THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

**2006,** *110,* 9983−9987
Published on Web 08/01/2006

# Explicit Dynamical Electron−Proton Correlation in the Nuclear−Electronic Orbital Framework

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

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

*Received: June 2, 2006; In Final Form: July 14, 2006*

A method that includes explicit electron−proton correlation directly into the nuclear−electronic orbital self-consistent-field framework is presented. This nuclear−electronic orbital explicitly correlated Hartree−Fock (NEO-XCHF) scheme is formulated using Gaussian basis functions for the electrons and the quantum nuclei in conjunction with Gaussian-type geminal functions. The NEO approach is designed for the quantum treatment of a relatively small number of nuclei, such as the hydrogen nuclei involved in key hydrogen bonding interactions or hydrogen transfer reactions. The conventional nuclear−electronic-orbital-based methods produce nuclear wave functions that are too localized, leading to severe overestimations of hydrogen vibrational frequencies, as well as inaccuracies in geometries, isotope effects, couplings, and tunneling splittings. The application of the NEO-XCHF approach to a model system illustrates that the description of the nuclear wave function is significantly improved by the inclusion of explicit electron−proton correlation. In contrast to the NEO-HF method, the NEO-XCHF method leads to hydrogen vibrational stretch frequencies that are in excellent agreement with those calculated from grid-based methods. This approach is computationally practical for many-electron systems because only a relatively small number of nuclei are treated quantum mechanically and only electron−proton correlation is treated explicitly. Electron−electron dynamical correlation can be included with density functional theory or perturbation theory methods.

## I. Introduction

Nuclear quantum effects such as zero point motion and hydrogen tunneling are often significant for hydrogen bonding interactions and hydrogen transfer reactions. In conventional treatments based on the Born−Oppenheimer approximation, nuclei are represented as classical point charges. In this case, the nuclear quantum effects are typically neglected or are included in the form of harmonic zero point energy corrections and Bell tunneling corrections.[1] Grid-based methods[2] can provide accurate nuclear wave functions for the Born−Oppenheimer potential energy surface but are computationally expensive for multidimensional systems.

Recently, methods have been developed to include nuclear quantum effects in electronic structure calculations without invoking the Born−Oppenheimer approximation. In the nuclear−electronic orbital (NEO) approach,[3−8] specified nuclei are treated quantum mechanically on the same level as the electrons by solving a mixed nuclear−electronic Schrödinger equation using molecular orbital techniques. The NEO approach is designed for the quantum mechanical treatment of a relatively small number of nuclei, such as the hydrogen nuclei involved in key hydrogen bonding interactions or hydrogen transfer reactions. This approach has been implemented at the Hartree−Fock (NEO-HF), configuration interaction (NEO-CI), multiconfigurational self-consistent-field (NEO-MCSCF), and second-order perturbation theory (NEO-MP2) levels. Similar techniques have been developed by other groups.[9−17]

These molecular-orbital-based methods typically produce nuclear wave functions that are too localized, leading to severe overestimations of hydrogen vibrational frequencies. The magnitudes of the errors in the calculated hydrogen vibrational stretch frequencies are often 2000−3000 $\text{cm}^{-1}$ (i.e., on the same order as the frequencies themselves).[13−20] The bending mode frequencies involving hydrogen are also often qualitatively incorrect. The overlocalization of the nuclear wave function impacts not only the frequencies but also the geometries, the isotope effects, and the tunneling splittings. We have demonstrated that the overlocalization of the ground state nuclear wave function can result in qualitative errors for the geometric isotope effects in hydrogen-bonded systems.[20,21] For example, grid-based methods and experimental data indicate that deuteration decreases the fluorine−fluorine distance in the hydrogen fluoride dimer, whereas the molecular-orbital-based methods predict that deuteration increases this distance.[20]

We have shown that dynamical electron−proton correlation strongly influences the delocalization of nuclear wave functions.[4,5] Unfortunately, the recovery of electron−proton correlation using orbital-based treatments suffers from slow convergence reminiscent of that found for precise treatments of electron−electron correlation. The qualitative impact of electron−proton dynamical correlation on the wave function is greater than that of electron−electron dynamical correlation because of the attractive electrostatic interaction between the

---

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

10.1021/jp0634297 CCC: $33.50

electron and the proton and the difference between the masses. The physical basis for the problems with the molecular-orbital-based approaches for treating electron−proton correlation can be understood by comparison to a Born−Oppenheimer grid-based calculation of the nuclear wave function. In this treatment, the external potential is computed at discrete points of a grid representing the nuclear coordinates by calculating a new electronic wave function for each set of nuclear coordinates. Thus, the electrons adjust instantaneously to the positions of the nuclei. The conventional molecular-orbital-based approaches do not include this type of explicit correlation between the electrons and the quantum nuclei. At the Hartree−Fock level, the quantum nuclei move in an average field of the electrons and the electrons move in an average field of the quantum nuclei. Corrections at the MP2 level and multiconfigurational methods are unable to fix the severe problems with the Hartree−Fock nuclear−electronic wave function.

