Multicomponent Coupled Cluster Singles and Doubles Theory within the Nuclear-Electronic Orbital Framework

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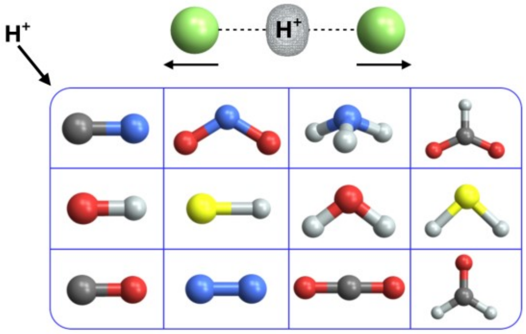
Abstract

The nuclear-electronic orbital (NEO) method treats all electrons and specified nuclei, typically protons, quantum mechanically on the same level with molecular orbital techniques. This approach directly includes nuclear delocalization, anharmonicity, and zero point energy contributions of the quantum nuclei in the self-consistent-field procedure for solving the time-independent Schrödinger equation. Herein the multicomponent wave function based methods configuration interaction singles and doubles (CISD) and coupled cluster singles and doubles (CCSD) are implemented within the NEO framework and are applied to molecular systems. In contrast to the NEO-HF (Hartree-Fock) and NEO-CISD methods, which produce proton densities that are much too localized, the NEO-CCSD method produces accurate proton densities in reasonable agreement with a grid-based reference. Moreover, the NEO-CCSD method also predicts accurate proton affinities in agreement with experimental measurements for a set of twelve molecules. An advantage of the NEO-CCSD method is its ability to include nuclear quantum effects, such as proton delocalization and zero point energy, during geometry optimizations and nuclear dynamics simulations. The NEO-CCSD method is a promising, parameter free approach for including nuclear quantum effects in high-level electronic structure calculations of molecular systems.

TOC Graphic



1 Introduction

A central approximation in computational quantum chemistry is the Born-Oppenheimer separation of electronic and nuclear motions. In this approximation, nuclei are treated classically as point charges during the solution of the time-independent electronic Schrödinger equation. However, many interesting chemical phenomena, such as hydrogen tunneling and proton-coupled electron transfer, require a quantum mechanical description of nuclei beyond the Born-Oppenheimer approximation.[1-6] A variety of methods has been developed in an effort to address these issues.[7-38] A computationally practical way of accurately incorporating nuclear quantum effects is provided by the nuclear-electronic orbital (NEO) approach.[10] In the NEO framework, select nuclei, typically protons, are treated quantum mechanically on the same level as the electrons, with at least two nuclei treated classically to avoid issues associated with translations and rotations. An advantage of the NEO method over conventional quantum chemistry methods is that anharmonicity, nuclear delocalization, and zero point energy contributions of the quantum nuclei are included directly in the self-consistent-field (SCF) procedure.

Due to the lack of electron-electron and, more importantly, electron-proton correlation effects, the NEO Hartree-Fock (NEO-HF) method, which represents the nuclear-electronic wavefunction as the product of a nuclear and electronic determinant, predicts highly over-localized proton densities. These problematic proton densities lead to inaccurate predictions of many molecular properties, including vibrationally averaged geometries, geometric isotope effects, proton affinities, and tunneling splittings.[14, 17] The NEO density functional theory (DFT) method includes both electron-electron and electron-proton correlation effects in a consistent and computationally practical manner.[9, 19, 21, 27] Recently our group developed a series of electron-proton correlation functionals, denoted epc17 and epc18, that are based on a multicomponent extension of the Colle-Salvetti approximation.[34, 38] The use of these electron-proton correlation functionals within the NEO-DFT framework represents a practical multicomponent quantum chemistry method that provides accurate proton densities and energies, such as proton affinities.[34-35, 38] Furthermore, the recently developed linear response NEO-TDDFT (time-dependent DFT) method enables the efficient calculation of accurate proton and electron excitation energies.[37] A significant advantage of the NEO-DFT method is its low computational cost (N^3 or N^4 in the case of exact electron exchange, where N is a measure of the system size), making it applicable to a wide range of chemical systems. However, a disadvantage of the NEO-DFT method is the lack of a clear path toward systematic improvement.

In contrast to the NEO-DFT approach, wavefunction methods within the NEO framework are systematically improvable and parameter free. Early work on these methods in our group includes the development of NEO-HF, second-order Møller-Plesset perturbation theory (NEO-MP2), configuration interaction (NEO-CI), and multiconfiguration self-consistent-field (NEO-MCSCF).[10, 15] Related methods have also been implemented independently at the HF[7] level and at the many-body perturbation theory (MBPTX, X=2,3,4),[12-13] CI,[8, 13] coupled cluster doubles (CCD), and Brueckner doubles[12] levels. Recently, the NEO method[10, 16] was implemented in the LOWDIN package[29] as the APMO (Any-Particle Molecular Orbital)[18, 22, 24] method. This method was extended to any-particle propagator theory and successfully used to predict proton and positron binding energies.[26, 28, 33] These methods either do not impact the proton density at all because they are implemented as energy corrections, such as the standard NEO-MP2 and propagator theory methods, or show very limited improvement in protonic density, such as current implementations of NEO-CI and NEO-MCSCF methods, due to insufficient treatment of electron-proton correlation. None of these wavefunction-based methods has been shown to provide accurate predictions of molecular properties that are dependent on the proton densities.

Another type of NEO wavefunction method incorporates explicit electron-proton correlation directly into the SCF procedure with Gaussian-type geminal functions, denoted the explicitly correlated HF (NEO-XCHF) method.[17, 20, 23, 30] These methods provide improved proton densities along the hydrogen stretching modes but do not provide accurate proton densities along the hydrogen bending modes; additionally, these explicitly correlated methods require computation of up to five-particle integrals, limiting applications to very small systems.[31] More recently, Chakraborty and coworkers presented a multicomponent coupled cluster method and applied it to positronium hydride, where the electrons and the positron were treated quantum mechanically, and to biexcitonic systems, where electrons and holes were treated quantum mechanically.[32, 36] Although the results for these electron-positron and electron-hole systems are very promising, such multicomponent coupled cluster methods have not yet been used to treat electrons and nuclei quantum mechanically on equal footing.

