J. Phys. Chem. A **2007,** *111,* 4522−4526

Density Functional Theory Treatment of Electron Correlation in the Nuclear−Electronic Orbital Approach

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

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

Received: January 18, 2007; In Final Form: March 7, 2007

This paper presents the nuclear−electronic orbital density functional theory [NEO-DFT(ee)] method for including electron−electron correlation and nuclear quantum effects self-consistently in quantum chemical calculations. The NEO approach is designed to treat a relatively small number of nuclei quantum mechanically, while the remaining nuclei are treated classically. In the NEO-DFT(ee) approach, the correlated electron density is used to obtain the nuclear molecular orbitals, and the resulting nuclear density is used to obtain the correlated electron density during an iterative procedure that continues until convergence of both the nuclear and electronic densities. This approach includes feedback between the correlated electron density and the nuclear wavefunction. The application of this approach to bihalides and acetylene indicates that the nuclear quantum effects do not significantly impact the electron correlation energy, but the quantum nuclear energy is enhanced in the NEO-DFT(ee) B3LYP method. The excellent agreement of the NEO-DFT(ee)-optimized bihalide structures with the vibrationally averaged geometries from grid-based quantum dynamical methods provides validation for the NEO-DFT(ee) approach. Electron−proton correlation could be included by the development of an electron−nucleus correlation functional. Alternatively, explicit electron−proton correlation could be included directly into the NEO self-consistent-field framework with Gaussian-type geminal functions.

I. Introduction

Conventional electronic structure calculations invoke the Born−Oppenheimer approximation, where the nuclei are represented as classical point charges. Nuclear quantum effects such as zero point motion and hydrogen tunneling, however, have been shown to be significant for systems involving hydrogen bonding interactions and hydrogen transfer reactions. Recently, methods have been developed to avoid the Born−Oppenheimer approximation and include nuclear quantum effects in electronic structure calculations.[1−16] In particular, the nuclear−electronic orbital (NEO) approach[1−7] is designed to treat selected nuclei (e.g., the hydrogen nuclei involved in hydrogen bonding interactions or hydrogen transfer reactions) quantum mechanically, while the remaining nuclei are treated classically. In the NEO approach, mixed nuclear−electronic wavefunctions are calculated variationally using molecular orbital techniques with Gaussian basis functions for the electrons and the nuclei.

In conventional electronic structure theory, electron correlation is defined as the difference between the exact energy and the single-configuration Hartree−Fock energy. Nondynamical electron correlation arises from the influence of other configurations that are close in energy to and mix strongly with the Hartree−Fock configuration, and dynamical electron correlation arises from interactions of electrons at close separation distances, which are difficult to describe. Typically, multiconfigurational methods are used to include nondynamical electron correlation, and methods such as perturbation theory, coupled cluster theory, configuration interaction, and density functional theory (DFT) are used to include dynamical electron correlation.

Within the framework of the NEO approach, both electron−electron and electron−proton correlation effects play important roles. We have shown that electron−proton dynamical correlation strongly impacts the calculation of nuclear−electronic wavefunctions because of the attractive electrostatic interaction between the electron and the proton.[2,3] Nondynamical electron−electron and electron−proton correlation effects have been included in the NEO framework with the configuration interaction (NEO-CI), multiconfigurational self-consistent-field (NEO-MCSCF), and nonorthogonal configuration interaction (NEO-NOCI) methods.[1−4] Dynamical electron−electron and electron−proton correlation effects have been included with second-order perturbation theory (NEO-MP2).[5] More recently, an explicitly correlated Hartree−Fock (NEO-XCHF) approach was developed to include explicit electron−proton correlation directly into the NEO self-consistent-field framework using Gaussian-type geminal functions.[7] In contrast to previous approaches, which produce nuclear wavefunctions that are too localized and that severely overestimate hydrogen vibrational frequencies,[12−20] the NEO-XCHF method provides accurate nuclear wavefunctions and hydrogen vibrational stretch frequencies.[7] The NEO-XCHF method is computationally practical for many-electron systems with a relatively small number of quantum nuclei because only electron−proton correlation is treated explicitly. A more computationally tractable method must be used to include electron−electron correlation for these types of systems.

