tilde{\rho}^e$ and $\tilde{\rho}^p$ with ρ^e and ρ^p, respectively, whenever they are multiplied by the geminal function g. This approximation leads to

$$\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p) = \frac{\tilde{\rho}^e\tilde{\rho}^p + \rho^e\rho^p g}{1 + \langle\rho^e\rho^p g N_e^{-1} N_p^{-1}\rangle_{ep}}. \tag{15}$$

Using ρ^{ep} from Eq. (15), the two sum-rule condition equations given above can be solved analytically to obtain the auxiliary densities in terms of the geminal one-particle densities [i.e., Eqs. (13) and (14) with the replacements used to obtain Eq. (15) from Eq. (12)]. The resulting expressions for the auxiliary densities can be substituted into Eq. (15) to obtain the geminal electron-proton pair density in terms of the geminal one-particle densities.

The final approximate expression for the geminal electron-proton pair density is

$$\begin{aligned} \rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p) = {}& \rho^e\rho^p + \rho^e\rho^p\langle\rho^e\rho^p g N_e^{-1} N_p^{-1}\rangle_{ep} \\ & - \rho^e\rho^p\langle\rho^e g N_e^{-1}\rangle_e - \rho^e\rho^p\langle\rho^p g N_p^{-1}\rangle_p \\ & + \frac{\rho^e\rho^p\langle\rho^p g N_p^{-1}\rangle_p\langle\rho^e g N_e^{-1}\rangle_e}{1 + \langle\rho^e\rho^p g N_e^{-1} N_p^{-1}\rangle_{ep}} \\ & + \frac{\rho^e\rho^p g}{1 + \langle\rho^e\rho^p g N_e^{-1} N_p^{-1}\rangle_{ep}}. \end{aligned} \tag{16}$$

Here the first term $\rho^e\rho^p$ is the uncorrelated electron-proton pair density and is responsible for the classical electron-proton Coulomb term J_{ep}. The remaining terms explicitly couple the electron and proton densities through the geminal function g. The electron-proton pair density in Eq. (16) was constructed to become $\rho^e\rho^p$ when $g = 0$ and to satisfy the sum-rule conditions. Other pair densities satisfying these criteria could be constructed using different approximations. Within the Kohn-Sham formalism, the electron-proton correlation functional is defined by substituting the geminal electron-proton pair density $\rho^{ep}(\mathbf{r}_1^e, \mathbf{r}_1^p)$ from

Eq. (16) into Eq. (9), where the one-particle densities ρ^e and ρ^p are obtained from the Kohn-Sham orbitals.

To test this electron-proton functional, we applied it to the $[\text{He-H-He}]^+$ system using NEO-DFT, an implementation of multicomponent DFT. The two helium nuclei are treated classically, and the hydrogen nucleus and four electrons are treated quantum mechanically. We used the same electronic and nuclear basis sets as in Ref. [9] to allow a consistent comparison to previously reported results using the NEO-XCHF and Fourier grid Hamiltonian (FGH) methods. The electronic and nuclear basis functions for the hydrogen were placed at the midpoint between the two helium nuclei. The distance between the two helium nuclei was chosen to be the equilibrium distance of 1.85 Å. Only a single Gaussian-type geminal was included in the electron-proton density functional. The values of b and γ for this geminal function were chosen to be those that were variationally optimized previously for a one-electron, one-proton model system using the NEO-XCHF method [8]. The values of these parameters are considered to be part of the electron-proton functional and are fixed during the NEO-DFT calculations. For these calculations, $v^e_{exc}(\mathbf{r}^e_1)$ is the Hartree-Fock electron exchange operator, but electron-electron correlation could be included with standard electronic functionals. With only a single quantum proton, the proton-proton Coulomb interaction and $v^p_{pxc}(\mathbf{r}^p_1)$ are omitted. This implementation is a hybrid DFT because it includes Hartree-Fock exchange for identical particles.

The results of these calculations are given in Table I. In general, the NEO-HF method produces nuclear wave functions that are too localized, leading to severe overestimations of hydrogen vibrational frequencies [8]. Table I indicates that the NEO-HF frequency is ~2000 cm^{-1} too high, whereas the NEO-DFT frequency is within ~50 cm^{-1} of the FGH and NEO-XCHF frequencies. This qualitative improvement in the nuclear density is critical for calculating all vibrationally averaged properties. The total NEO-DFT energy is significantly lower than the total NEO-HF energy but is still above the NEO-XCHF energy. The NEO-DFT approach is computationally much faster than the NEO-XCHF approach because it requires significantly fewer computationally expensive atomic orbital integrals involving geminal functions. Even for this small system, the NEO-DFT calculations are ~1400 times faster than the NEO-XCHF calculations. Thus, this electron-proton functional solves the pervasive problem of overlocalization of the nuclear density in a computationally practical manner.

The strategy presented here for deriving electron-proton density functionals can be improved and extended in many directions. The expressions in Eqs. (12)–(14) could be solved using density fitting methods or by invoking alternative approximations that still satisfy the sum rules. Higher-order density terms could be included in these expressions. Moreover, the parameters in the geminal functions could be used as free parameters fit to molecular properties of a chosen data set.

TABLE I. The frequencies in cm^{-1} for the $[\text{He-H-He}]^+$ system with H, D, and T as the central nucleus. The frequencies were determined from a Gaussian fit of the nuclear density along the He-He axis.

	NEO-HF[a,b]	NEO-XCHF[a,b]	FGH[a]	NEO-DFT[b,c]	ΔE[d]
H	3759	1030	1107	1072	−0.052
D	2738	725	783	770	−0.044
T	2274	588	639	630	−0.041

[a] Results from Ref. [9]. NEO-HF is Eq. (10) with $g = 0$.
[b] NEO calculations used a five $1s$ proton basis set [8].
[c] The electron-proton functional used a single geminal function with $b = 0.852$ a.u. and $\gamma = 1.962$ a.u.
[d] $\Delta E = E_{\text{NEO-DFT}} - E_{\text{NEO-HF}}$ is total energy difference in a.u.

We have proposed a general strategy for the development of electron-proton density functionals using an explicitly correlated electron-proton pair density. In NEO-DFT, typically only the chemically relevant hydrogen nuclei are treated quantum mechanically. This approach provides accurate ground-state hydrogen nuclear densities, enabling the reliable calculation of geometries, energies, frequencies, and isotope effects. Because of the local nature of the hydrogen nuclear densities in molecular systems, the scaling of this approach with the number of electrons will be similar to that of conventional electronic DFT. Thus, this approach is potentially applicable to relatively large, many-electron molecular systems of chemical and biological significance.

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*shs@chem.psu.edu

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