Herein we present an implementation of the NEO-CCSD (coupled cluster singles and doubles) method, as well as the NEO-CISD (configuration interaction singles and doubles) method, for treating electrons and specified nuclei quantum mechanically on the same level. Our applications to molecular systems indicate that the NEO-CCSD method provides much more accurate proton densities and proton affinities than does the NEO-CISD method. An advantage of using the NEO-CCSD approach rather than conventional electronic CCSD methods[39-43] for computing quantities such as proton affinities is that the NEO-CCSD approach inherently includes the zero point energy associated with the quantum hydrogen and thus does not require the calculation of the Hessian, which can be computationally expensive. Moreover, an advantage of NEO-CCSD over energy correction approaches, such as the any-particle propagator theory, is that the NEO-CCSD approach provides accurate proton densities, which is important for incorporating nuclear delocalization and zero point energy effects into geometry optimizations, reaction paths, and reaction dynamics.

We emphasize that this paper does not present new theory because the NEO-CCSD and NEO-CISD equations are straightforward extensions of the conventional electronic CCSD and CISD equations.[39-40, 44-45] Related multicomponent methods have been published previously[12-13, 32] but have not been used to investigate nuclear quantum effects in molecular systems with more than two atoms. The main goal of this paper is to present the complete equations and implementation of the NEO-CCSD approach for larger molecules and to illustrate that this approach provides accurate proton affinities, approximate proton densities, and vibrationally averaged optimized geometries for molecular systems. The programmable equations are also provided in the Supporting Information (SI) to enable others to implement this approach.

The manuscript is organized as follows. In Section 2, we describe the theoretical foundation of the NEO-CISD and NEO-CCSD formalism. In Section 3, we discuss the validation of the implementation for the small model system positronium hydride (PsH), where the electrons and positron are treated quantum mechanically. Then we present results on molecular systems in which all electrons and a proton are treated quantum mechanically, illustrating the level of accuracy for calculating proton densities, vibrationally averaged optimized geometries, and proton affinities. Concluding remarks are provided in Section 4.

2 Theory

In this section, we introduce the multicomponent CISD and CCSD formalism. A multicomponent system is a system where at least two types of particles, such as electrons and positrons or electrons and nuclei, are treated quantum mechanically. Here we present the formalism for a multicomponent system composed of electrons and protons, but the extension to any multicomponent system is straightforward. In this case, all electrons and specified protons are treated quantum mechanically, while the remaining nuclei are treated classically. The NEO Hamiltonian using second quantization notation is given by:

$$\hat{H} = h_q^p a_p^q + \frac{1}{4}\bar{g}_{rs}^{pq} a_{pq}^{rs} + h_Q^P a_P^Q + \frac{1}{4}\bar{g}_{RS}^{PQ} a_{PQ}^{RS} - g_{qQ}^{pP} a_{pP}^{qQ}. \tag{1}$$

Occupied electronic molecular orbitals in the NEO-HF reference are denoted by $i, j, \ldots$, unoccupied orbitals are denoted by $a, b, \ldots$, and general orbitals are denoted by $p, q, \ldots$. The same notation is used for the nuclear orbitals with upper-case letters. The Einstein summation convention is assumed over repeated indices, unless noted otherwise. Additionally, we use the standard tensor notation introduced by Kutzelnigg and Mukherjee,[46] where the excitation operators $a_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n}$ are defined as a string (product) of creation $(a_p^\dagger)$ and annihilation (a_p) operators: $a_{q_1 q_2 \cdots q_n}^{p_1 p_2 \cdots p_n} \equiv a_{p_1}^\dagger a_{p_2}^\dagger \ldots a_{p_n}^\dagger a_{q_n} \ldots a_{q_2} a_{q_1}$. Equivalent notations and definitions are used for the protonic excitation operators. The mixed excitation operators acting on the space of both electrons and protons are defined analogously. In Eq. (1), $h_q^p \equiv \langle q | \hat{h}^{\mathrm{e}} | p \rangle$ corresponds to a matrix element of the electronic one-particle Hamiltonian, while $\bar{g}_{rs}^{pq} \equiv \langle rs || pq \rangle = \langle rs | pq \rangle - \langle rs | qp \rangle$ is the antisymmetrized two-electron Coulomb repulsion tensor element. The protonic counterparts, h_Q^P and $\bar{g}_{RS}^{PQ}$, are defined analogously. The electron-proton Coulomb attraction tensor element is defined as $g_{qQ}^{pP} \equiv \langle qQ | pP \rangle$.

The NEO Hamiltonian given by Eq. (1) can be recast into normal ordered form relative to the reference state, which in this case is the NEO-HF wavefunction: $\Psi_{\mathrm{NEO-HF}}(\mathbf{r}_{\mathrm{e}}, \mathbf{r}_{\mathrm{p}}) = \Phi_0^{\mathrm{e}}(\mathbf{r}_e)\Phi_0^{\mathrm{p}}(\mathbf{r}_p) \equiv |0^{\mathrm{e}}0^{\mathrm{p}}\rangle$. Using Wick's theorem contraction rules,[39, 46-47] the NEO Hamiltonian is now given by