In this paper, we present the NEO-DFT(ee) approach for including electron−electron correlation within the NEO framework in a self-consistent and computationally practical manner. The theoretical foundation for non-Born−Oppenheimer density functional theory was provided by Parr and co-workers.[21] More recently, Shigeta and co-workers presented a theoretical for-

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* To whom correspondence should be addressed. E-mail: shs@chem.psu.edu.

10.1021/jp0704463 CCC: $37.00

mulation and numerical scheme for non-Born−Oppenheimer DFT calculations.[8] In addition, Kreibich and Gross developed a multicomponent density functional theory for a combined system of electrons and nuclei and provided approximate functionals for the electron−nuclear correlation energy.[14] These previous methods were developed for systems in which all of the nuclei and all of the electrons were treated quantum mechanically, and the electron−proton correlation was included via an electron−nuclear functional. In contrast, the NEO approach is designed to treat a relatively small number of nuclei quantum mechanically, while the remaining nuclei are treated classically.[22] Moreover, an alternative to developing an electron−nuclear functional is to include only electron−electron correlation with density functional theory and to include electron−proton correlation explicitly with the NEO-XCHF approach.

The paper is organized as follows. Section II presents the the oretical formulation and implementation of the NEO-DFT(ee) method. Section III describes the application of this approach to bihalides and acetylene for benchmarking purposes. The electron correlation effects and the nuclear quantum effects are analyzed, and the bihalide structures are compared to results from grid-based quantum dynamical methods and to experimental data. Concluding remarks are provided in Section IV.

II. Theory and Methods

A. Theoretical Formulation and Implementation of NEO-DFT(ee). The NEO approach is formulated for a system with N_e electrons, N_p quantum nuclei, and N_c classical nuclei. This approach is designed for systems in which at least two nuclei are treated classically, thereby eliminating the difficulties associated with translations and rotations.[23] For simplicity, here we assume that the quantum nuclei are protons with a charge of +1. The equations are easily extended for other types of quantum nuclei. In this case, the NEO-HF (Hartree−Fock) Hamiltonian is defined as

$$\hat{H}_{\mathrm{tot}} = \sum_i^{N_e} h^e(i) + \sum_{i'}^{N_p} h^p(i') + \sum_{i'}^{N_p}\sum_{j'>i'}^{N_p}\frac{1}{\mathrm{r}_{i'j'}} + \sum_i^{N_e}\sum_{j>i}^{N_e}\frac{1}{\mathrm{r}_{ij}} - \sum_i^{N_e}\sum_{i'}^{N_p}\frac{1}{r_{ii'}} \tag{1}$$

where the unprimed indices i, j refer to electrons and the primed indices i', j' refer to the quantum protons. h^e and h^p are the one-particle terms for the electrons and protons, respectively, and are defined as

$$h^e(i) = -\frac{1}{2}\nabla_i^2 - \sum_A^{N_c}\frac{Z_A}{r_{iA}} \tag{2}$$

$$h^p(i') = -\frac{1}{2M}\nabla_{i'}^2 + \sum_A^{N_c}\frac{Z_A}{r_{i'A}} \tag{3}$$

where the mass of the proton is denoted by M, the index A refers to classical nuclei, and the charges of the classical nuclei are represented by Z_A.

We have derived the NEO-HF equations for a restricted Hartree−Fock (RHF) treatment of the electrons and a high-spin open-shell treatment of the quantum nuclei. The extension to other spin configurations is straightforward and has been implemented. For this case, the electronic and nuclear Fock equations are

$$f^e(1)\psi_i^e(1) = (h^e(1) + \nu_{ee}(1) + \nu_{ep,e}(1))\psi_i^e(1) = \epsilon_i^e\,\psi_i^e(1) \tag{4}$$

$$f^p(1')\psi_{i'}^p(1') = (h^p(1') + \nu_{pp}(1') + \nu_{ep,p}(1'))\psi_{i'}^p(1') = \epsilon_{i'}^p\,\psi_{i'}^p(1') \tag{5}$$