In this Letter, we present the nuclear−electronic orbital explicitly correlated Hartree−Fock (NEO-XCHF) method, which includes explicit electron−proton correlation directly into the nuclear−-electronic orbital self-consistent-field framework. This scheme is formulated using Gaussian basis functions for the electrons and the quantum nuclei in conjunction with Gaussian-type geminal functions that depend on the distance between an electron and a quantum nucleus. Previously explicit electron−electron correlation has been included in MP2 corrections for electronic structure calculations[22,23] but, to our knowledge, not in the self-consistent-field procedure. Geminals have also been used in other contexts within electronic structure theory.[24,25] Adamowicz and co-workers have developed a non-Born−Oppenheimer approach in which all electrons and nuclei are treated quantum mechanically with explicit correlation between all particles.[26] This approach is restricted to relatively small systems. In the NEO-XCHF approach, only a small number of nuclei are treated quantum mechanically, and only electron−proton correlation is treated explicitly with Gaussian-type geminals. As a result, the NEO-XCHF approach is applicable to larger systems of chemical and biological interest. We demonstrate that the hydrogen vibrational frequencies calculated at the NEO-HF level are improved significantly with the NEO-XCHF method for a model system. We also present a general form of the NEO-XCHF nuclear−electronic wave function that will enable calculations of larger many-electron systems.

## II. Theory

For a system with one electron, one proton, and $N_c$ classical point charges, the Hamiltonian is

$$\hat{H} = -\frac{1}{2}\nabla_e^{\ 2} - \frac{1}{2m_p}\nabla_p^{\ 2} - \sum_A^{N_c}\frac{Z_A}{|\mathbf{r}^e - \mathbf{r}_A^c|} + \sum_A^{N_c}\frac{Z_A}{|\mathbf{r}^p - \mathbf{r}_A^c|} - \frac{1}{|\mathbf{r}^e - \mathbf{r}^p|} \qquad (1)$$

Here, $\mathbf{r}^e$ and $\mathbf{r}^p$ denote the spatial coordinates of the electron and proton, respectively, and $\mathbf{r}_A^c$ and $Z_A$ denote the spatial coordinates and the charges of the classical point charges. At the NEO-XCHF level, the total nuclear−electronic wave function for a system comprised of one electron and one proton is

$$\Psi_{tot}(\mathbf{r}^e,\mathbf{r}^p) = \psi^e(\mathbf{r}^e)\psi^p(\mathbf{r}^p)(1 + \sum_k^{N_{gem}} b_k \exp[-\gamma_k|\mathbf{r}^e - \mathbf{r}^p|^2]) \qquad (2)$$

where $\psi^e(\mathbf{r}^e)$ and $\psi^p(\mathbf{r}^p)$ are spatial orbitals representing the electron and the proton, respectively. In eq 2, the summation term is the Gaussian-type geminal (GTG) expansion, which couples the electron and the proton. For notational convenience, we define the GTG factor as

$$G(\mathbf{r}^e,\mathbf{r}^p) \equiv 1 + \sum_k^{N_{gem}} b_k \exp[-\gamma_k|\mathbf{r}^e - \mathbf{r}^p|^2] \qquad (3)$$

We have derived modified Hartree−Fock equations using the standard variation method to minimize the energy $\langle\Psi_{tot}|\hat{H}|\Psi_{tot}\rangle$ with respect to both the electronic and the nuclear molecular orbitals subject to the normalization constraint $\langle\Psi_{tot}|\Psi_{tot}\rangle = 1$. The resulting Hartree−Fock equations for the electron and the proton are

$$f^e(\mathbf{r}^e)\ \psi^e(\mathbf{r}^e) = \epsilon^e s^e(\mathbf{r}^e)\ \psi^e(\mathbf{r}^e) \qquad (4)$$

$$f^p(\mathbf{r}^p)\ \psi^p(\mathbf{r}^p) = \epsilon^p s^p(\mathbf{r}^p)\ \psi^p(\mathbf{r}^p) \qquad (5)$$

where the Fock operators are defined as

$$f^e(\mathbf{r}^e) = \int \mathrm{d}\mathbf{r}_p\ \psi^p(\mathbf{r}^p)\ G(\mathbf{r}^e,\mathbf{r}^p)\ \hat{H}\psi^p(\mathbf{r}^p)\ G(\mathbf{r}^e,\mathbf{r}^p) \qquad (6)$$

$$f^p(\mathbf{r}^p) = \int \mathrm{d}\mathbf{r}_e\ \psi^e(\mathbf{r}^e)\ G(\mathbf{r}^e,\mathbf{r}^p)\ \hat{H}\psi^e(\mathbf{r}^e)\ G(\mathbf{r}^e,\mathbf{r}^p) \qquad (7)$$

and the overlap operators $s^e(\mathbf{r}^e)$ and $s^p(\mathbf{r}^p)$ are defined analogously without the operator $\hat{H}$.