$$\begin{aligned}\hat{H} &= (h_q^p + \textstyle\sum_i \bar{g}_{qi}^{pi} - \sum_I g_{qI}^{pI})\tilde{a}_p^q + \frac{1}{4}\bar{g}_{rs}^{pq}\tilde{a}_{pq}^{rs} \\ &+ (h_Q^P + \textstyle\sum_I \bar{g}_{QI}^{PI} - \sum_i g_{Qi}^{Pi})\tilde{a}_P^Q + \frac{1}{4}\bar{g}_{RS}^{PQ}\tilde{a}_{PQ}^{RS} - g_{qQ}^{pP}\tilde{a}_{pP}^{qQ} \\ &+ \textstyle\sum_i h_i^i + \frac{1}{2}\sum_{ij} \bar{g}_{ij}^{ij} + \sum_I h_I^I + \frac{1}{2}\sum_{IJ} \bar{g}_{IJ}^{IJ} - \sum_{iI} g_{iI}^{iI}\end{aligned} \tag{2}$$

which can be written as

$$\hat{H} = \hat{F}_N^{\mathrm{e}} + \hat{W}_N^{\mathrm{ee}} + \hat{F}_N^{\mathrm{p}} + \hat{W}_N^{\mathrm{pp}} + \hat{W}_N^{\mathrm{ep}} + \langle 0^{\mathrm{e}}0^{\mathrm{p}}|\hat{H}|0^{\mathrm{e}}0^{\mathrm{p}}\rangle \tag{3}$$

where $\hat{F}_N^{\mathrm{e}}$ and $\hat{W}_N^{\mathrm{ee}}$ are the normal-ordered NEO electronic Fock and fluctuation operators, respectively, in the spin-orbital basis. Protonic normal-ordered operators are defined analogously, and $\hat{W}_N^{\mathrm{ep}} \equiv -g_{qQ}^{pP}\tilde{a}_{pP}^{qQ}$ is the normal-ordered electron-proton fluctuation operator. Operators with a tilde correspond to normal-ordered (with respect to $|0^{\mathrm{e}}0^{\mathrm{p}}\rangle$) excitation operators. Finally, the normal-ordered Hamiltonian is

$$\hat{H}_N = \hat{H} - \langle 0^{\mathrm{e}}0^{\mathrm{p}}|\hat{H}|0^{\mathrm{e}}0^{\mathrm{p}}\rangle. \tag{4}$$

There are two equivalent methods for constructing the exact wavefunction: the full configuration interaction (FCI) and the full coupled cluster (FCC) expansions. The former assumes a linear expansion ($|\mathrm{NEO-FCI}\rangle = (1+\hat{C})|0^{\mathrm{e}}0^{\mathrm{p}}\rangle$), while the latter assumes an exponential expansion ($|\mathrm{NEO-FCC}\rangle = e^{\hat{T}}|0^{\mathrm{e}}0^{\mathrm{p}}\rangle$). The operators $\hat{C} \equiv \sum_i \hat{C}_i$ and $\hat{T} \equiv \sum_i \hat{T}_i$ are defined in terms of the cluster operators $\hat{C}_i$ or $\hat{T}_i$ that generate excited determinants by acting on the reference state, and the index i corresponds to the excitation rank. Because these methods scale factorially with the system size, we include only single- and double-excitations ($\hat{C} \equiv \hat{C}_1^{\mathrm{e}} + \hat{C}_2^{\mathrm{e}} + \hat{C}_1^{\mathrm{p}} + \hat{C}_2^{\mathrm{p}} + \hat{C}_{11}^{\mathrm{ep}}$ and $\hat{T} \equiv \hat{T}_1^{\mathrm{e}} + \hat{T}_2^{\mathrm{e}} + \hat{T}_1^{\mathrm{p}} + \hat{T}_2^{\mathrm{p}} + \hat{T}_{11}^{\mathrm{ep}}$), defining the NEO-CISD and NEO-CCSD methods, respectively, to make these methods computationally practical. The operators $\hat{T}_1^{\mathrm{e}} = t_a^i\tilde{a}_i^a$ and $\hat{T}_2^{\mathrm{e}} = \frac{1}{4}t_{ab}^{ij}\tilde{a}_{ij}^{ab}$ are the conventional electronic single- and double-cluster operators, while $\hat{T}_1^{\mathrm{p}} = t_A^I \tilde{a}_I^A$ and $\hat{T}_2^{\mathrm{p}} = \frac{1}{4} t_{AB}^{IJ} \tilde{a}_{IJ}^{AB}$ are the protonic single- and double-cluster operators. Finally, the mixed cluster operator $\hat{T}_{11}^{\mathrm{ep}} = t_{aA}^{iI} \tilde{a}_{iI}^{aA}$ replaces single electronic and protonic occupied orbitals with unoccupied ones from the reference configuration. The cluster operators that occur in the NEO-CISD method are defined similarly as $\hat{C}_1^{\mathrm{e}} = c_a^i \tilde{a}_i^a$, $\hat{C}_2^{\mathrm{e}} = \frac{1}{4} c_{ab}^{ij} \tilde{a}_{ij}^{ab}$, $\hat{C}_1^{\mathrm{p}} = c_A^I \tilde{a}_I^A, \hat{C}_2^{\mathrm{p}} = \frac{1}{4} c_{AB}^{IJ} \tilde{a}_{IJ}^{AB}$ and $\hat{C}_{11}^{\mathrm{ep}} = c_{aA}^{iI} \tilde{a}_{iI}^{aA}$. The coefficients c and t are unknown NEO-CISD and NEO-CCSD amplitudes that need to be determined. These unknown coefficients can be obtained from left projection by excited determinants.

In the case of NEO-CISD, the c amplitude equations are given by

$$c_a^i E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle {}_i^a | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{5}$$

$$c_{ab}^{ij} E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle {}_{ij}^{ab} | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{6}$$

$$c_A^I E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle {}_I^A | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{7}$$

$$c_{AB}^{IJ} E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle {}_{IJ}^{AB} | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{8}$$

$$c_{aA}^{iI} E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle {}_{iI}^{aA} | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{9}$$

and the corresponding programmable expressions are obtained by utilizing the generalized Wick's theorem.[46] The electronic excited determinants are defined as $\langle {}_i^a | = \langle 0^e 0^p | \tilde{a}_a^i$, etc. while protonic and electronic-protonic excited determinants are defined analogously. The NEO-CISD correlation energy is defined as

$$E_{\mathrm{NEO-CISD}}^{\mathrm{corr}} = \langle 0^e 0^p | \hat{H}_N (1 + \hat{C}) | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle. \tag{10}$$

The programmable NEO-CISD energy and amplitude equations are provided in the SI.