The two particle operators are defined as

$$\nu_{ee}(1)\psi_j^e(1) = 2\sum_b \langle\psi_b^e(2)|r_{12}^{-1}|\psi_b^e(2)\rangle\psi_j^e(1) - \sum_b \langle\psi_b^e(2)|r_{12}^{-1}|\psi_j^e(2)\rangle\psi_b^e(1) \tag{6}$$

$$\nu_{pp}(1')\psi_{j'}^p(1') = \sum_{b'} \langle\psi_{b'}^p(2')|r_{1'2'}^{-1}|\psi_{b'}^p(2')\rangle\psi_{j'}^p(1') - \sum_{b'} \langle\psi_{b'}^p(2')|r_{1'2'}^{-1}|\psi_{j'}^p(2')\rangle\psi_{b'}^p(1') \tag{7}$$

$$\nu_{ep,e}(1)\psi_j^e(1) = -\sum_{b'} \langle\psi_{b'}^p(1')|r_{11'}^{-1}|\psi_{b'}^p(1')\rangle\psi_j^e(1) \tag{8}$$

$$\nu_{ep,p}(1')\psi_{j'}^p(1') = -2\sum_b \langle\psi_b^e(1)|r_{11'}^{-1}|\psi_b^e(1)\rangle\psi_{j'}^p(1') \tag{9}$$

where the symbol ψ denotes the spatial orbitals, and the summations of b and b' are over the occupied electronic and proton spatial orbitals, respectively. Here, $\nu_{ee}(i)$ and $\nu_{pp}(i')$ are the Coulomb-exchange operators for the electrons and protons, respectively, and $\nu_{ep,e}(i)$ and $\nu_{ep,p}(i')$ are the electron−proton Coulomb operators for the electrons and protons, respectively.

The electron−proton Coulomb operator for the proton can be expressed in terms of the total electron density

$$\rho^e(\mathbf{r}) = 2\sum_b |\psi_b^e(\mathbf{r})|^2$$

where

$$\nu_{ep,p}(\mathbf{r}_{1'}) = -\int \frac{\rho^e(\mathbf{r}_1)}{r_{11'}}\,\mathrm{d}\mathbf{r}_1 \tag{10}$$

In the NEO-DFT(ee) approach, the total electron density $\rho^e(\mathbf{r})$ is obtained from a conventional electronic structure DFT calculation, thereby reflecting the changes in the electronic environment due to electron−electron correlation. The modified electron−proton Coulomb operator in eq 10 is used in eq 5 for the solution of the nuclear Fock equations to obtain the nuclear molecular orbitals for the quantum protons.

Conventional electronic structure DFT calculations are based on the Kohn−Sham orbital equations[24,25]

$$\left(-\frac{1}{2}\nabla_1^2 + \nu_{\mathrm{eff}}^e(1)\right)\psi_i^e(1) = \epsilon_i^e\,\psi_i^e(1) \tag{11}$$

where the effective potential $\nu_{\mathrm{eff}}^e(\mathbf{r})$ is

$$\nu_{\mathrm{eff}}^e(\mathbf{r}_1) = -\sum_A^{N_c}\frac{Z_A}{r_{1A}} + \int\frac{\rho^e(\mathbf{r}_2)}{r_{12}}\,\mathrm{d}\mathbf{r}_2 + \nu_{\mathrm{xc}}^e(\mathbf{r}_1) \tag{12}$$

and $\nu_{\mathrm{xc}}^e(\mathbf{r})$ is the exchange-correlation potential. In the NEO-DFT(ee) approach, the contribution to the effective potential associated with the external potential created by the classical nuclei is modified to account for the quantum treatment of selected nuclei

$$\nu^{\mathrm{e}}_{\mathrm{eff}}(\mathbf{r}_1) = -\sum_{A}^{N_{\mathrm{c}}} \frac{Z_A}{r_{1A}} - \sum_{b'}^{N_{\mathrm{p}}} \int \frac{|\psi^{\mathrm{p}}_{b'}(\mathbf{r}_{1'})|^2}{r_{11'}} \mathrm{d}\mathbf{r}_{1'} + \int \frac{\rho^{\mathrm{e}}(\mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_2 + \nu^{\mathrm{e}}_{\mathrm{xc}}(\mathbf{r}_1) \qquad (13)$$

The modified effective potential in eq 13 is used in eq 11 to calculate the total electron density.