The NEO-CCSD energy and t amplitude equations are obtained analogously to the derivation of the conventional electronic CCSD equations.[32, 39, 44] The first step is to multiply the coupled cluster Schrödinger equation $\hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle = E_{\mathrm{NEO-CCSD}}^{\mathrm{corr}} e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle$ by $e^{-\hat{T}}$ from the left, followed by left projection by the ground state ($\langle 0^e 0^p|$) and excited determinants ($\langle \mu|$) to obtain the energy and amplitude equations, respectively, giving

$$E^{\mathrm{corr}}_{\mathrm{NEO-CCSD}} = \langle 0^{\mathrm{e}} 0^{\mathrm{p}} | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle \tag{11}$$

$$0 = \langle \mu \big| e^{-\hat{T}} \hat{H}_N e^{\hat{T}} \big| 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle. \tag{12}$$

Application of the Baker-Campbell-Hausdorff (BCH) expansion,[48] which naturally truncates after the fourth-fold commutator, leads to

$$e^{-\hat{T}} \hat{H}_N e^{\hat{T}} = \hat{H}_N + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}_N, \hat{T}], \hat{T}]$$

$$+ \frac{1}{3!} [[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}], \hat{T}]. \tag{13}$$

This expression can be further simplified because the only terms that contribute are those for which the normal-ordered Hamiltonian has at least one contraction with all cluster operators on the right side, as indicated by the subscript C in the following NEO-CCSD amplitude equations:[39]

$$0 = \langle {}^{a}_{i} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C \tag{14}$$

$$0 = \langle {}^{ab}_{ij} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C \tag{15}$$

$$0 = \langle {}^{A}_{I} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C \tag{16}$$

$$0 = \langle {}^{AB}_{IJ} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C \tag{17}$$

$$0 = \langle {}^{aA}_{iI} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C \tag{18}$$

and in the NEO-CCSD energy equation

$$E^{\mathrm{corr}}_{\mathrm{NEO-CCSD}} = \langle 0^{\mathrm{e}} 0^{\mathrm{p}} | \hat{H}_N e^{\hat{T}} | 0^{\mathrm{e}} 0^{\mathrm{p}} \rangle_C. \tag{19}$$

Similar to the NEO-CISD method, applying the generalized Wick's theorem gives the programmable expressions for the t amplitude equations and energy. In contrast to the NEO-CISD method, the NEO-CCSD method is size-consistent even in the truncated form, making it more robust and preferable. The programmable NEO-CCSD energy and amplitude equations are provided in the SI.

In addition to the spin-orbital formalism discussed above, we have also used a spin-free formalism for derivation of the computationally efficient programmable amplitude and energy equations.[42-43] The difference in this approach is that in place of the excitation operators $a^{p_1 p_2 \cdots p_n}_{q_1 q_2 \cdots q_n}$, the spin-free one- and two-particle replacement operators E^p_q and E^{pq}_{rs} are used.[46] These operators are defined in terms of the spin-orbital creation and annihilation operators a and $a^\dagger$, respectively, as

$$E^p_q \equiv \sum_{\sigma=\uparrow,\downarrow} a^\dagger_{p_\sigma} a_{q_\sigma} \tag{20}$$

$$E^{pq}_{rs} \equiv \sum_{\sigma,\rho=\uparrow,\downarrow} a^\dagger_{p_\sigma} a^\dagger_{q_\rho} a_{s_\rho} a_{r_\sigma} \tag{21}$$

where σ and ρ denote indices for spin-up ($m_s = 1/2$) and spin-down ($m_s = -1/2$) magnetic quantum numbers, and p_σ denotes the spin orbital corresponding to spatial orbital p with spin σ.[46, 49]

3 Results and discussion

The NEO-CISD and NEO-CCSD amplitude and energy equations defined in Section 2 have been implemented in an in-house code developed in our group in both the spin-orbital and spin-free basis. The code is built on top of the Libint integral library.[50] Additionally, the programmable energy and amplitude equations were derived with the SeQuant package. The implementation was validated using the positronium hydride (PsH) system, which consists of two quantum electrons, one quantum positron, and a classical hydrogen nucleus.[8, 51] The exact solution for this system can be obtained by extending the cluster operators $\hat{C}$ and $\hat{T}$ to include $\hat{C}^{\mathrm{ep}}_{21} = \frac{1}{4} c^{ijI}_{abA} \tilde{a}^{abA}_{ijI}$ and $\hat{T}^{\mathrm{ep}}_{21} = \frac{1}{4} t^{ijI}_{abA} \tilde{a}^{abA}_{ijI}$, respectively, which are equivalent to the multicomponent FCI and FCC methods, respectively, for this particular system.[13, 32, 51] Because they are both exact solutions for a given basis set, the FCI and FCC approaches should give the same result for this system and have been confirmed to do so for our implementation. Details of these calculations are provided in the SI. The NEO-CISD and NEO-CCSD methods have also been used to calculate the proton densities and the optimized geometry for the FHF^{-} molecule and to compute the proton affinities of twelve small molecules. These results are presented in the next two subsections.

3.1 Calculation of the proton density and optimized geometry for the FHF^{-} molecule

The proton density is calculated by evaluating the expression

$$\rho_{\mathrm{p}}(\mathbf{r}_{\mathrm{p}}) = \sum_{PQ} \phi_Q(\mathbf{r}_{\mathrm{p}})\gamma_{QP}\phi_P^*(\mathbf{r}_{\mathrm{p}}). \tag{22}$$

Here $\{\phi_P\}$ are protonic orbitals and γ_{QP} is the matrix element of the one-particle reduced proton density matrix defined by $\gamma_{QP} = \frac{\langle \Psi^{\mathrm{NEO}} | a_Q^P | \Psi^{\mathrm{NEO}} \rangle}{\langle \Psi^{\mathrm{NEO}} | \Psi^{\mathrm{NEO}} \rangle}$,[40, 52] where $|\Psi^{\mathrm{NEO}}\rangle$ can be a NEO-HF, NEO-CISD, or NEO-CCSD wavefunction. In the case of the NEO-CCSD density matrix, we include up to quadratic terms in the wavefunction expansion, $|\Psi^{\mathrm{NEO}}\rangle = (1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \cdots)|0^{\mathrm{e}}0^{\mathrm{p}}\rangle$.[40] Note that the NEO-CCSD density matrix has a nonterminating expansion, but truncation after second order serves as a qualitative estimate of the NEO-CCSD density, as discussed by Noga and Urban.[40, 53] Although this approach is only an approximation of the true NEO-CCSD density, it provides a qualitatively reasonable description of the proton density, as supported by the vibrationally averaged geometry optimizations discussed below. A more accurate, but technically more complicated, method for calculating the one-particle reduced proton density matrix is based on solving the Λ-CC equations,[39, 44, 52, 54] which is beyond the scope of the current work.

The proton density was calculated for the FHF^- molecule optimized at the CCSD/aug-cc-pVTZ level of theory. The fluorine-fluorine distance was 2.267 Å with the hydrogen atom positioned at the midpoint between the two fluorines. For the NEO calculations, the aug-cc-pVTZ electronic basis set was used for the two classical nuclei, and the quantum hydrogen was represented by electronic and nuclear basis functions centered at the midpoint between the two fluorine atoms. Specifically, the aug-cc-pVQZ electronic basis set and an even-tempered $8s8p8d$ nuclear basis with exponents ranging from $2\sqrt{2}$ to 32 were used for the quantum hydrogen.[55-57]

As a benchmark, the proton densities were also calculated with the Fourier grid Hamiltonian (FGH) method,[58] treating the hydrogen nucleus quantum mechanically with the two fluorine atoms fixed. In this approach, the hydrogen nucleus was moved on a three-dimensional grid spanning the region between the two fluorine atoms, and single-point energy calculations were performed at each grid point using the conventional electronic CCSD/aug-cc-pVTZ method. Subsequently, the FGH method was used to solve the three-dimensional Schrödinger equation for the proton, yielding the three-dimensional proton vibrational wavefunctions and energy levels. The proton density corresponding to the ground vibrational state was computed from the square of the ground state proton vibrational wavefunction. This approach is numerically exact for electronically adiabatic systems, in which the Born-Oppenheimer separation between electrons and nuclei is valid. The FHF^- molecule is expected to be electronically adiabatic and therefore serves as a useful example in this regime. Although the NEO methods should be valid in the nonadiabatic or non-Born-Oppenheimer regime, the proton densities must also be accurate and are more easily benchmarked in the electronically adiabatic regime.

Figure 1 shows two slices of the proton density calculated for the FHF^- molecule using the NEO-HF, NEO-CISD, and NEO-CCSD methods, as well as the FGH method, which is viewed as the reference. As demonstrated previously, NEO-HF predicts a highly localized proton density due to an inadequate description of electron-proton correlation effects.

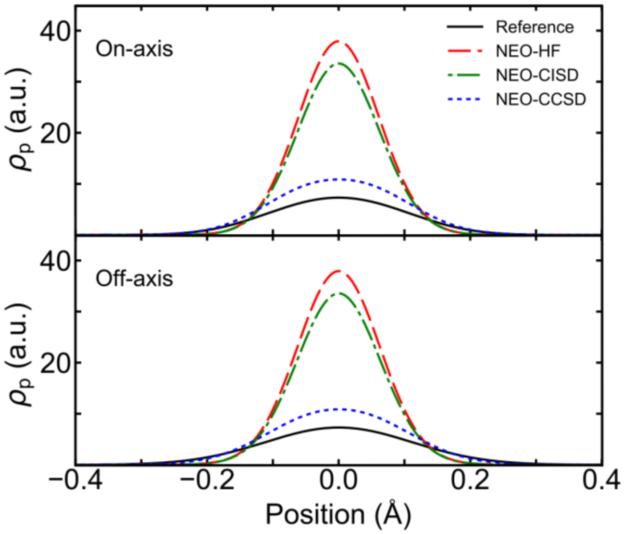


Figure 1. On-axis (top) and off-axis (bottom) proton density for the FHF^- molecule calculated with the reference FGH (solid black), NEO-HF (dashed red), NEO-CISD (dashed-dotted green), and NEO-CCSD (dotted blue) methods. The fluorine atoms are fixed at a distance of 2.267 Å, and the quantum proton basis functions are positioned at the origin. Note that all proton densities are normalized in three-dimensional space, with the tails contributing more than the peak region due to the volume element in the integration.

The NEO-CISD method leads to only a very small improvement in the proton density because it does not recover enough electron-proton correlation energy. In contrast, the NEO-CCSD method leads to a significant improvement in the proton density, exhibiting much better agreement with the grid-based reference density. To the best of our knowledge, NEO-CCSD is the first parameter-free quantum chemistry approach that produces qualitatively accurate proton densities. We expect that including excitation operators of higher rank, in addition to rigorous construction of the one-particle reduced proton density matrix, would further improve the proton density, but unfortunately at greater computational expense.