The NEO-DFT(ee) approach requires the iterative solution of the nuclear NEO-HF equations (eq 5) and the conventional electronic structure DFT equations (eq 11) until convergence of both the nuclear and electronic densities. The NEO-HF equations for the quantum nuclei depend on the total electron density and provide the nuclear molecular orbitals. The expression for the nuclear HF energy is

$$E^{\mathrm{HF}}_{\mathrm{p}} = \sum_{b'}^{N_{\mathrm{p}}} \left[\langle \psi^{\mathrm{p}}_{b'} | h^{\mathrm{p}} | \psi^{\mathrm{p}}_{b'} \rangle + \frac{1}{2} \langle \psi^{\mathrm{p}}_{b'} | \nu_{\mathrm{pp}} | \psi^{\mathrm{p}}_{b'} \rangle - \int\int \frac{\rho^{\mathrm{e}}(\mathbf{r}_1) |\psi^{\mathrm{p}}_{b'}(\mathbf{r}_{1'})|^2}{r_{11'}} \mathrm{d}\mathbf{r}_{1'} \mathrm{d}\mathbf{r}_1 \right] \qquad (14)$$

The conventional electronic structure DFT equations depend on the nuclear molecular orbitals and provide the total electron density. The expression for the electronic DFT energy is

$$E^{\mathrm{DFT}}_{\mathrm{e}} = 2\sum_{b}^{N_{\mathrm{e}}/2} \left\langle \psi^{\mathrm{e}}_{b} \middle| -\frac{1}{2}\nabla^2 \middle| \psi^{\mathrm{e}}_{b} \right\rangle + \frac{1}{2} \int\int \frac{\rho^{\mathrm{e}}(\mathbf{r}_1)\rho^{\mathrm{e}}(\mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 + \int \upsilon_{\mathrm{xc}}(\mathbf{r}_1)\rho^{\mathrm{e}}(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 - \sum_{A}^{N_{\mathrm{c}}} \int \frac{\rho^{\mathrm{e}}(\mathbf{r}_1) Z_A}{r_{1A}} \mathrm{d}\mathbf{r}_1 - \sum_{b'}^{N_{\mathrm{p}}} \int\int \frac{\rho^{\mathrm{e}}(\mathbf{r}_1) |\psi^{\mathrm{p}}_{b'}(\mathbf{r}_{1'})|^2}{r_{11'}} \mathrm{d}\mathbf{r}_{1'} \mathrm{d}\mathbf{r}_1 \qquad (15)$$

After convergence of the nuclear and electronic densities, the total energy is calculated as

$$E = E^{\mathrm{HF}}_{\mathrm{p}} + E^{\mathrm{DFT}}_{\mathrm{e}} + \sum_{b'}^{N_{\mathrm{p}}} \int\int \frac{\rho^{\mathrm{e}}(\mathbf{r}_1) |\psi^{\mathrm{p}}_{b'}(\mathbf{r}_{1'})|^2}{r_{11'}} \mathrm{d}\mathbf{r}_{1'} \mathrm{d}\mathbf{r}_1 \qquad (16)$$

In this expression for the total energy, the electron−proton interaction term is subtracted from the sum of the nuclear HF and the electronic DFT energies to avoid double counting of this interaction, which is included in both the nuclear HF and the electronic DFT energies.

Since only the external potential part of the DFT effective potential is effected by these modifications, this procedure can be applied in conjunction with any kind of DFT functional (i.e., purely exchange or mixed exchange-correlation functionals). This general procedure is closely related to the formulation proposed by Parr and co-workers[21] for the quantum mechanical treatment of all nuclei. The NEO-DFT(ee) method, however, is designed to treat only a relatively small number of nuclei quantum mechanically and the remaining nuclei classically. The NEO-DFT(ee) method has been incorporated into the GAMESS electronic structure code.[26]

B. Grid-Based Methods. For benchmarking purposes, we calculated vibrationally averaged geometries for the bihalides with the vibrational self-consistent-field (VSCF) method.[27] At the VSCF level, the total molecular vibrational wavefunction is constructed as a product of single-mode wavefunctions. The single-mode wavefunctions are generated on a grid and are optimized using a self-consistent-field procedure. The expectation values of the Cartesian coordinates with respect to the VSCF ground-state wavefunction are determined through linear transformations. For the VSCF calculations presented below, we used a locally modified version of GAMESS that includes the option to calculate vibrationally averaged molecular structures within the VSCF framework.[19,26] For these calculations, 16 directly computed quadrature points along each normal mode were used to construct the VSCF potential.