Another important feature of the NEO approach is that it incorporates the nuclear quantum effects of the proton, such as proton delocalization and zero point energy, during geometry optimizations of the classical nuclei or nuclear dynamics simulations. In contrast, conventional electronic structure calculations typically include the zero point energy as a correction to the total energy at the optimized geometry based on frequencies obtained from the Hessian and thus do not include these nuclear quantum effects during geometry optimizations or dynamics. Previously studied methods such as NEO-HF, NEO-MP2, and NEO-CISD, as well as the APMO/PP2 method, do not provide even qualitatively accurate proton densities and therefore are not suitable for this purpose. The NEO-DFT/epc17 approach, however, has been shown to produce accurate proton densities as well as to correctly predict the impact of nuclear quantum effects on the optimized geometries.[35]

To investigate this feature for wavefunction-based methods, we calculated the impact of proton quantization on the equilibrium, minimum-energy F−F distance for the FHF^- molecule. The results obtained with the NEO-HF, NEO-CISD, NEO-CCSD, and conventional electronic CCSD methods are shown in Figure 2. The equilibrium distance obtained with the FGH method, which is numerically exact for electronically adiabatic systems, is indicated with a vertical black line and serves as the benchmark. Due to a combination of proton delocalization, zero point energy, and anharmonicity effects, the equilibrium F−F distance determined from the FGH method is increased by 0.022 Å with respect to the equilibrium distance determined from conventional electronic CCSD. In contrast, the NEO-HF and NEO-CISD methods increase the equilibrium F−F distance by only 0.011 Å and 0.013 Å, respectively. The similarity of the equilibrium distances obtained from the NEO-HF and NEO-CISD methods is consistent with the similar, highly over-localized proton densities generated by these methods (Figure 1). The equilibrium F−F distance obtained with the NEO-CCSD method is increased by 0.026 Å relative to the distance obtained with conventional electronic CCSD, representing much better agreement with the reference FGH distance. Because accurate proton densities are essential for obtaining accurate vibrationally averaged geometries, the more accurate optimized geometry obtained with the NEO-CCSD method provides further validation of the improved proton densities shown in Figure 1.

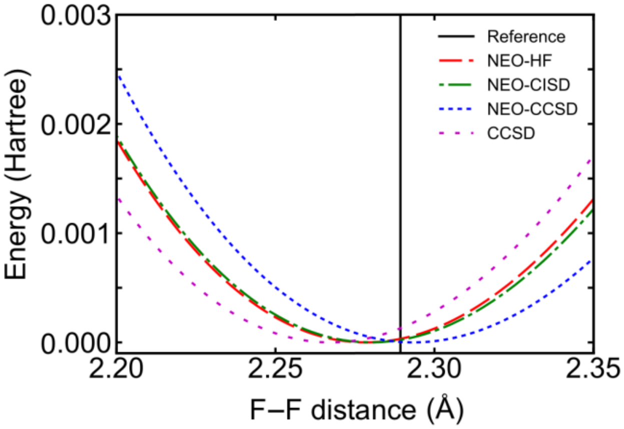


Figure 2. Energy as a function of the fluorine-fluorine distance in the FHF^- molecule calculated with the reference FGH (solid black vertical line), NEO-HF (dashed red), NEO-CISD (dashed-dotted green), NEO-CCSD (dotted blue), and conventional CCSD (dotted magenta) methods. All minimum energies are set to 0.0 Hartree.

3.2 Calculation of proton affinities

In this section, we use the NEO-CISD and NEO-CCSD methods to compute the proton affinities for a set of small molecules. The proton affinity (PA) of a molecular system A is the negative enthalpy change of the reaction $\mathrm{A} + \mathrm{H}^+ \rightarrow \mathrm{AH}^+$:

$$\mathrm{PA(A)} = -\Delta H = -\Delta E + RT \tag{23}$$

where R is the universal gas constant, T is the absolute temperature, and $\Delta E(T)$ is the energy difference between the product (AH^+) and the reactant (A) species. The change in energy for a nonlinear polyatomic molecule can be approximated as $\Delta E(T) = \Delta E_{\mathrm{trans}}(T) + \Delta E_{\mathrm{rot}}(T) + \Delta E_{\mathrm{vib}}(T) + \Delta E_{\mathrm{elec}}$, which accounts for the translational, rotational, vibrational, and electronic contributions, respectively.[59] Further simplifications can be achieved by assuming the ideal gas approximation, $\Delta E_{\text{trans}}(T) = -\frac{3}{2}RT$, and by neglecting the difference in rotational energy between the A and AH$^+$ species, i.e., assuming $\Delta E_{\text{rot}}(T) = 0$. Therefore, the PA for the species A is given by

$$\text{PA(A)} = -\Delta E_{\text{elec}} - \Delta E_{\text{vib}}(T) + \frac{5}{2}RT. \tag{24}$$

We calculated the proton affinities using conventional electronic structure CISD and CCSD methods and the corresponding NEO methods. In addition to the calculation of the electronic energy, conventional electronic structure calculations of proton affinities require the calculation of the Hessian, from which the vibrational energy contributions (i.e., the zero point energies) are determined. Within the NEO framework, the zero point energy of the quantum proton is included in the total energy calculation. We invoked the reasonable approximation that the vibrational modes of the classical nuclei are predominantly separable from those of the quantum hydrogen and that their corresponding zero point energies remain mostly unchanged upon protonation. As discussed below, we tested this approximation for this set of molecules and estimated the error introduced by it. In this case, the proton affinity of molecule A within the NEO framework is given by

$$\text{PA(A)} = E_{\text{A}} - E_{\text{AH}^+} + \frac{5}{2}RT, \tag{25}$$

where E_{A} is obtained with a conventional electronic structure calculation and E_{AH^+} is obtained with its NEO counterpart.[26, 35]

Table 1. Absolute Deviation, Mean Absolute Error (MAE), and Maximum Absolute Error (MaxAE) with Respect to Experimentally Determined Proton Affinities[a]