TABLE 1: Electron Correlation Energies and Quantum Nuclear Energies for the $(\mathrm{FHF})^-$ Molecule[a]

method	E_{corr} (classical H)	E_{corr} (quantum H)	ΔE_{QN}
HF	0.0000000	0.000000	0.032118
DFT BLYP	−0.734705	−0.734783	0.032040
DFT B3LYP	−0.804013	−0.800583	0.035547
MP2	−0.578704	−0.577176	0.033645
CCSD(T)	−0.591654	−0.590109	0.033663

[a] E_{corr} is defined as the difference between the HF energy and the energy obtained with the specified electronic structure method. ΔE_{QN} is defined as the difference between the energies obtained with a quantum H and a classical H for the specified electronic structure method. Energies are given in atomic units.

We also performed two-dimensional (2D) vibrational configuration interaction (VCI) calculations that did not include the bending modes of the bihalides. In the 2D VCI method,[28−30] the two-dimensional vibrational wavefunction is represented as a linear combination of two-dimensional harmonic oscillator wavefunctions, and the expansion coefficients are obtained variationally by diagonalizing the Hamiltonian matrix in the two-dimensional harmonic oscillator basis. These calculations were carried out using seven harmonic oscillator basis functions per mode and an eleven-point Gauss−Hermite quadrature scheme for the numerical integration. Convergence with respect to the number of basis functions and quadrature points was investigated by repeating the calculations with five harmonic oscillator basis functions and seven Gauss−Hermite quadrature points per mode. The vibrationally averaged distances differed by only 0.001 Å for these two sets of calculations, thereby confirming convergence.

III. Results and Discussion

In this section, we present calculations for the bihalides $(\mathrm{FHF})^-$ and $(\mathrm{ClHCl})^-$ and for acetylene. The aug′-cc-pVTZ electronic basis set,[31−33] in which the prime indicates that diffuse functions were placed only on the heavy atoms, was used for the bihalide calculations, and the 6-311G electronic basis set[34] was used for the acetylene calculations. For the NEO calculations, all hydrogen nuclei were treated quantum mechanically with the DZSPDN nuclear basis set.[1]

We calculated both the electron correlation energies and the quantum nuclear energies for all three molecules with second-order perturbation theory (MP2),[35] coupled cluster theory [CCSD(T)],[36,37] and DFT with the BLYP[38] and B3LYP[39−41] functionals. These calculations were performed at the equilibrium Hartree−Fock geometries. The electron correlation energy E_{corr} is defined to be the difference between the Hartree−Fock (HF) energy and the energy obtained with the specified electronic structure method. When the hydrogen nuclei are treated classically, the electron correlation energies are determined relative to the conventional HF energy, and when the

TABLE 2: Electron Correlation Energies and Quantum Nuclear Energies for the $(ClHCl)^-$ Molecule[a]

method	E_{corr} (classical H)	E_{corr} (quantum H)	ΔE_{QN}
HF	0.000000	0.000000	0.030822
DFT BLYP	−1.350802	−1.344543	0.030901
DFT B3LYP	−1.460847	−1.460767	0.037080
MP2	−0.429777	−0.428383	0.032216
CCSD(T)	−0.479245	−0.477675	0.032393

[a] E_{corr} is defined as the difference between the HF energy and the energy obtained with the specified electronic structure method. ΔE_{QN} is defined as the difference between the energies obtained with a quantum H and a classical H for the specified electronic structure method. Energies are given in atomic units.

TABLE 3: Electron Correlation Energies and Quantum Nuclear Energies for the Acetylene Molecule[a]

method	E_{corr} (classical H)	E_{corr} (quantum H)	ΔE_{QN}
HF	0.000000	0.000000	0.065776
DFT BLYP	−0.642525	−0.642723	0.065578
DFT B3LYP	−0.723615	−0.718516	0.070875
MP2	−0.254133	−0.254782	0.065127
CCSD(T)	−0.270923	−0.270701	0.065997

[a] E_{corr} is defined as the difference between the HF energy and the energy obtained with the specified electronic structure method. ΔE_{QN} is defined as the difference between the energies obtained with a quantum H and a classical H for the specified electronic structure method. Energies are given in atomic units.

TABLE 4: Experimental and Theoretical X−X Distances for the Bihalide Systems $(FHF)^-$ and $(ClHCl)^-$[a]

method	$(FHF)^-$ R_{FF}	$(ClHCl)^-$ R_{ClCl}
experimental R_e	2.277 71[b]	3.1122(26)[c]
experimental R_0	2.304[d]	3.14676(5)[c]
MP2[e]	2.288	3.110
4D VSCF-MP2[e]	2.311	3.131
2D grid-MP2[f]	2.324	3.152
2D VCI-MP2	2.324	3.152
NEO-MP2(ee)[e]	2.321	3.150
DFT	2.301	3.153
4D VSCF-DFT	2.325	3.175
2D VCI-DFT	2.336	3.196
NEO-DFT(ee)	2.329	3.184

[a] The aug′-cc-pVTZ electronic basis set was used in all calculations. The DZSPDN nuclear basis set was used in all of the NEO calculations. The DFT calculations use the B3LYP functional. Distances are given in angstroms. [b] Ref 44. [c] Ref 45. [d] Calculated using the rigid rotor approximation and B_0 from ref 44. [e] Ref 19. [f] Ref 42.

hydrogen nuclei are treated quantum mechanically, the electron correlation energies are determined relative to the NEO-HF energy. The quantum nuclear energy ΔE_{QN} is defined to be the difference between the energies obtained with quantum hydrogen nuclei and classical hydrogen nuclei for the specified electronic structure method.

The electron correlation effects are treated in a different manner for the MP2, CCSD(T), and DFT methods. In both the NEO-MP2 and NEO-CCSD(T) approaches, initially the nuclear and electronic molecular orbitals are obtained from a NEO-HF calculation, and subsequently the electron correlation corrections are evaluated with either the MP2 or the CCSD(T) method. Thus, the impact of electron correlation on the nuclear wavefunction is not included in these approaches. In the NEO-DFT approach, however, the correlated electron density is used to obtain the nuclear molecular orbitals at each step of the iterative procedure, and the resulting nuclear density is used to calculate the correlated electron density for the subsequent step of this procedure. Thus, the NEO-DFT approach includes feedback between the correlated electron density and the nuclear wavefunction.

The results for the $(FHF)^-$, $(ClHCl)^-$, and acetylene molecules are given in Tables 1, 2, and 3, respectively. These tables illustrate several qualitative trends for all three systems. The DFT method appears to recover more electron correlation energy than the MP2 and CCSD(T) methods. More importantly, these results show that the electron correlation energy is similar for the conventional and the NEO calculations at each level of electronic structure theory. This observation indicates that the quantum treatment of the hydrogen nuclei does not significantly impact the electron correlation energy for the MP2, CCSD(T), and DFT methods. The results also show that the quantum nuclear energies are similar for the MP2, CCSD(T), and DFT methods. This observation indicates that the impact of the quantum treatment of the hydrogen nuclei on the energy is relatively independent of the level of electronic structure theory. For all three molecules, however, the quantum nuclear energies are greatest at the NEO-DFT(ee) B3LYP level. This observation suggests that the quantum nuclear energy is enhanced by the combination of the larger electron correlation energy and the feedback between the correlated electron density and the nuclear wavefunction included in the NEO-DFT(ee) B3LYP approach.

In order to benchmark the NEO-DFT(ee) method, we compare the F−F and Cl−Cl distances for the bihalides optimized with the NEO approach to vibrationally averaged geometries obtained with the full-dimensional VSCF method and the 2D VCI method. The optimized NEO X−X distances correspond to the minimum energy geometry at the specified level of electronic structure theory within the NEO framework. The results for these calculations at both the MP2 and DFT B3LYP levels of electronic structure theory are given in Table 4. The agreement between the 2D VCI-MP2 and the 2D grid-MP2 calculations from Del Bene and Jordan[42] to within 0.001 Å provides validation for the VCI results. We emphasize that the NEO calculations are much faster than the full-dimensional VSCF and 2D VCI calculations. For the $(FHF)^-$ system, the NEO-DFT(ee) optimization required ∼10 min of CPU time, while the full-dimensional VSCF and 2D VCI calculations required ∼35 and ∼2 h of CPU time, respectively.