Molecule	CISD	CCSD	NEO-HF	NEO-CISD	NEO-CCSD
CN^-	0.06	0.04	0.91	0.31	0.11
NO_2^-	0.19	0.14	0.53	0.15	0.01
NH_3	0.07	0.04	0.52	0.17	0.05
$HCOO^-$	0.17	0.09	0.55	0.21	0.04
HO^-	0.21	0.13	0.36	0.08	<0.01
HS^-	0.08	0.05	0.84	0.27	0.10
H_2O	0.07	0.04	0.52	0.17	0.06
H_2S	0.12	0.11	0.65	0.17	<0.01
CO	0.07	0.09	0.84	0.24	0.04
N_2	0.08	0.09	0.76	0.25	0.07
CO_2	0.07	0.07	0.60	0.22	0.04
CH_2O	0.14	0.09	0.33	0.10	<0.01
MAE	0.11	0.08	0.62	0.20	0.04
MaxAE	0.21	0.14	0.91	0.31	0.11

[a]All values given in units of eV.

These methods were used to compute the proton affinities for a set of twelve molecules. The geometries of these molecules were optimized at the CISD and CCSD levels of theory employing the aug-cc-pVTZ basis set.[55-57] At the optimized structures, the harmonic zero point energy corrections were computed to generate the proton affinities at the conventional electronic CISD and CCSD levels. These calculations were performed with the ORCA quantum chemistry package.[60] The NEO calculations were performed on the optimized CISD and CCSD geometries employing the aug-cc-pVTZ electronic basis set centered on the classical nuclei. The aug-cc-pVQZ electronic basis set and an even-tempered 8*s*8*p*8*d* nuclear basis set with exponents ranging from $2\sqrt{2}$ to 32 were centered at the hydrogen position optimized with conventional CISD or CCSD.

The absolute deviations of the proton affinities obtained with each method with respect to the experimentally determined proton affinities are given in Table 1.[61-65] These results indicate that conventional electronic CCSD yields a mean absolute error (MAE) of 0.08 eV, which is more accurate than the conventional electronic CISD method, which has an MAE of 0.11 eV. The performance of the CCSD method can be significantly improved by inclusion of the perturbative treatment of the triples excitations (T) along with a larger basis set. Thus, for the same set of molecules, conventional electronic CCSD(T)/aug-cc-pVQZ produces an MAE below 0.03 eV (Table S2). This result is consistent with previous studies of proton affinities computed with post-HF composite methods.[59] The NEO-HF method produces extremely large errors in the proton affinities with an MAE of 0.62 eV, presumably due to the lack of both electron-electron and electron-proton correlation effects. While the NEO-CISD method exhibits a significant improvement over NEO-HF for the proton affinities, it still yields a relatively large MAE of 0.20 eV, which is beyond the experimental uncertainty of ~0.09 eV reported by Hunter and Lias.[62] Finally, the NEO-CCSD method produces the smallest deviations with an MAE of only 0.04 eV, which is within both chemical accuracy (~0.04 eV) and experimental accuracy (~0.09 eV). Similar to our findings for conventional electronic structure methods, NEO-CCSD(T) calculations with a larger electronic basis set are expected to produce an MAE below 0.03 eV (Table S2).

The NEO-CCSD method yields similar proton densities and proton affinities to those obtained with the NEO-DFT/epc17-2 method.[35] The main advantages of the NEO-CCSD method are that it is a parameter-free approach and can be improved systematically. The main disadvantage is that it is more computationally expensive, formally scaling as N^6. Both NEO-CCSD and NEO-DFT invoke the assumption that the vibrational energy effects associated with the classical nuclei predominantly cancel in the calculation of the proton affinities. Here the "classical" nuclei refer to all nuclei in the conventional electronic structure calculations and to all nuclei except the quantum protons in the NEO calculations, although the quantum effects of such "classical" nuclei can be included in the form of zero point energies (ZPEs).

Table 2. Zero Point Energies in eV Calculated from Harmonic Vibrational Frequencies with CCSD and NEO-CCSD Methods.

Molecule A	Conv. ZPE(A)[a]	NEO ZPE(AH^+)[b]	ΔZPE[c]
CN^-	0.13	0.14	-0.01
HO^-	0.24	0.24	<-0.01
HS^-	0.17	0.17	<-0.01
CO	0.14	0.15	-0.01
N_2	0.15	0.15	<-0.01

[a] ZPE calculated from the harmonic vibrational frequencies at the conventional CCSD level, as obtained from the CCSD Hessian.

[b] ZPE calculated from the harmonic vibrational frequencies of the "classical" nuclei at the NEO-CCSD level. Note that the ZPE associated with the quantum proton is included directly in the NEO-CCSD energy, and the ZPE reported here is calculated from the vibrational frequencies obtained from the NEO-CCSD Hessian computed for the other nuclei.

[c] ΔZPE = Conv. ZPE(A) - NEO ZPE(AH^+).

To investigate the validity of the assumption that the vibrational energy effects associated with the classical nuclei predominantly cancel in the proton affinity calculations, we compared the ZPE associated with the classical nuclei for A and AH^+ using the conventional electronic CCSD and NEO-CCSD methods, respectively. This comparison is provided in Table 2 for a subset of the systems in Table 1. The ZPE for A was calculated using the harmonic vibrational frequencies obtained by diagonalizing the Hessian computed with the conventional CCSD method. The ZPE for AH^+ was calculated using the harmonic vibrational frequencies associated with the "classical" nuclei obtained by diagonalizing the Hessian computed with the NEO-CCSD method. As discussed previously,[11] the NEO-CCSD potential energy surface depends on only the classical nuclear coordinates and is defined such that the centers of the electronic and nuclear basis functions associated with the quantum proton(s) are optimized variationally for each configuration of the classical nuclear coordinates. Within this framework, the NEO-CCSD Hessian can be computed numerically, and diagonalization of this Hessian produces the vibrational frequencies associated with the classical nuclei, allowing the calculation of the associated ZPE. The results shown in Table 2 indicate that the ZPEs associated with the classical nuclei for A and AH^+ predominantly cancel. Specifically, the assumption of this cancellation introduces a maximum error of ~0.01 eV and therefore has a negligible impact on the proton affinities reported in Table 1. We have also used an alternative, less consistent analysis to assess the validity of this assumption (Table S3), leading to a slightly larger estimated error that is still well within the experimental uncertainty for proton affinities.