As discussed previously,[19] the X−X distances are shorter for the full-dimensional VSCF calculations than for the 2D VCI calculations because the inclusion of the bending motions tends to decrease the X−X distance. The NEO approach is capable of including the nuclear quantum effects of the bending mode with an adequate nuclear basis set and sufficient electron−proton correlation, but the present implementation is directed at an accurate description of the stretching modes and is not optimized for the description of the lower-frequency bending modes. As a result, the NEO-MP2(ee) X−X distances are within 0.003 Å of the 2D VCI-MP2 distances and are greater than the full-dimensional VSCF-MP2 distances by ∼0.01−0.02 Å.

Similar trends are observed for the NEO-DFT(ee) X−X distances, which are within ∼0.01 Å of the 2D VCI−DFT distances. The slightly larger differences between the NEO and 2D VCI calculations observed for DFT may arise from the feedback between the correlated electron density and the nuclear molecular orbitals in the NEO-DFT(ee) approach. This feedback is not present in the 2D VCI and NEO-MP2(ee) methods, and it may lead to a better description of the bending mode. Table 4 indicates that the NEO-DFT(ee) X−X distances are slightly closer to the full-dimensional VSCF-DFT distances than to the 2D VCI-DFT distances. This better agreement with the full-dimensional grid-based calculations also suggests that the NEO-

DFT(ee) approach describes the bending mode more accurately than the NEO-MP2(ee) method. Note that the DFT distances do not agree as well as the MP2 distances with the experimental distances. The larger bond lengths for DFT than for MP2 are a characteristic of the DFT B3LYP method for these molecules with this electronic basis set and are not a reflection of the accuracy of the NEO methodology. Similar trends were observed in previous conventional electronic structure studies.[43] For benchmarking purposes, our goal is to compare the NEO-DFT(ee) method to grid-based quantum dynamical methods at the same level of electronic structure theory. The excellent agreement between the distances obtained with the NEO-DFT(ee) method and the 2D VCI-DFT and full-dimensional VSCF-DFT methods provides validation for the NEO-DFT(ee) approach.

IV. Concluding Remarks

In this paper, we presented the NEO-DFT(ee) approach for including both electron−electron correlation and nuclear quantum effects self-consistently within the NEO framework. The NEO approach is designed to treat a relatively small number of nuclei quantum mechanically, while the remaining nuclei are treated classically. In the NEO-DFT(ee) approach, the correlated electron density is used to obtain the nuclear molecular orbitals, and the resulting nuclear density is used to obtain the correlated electron density during an iterative procedure that continues until convergence of both the nuclear and electronic densities. As a result, this approach includes feedback between the correlated electron density and the nuclear wavefunction. Our analysis of NEO and conventional electronic structure calculations at various levels of theory for bihalides and acetylene indicates that the nuclear quantum effects do not significantly impact the electron correlation energy. This analysis also suggests that the quantum nuclear energy is enhanced in the NEO-DFT(ee) B3LYP method due to the combination of greater electron correlation energy and feedback between the correlated electron density and the nuclear wavefunction. Benchmarking calculations on the bihalides by comparison of the NEO-DFT(ee) method to grid-based quantum dynamical methods provide an assessment of the accuracy of this approach.

The current version of the NEO-DFT(ee) method includes only electron−electron correlation with density functional theory. Electron−proton correlation plays a vital role in the description of nuclear−electronic wavefunctions because of the attractive electron−proton electrostatic interaction. Inadequate treatment of electron−proton correlation produces nuclear wavefunctions that are too localized and leads to severe overestimations of hydrogen vibrational frequencies. One potential direction for the inclusion of electron−proton correlation is to develop an electron−nucleus correlation functional within the density functional theory framework. Alternatively, explicit electron−proton correlation can be included directly into the NEO self-consistent-field framework with Gaussian-type geminal functions using the NEO-XCHF method.[7] The NEO-XCHF method has already been shown to provide accurate descriptions of nuclear−electronic wavefunctions. The combination of the NEO-DFT(ee) approach for electron−electron correlation and the NEO-XCHF approach for electron−proton correlation would provide a computationally practical and highly accurate method for inclusion of nuclear quantum effects in electronic structure calculations.

Acknowledgment. We gratefully acknowledge the support of AFOSR Grant No. FA9550-07-1-0143 and helpful discussions with Simon Webb and Chet Swalina.

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