Additionally, we calculated the proton affinities for the same set of molecules with the CID, CCD, NEO-CID, and NEO-CCD methods, which include double excitations but not single excitations, to investigate the impact of the single excitations ($\hat{\boldsymbol{C}}_{\boldsymbol{1}}$ and $\hat{\boldsymbol{T}}_{\boldsymbol{1}}$) on the proton affinities. The results given in Table S4 illustrate that inclusion of single excitations has negligible impact on the results obtained with the NEO-CISD and conventional electronic CISD and CCSD methods, but it significantly impacts the results obtained with the NEO-CCSD method. The single excitation cluster operator, $\boldsymbol{e}^{\hat{\boldsymbol{T}}_{\boldsymbol{1}}}$, in the NEO-CCSD method accounts for orbital optimization and relaxation effects, according to the Thouless theorem.[66-68] These observations are in agreement with the findings by Nakai and Sodeyama in the context of Brueckner doubles.[12] Thus, the NEO-CCSD method produces significantly more accurate proton affinities than the NEO-HF, NEO-CID, NEO-CCD, and NEO-CISD methods.

The APMO/PP2 method, which is a multicomponent propagator theory, has been extensively benchmarked for proton affinities on a large number of molecules.[26, 33] The APMO/PP2 method was found to produce a very small MAE of 0.03 eV for a set of 150 organic molecules with MaxAE of 0.15 eV. This maximum absolute error (MaxAE) is observed on the CH_2O molecule.[33] For the same system, CH_2O, the NEO-CCSD method produces a much smaller deviation of 0.001 eV. The APMO/PP2 method also produced relatively large deviations for the molecules CN^- and HS^-, where the APMO/PP2 method deviated from experiment by 0.51 and 0.49 eV, respectively, while the NEO-CCSD method deviates by only 0.11 and 0.10 eV, respectively. These two molecules also exhibit the largest deviations among the twelve molecules studied with the NEO-CCSD method. For the six molecules that have been studied with both the APMO/PP2 and NEO-CCSD methods (i.e., CN^-, NO_2^-, NH_3, $HCOO^-$, HS^-, and CH_2O), the MAE is 0.22 eV for the APMO/PP2 method and 0.05 eV for the NEO-CCSD method. The larger error for the APMO/PP2 method for this set of challenging molecules may be due in part to the use of relatively small electronic and nuclear basis sets,[69-70] but it also may be due to limitations of the overall approach. Although the APMO/PP2 method is less computationally expensive than the NEO-CCSD method, the NEO-CCSD method possesses several significant advantages. In contrast to the APMO/PP2 method, the NEO-CCSD method includes electron-electron correlation and the geometry changes that occur upon protonation. Another distinction from the APMO/PP2 method is that the NEO-CCSD method generates accurate proton densities and is therefore more generally suitable for computing other molecular properties, such as vibrationally averaged geometries. Nevertheless, it is very useful to have several different methods available for computing proton affinities.

4 Conclusions

In this paper, we presented the implementation of the multicomponent wavefunction based methods NEO-CISD and NEO-CCSD for molecular systems, in which all electrons and specified protons are treated quantum mechanically on the same level. The computational complexity of the NEO-CISD and NEO-CCSD methods is the same as their conventional electronic counterparts, with scaling as N^6 where N is a measure of the system size. However, the NEO methods are technically more complex because of three additional amplitude equations, as well as more terms that enter the conventional amplitude equations.

The NEO-HF, NEO-CISD, and NEO-CCSD methods were used to calculate the proton density for the FHF^- molecule, and the resulting proton densities were compared to the proton density obtained with a reference grid-based method. The NEO-CCSD method was found to exhibit a major improvement over both the NEO-HF and NEO-CISD methods, which do not provide even qualitatively accurate proton densities. In particular, the NEO-HF and NEO-CISD methods produce proton densities that are much too localized compared to the proton densities obtained with the NEO-CCSD and reference grid-based methods. Moreover, the NEO-CCSD method also produces accurate proton affinities that are in good agreement with experimentally measured values for the set of twelve molecules studied. Our conjecture is that NEO-CCSD produces significantly more accurate proton densities and affinities than NEO-CISD because of the additional orbital optimization and the cluster operators that generate higher excitations in NEO-CCSD that are not present in NEO-CISD.[39-40, 44, 68, 71-72]

A significant advantage of the NEO-CCSD approach over post-Hartree-Fock approaches, such as methods based on many-body perturbation theory or propagator theory, is that the proton densities are improved, enabling meaningful calculations of other molecular properties, such as vibrationally averaged geometries. To investigate this capability, the NEO-CISD and NEO-CCSD methods were used to optimize the geometry of the FHF^- molecule. The F−F distance determined with the NEO-CCSD method was found to agree well with the grid-based reference distance, suggesting that inclusion of proton delocalization, zero point energy, and anharmonicity increases the F−F distance. In addition to geometry optimizations, the NEO-CCSD method could be used to calculate reaction paths and reaction dynamics of molecular systems. The development and implementation of the NEO-CCSD approach opens up many possible directions in terms of both method development and applications.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website: Programmable NEO-CCSD and NEO-CISD energy and amplitude equations, results for positronium hydride (PsH), absolute errors of proton affinities for twelve molecules calculated with the CCSD(T), CID, CCD, NEO-CID and NEO-CCD methods, and analysis of errors in proton affinities.

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