The spatial orbitals for the electron and the proton are expanded in Gaussian basis sets:

$$\psi_i^e(\mathbf{r}^e) = \sum_\mu^{N_{bf}^e} c_{\mu i}^e \varphi_\mu^e(\mathbf{r}^e) \qquad (8)$$

$$\psi_{i'}^p(\mathbf{r}^p) = \sum_{\mu'}^{N_{bf}^p} c_{\mu' i'}^p \varphi_{\mu'}^p(\mathbf{r}^p) \qquad (9)$$

where the unprimed indices refer to electronic basis functions and the primed indices refer to nuclear basis functions. Substitution of these expansions into eqs 4 and 5 leads to the Hartree−Fock−Roothaan equations for the electron and the proton:

$$\sum_\nu^{N_{bf}^e} F_{\mu\nu}^e c_{\nu i}^e = \epsilon_i^e \sum_\nu^{N_{bf}^e} S_{\mu\nu}^e c_{\nu i}^e \qquad (10)$$

$$\sum_{\nu'}^{N_{bf}^p} F_{\mu'\nu'}^p c_{\nu' i'}^p = \epsilon_{i'}^p \sum_{\nu'}^{N_{bf}^p} S_{\mu'\nu'}^p c_{\nu' i'}^p \qquad (11)$$

where the Fock matrix elements are defined as

$$F_{\mu\nu}^e = \sum_{\mu'\nu'}^{N_{bf}^p} c_{\mu' i'}^p c_{\nu' i'}^p H_{\mu\mu'\nu\nu'} \qquad (12)$$

$$F_{\mu'\nu'}^p = \sum_{\mu\nu}^{N_{bf}^e} c_{\mu i}^e c_{\nu i}^e H_{\mu\mu'\nu\nu'} \qquad (13)$$

$$H_{\mu\mu'\nu\nu'} = \int\int \mathrm{d}\mathbf{r}^e\ \mathrm{d}\mathbf{r}^p\ \varphi_\mu^e(\mathbf{r}^e)\ \varphi_{\mu'}^p(\mathbf{r}^p)\ G(\mathbf{r}^e,\mathbf{r}^p)\ \hat{H}\varphi_\nu^e(\mathbf{r}^e)\ \varphi_{\nu'}^p(\mathbf{r}^p)\ G(\mathbf{r}^e,\mathbf{r}^p) \qquad (14)$$

and the overlap matrix elements $S_{\mu\nu}^e$ and $S_{\mu'\nu'}^p$ are defined analogously without the operator $\hat{H}$. Note that these Fock and overlap matrixes are different from those used in conventional electronic structure theory. As long as the overlap matrixes are invertible, however, eqs 10 and 11 can be solved using standard matrix methods for generalized eigenvalue equations. The integrals over GTGs are evaluated using the McMurchie−Davidson approach by expanding them as linear combinations of Gaussian Hermite integrals.[23,27−29] The NEO-XCHF approach has been incorporated into the GAMESS electronic structure code.[30]

In addition, we have derived alternative modified Hartree−Fock equations using the variation method to minimize the total energy $\langle\Psi_{tot}|\hat{H}|\Psi_{tot}\rangle/\langle\Psi_{tot}|\Psi_{tot}\rangle$ with respect to both the electronic and the nuclear molecular orbitals subject to orthonormalization constraints for the electronic and nuclear molecular orbitals. In this case, the total wave function is not normalized. The resulting Hartree−Fock equations for the electron and the proton are

$$\left[\frac{1}{\langle\Psi_{tot}|\Psi_{tot}\rangle} f^{e}(\mathbf{r}^{e}) - \frac{\langle\Psi_{tot}|\hat{H}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle^{2}}\Lambda^{e}(\mathbf{r}^{e})\right]\psi^{e}(\mathbf{r}^{e}) = \tilde{\epsilon}^{e}\psi^{e}(\mathbf{r}^{e}) \tag{15}$$

$$\left[\frac{1}{\langle\Psi_{tot}|\Psi_{tot}\rangle} f^{p}(\mathbf{r}^{p}) - \frac{\langle\Psi_{tot}|\hat{H}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle^{2}}\Lambda^{p}(\mathbf{r}^{p})\right]\psi^{p}(\mathbf{r}^{p}) = \tilde{\epsilon}^{p}\psi^{p}(\mathbf{r}^{p}) \tag{16}$$

where the operators $\Lambda^{e}(\mathbf{r}^{e})$ and $\Lambda^{p}(\mathbf{r}^{p})$ are defined as

$$\Lambda^{e}(\mathbf{r}^{e}) = \int d\mathbf{r}_{p}\, \psi^{p}(\mathbf{r}^{p})[G^{2}(\mathbf{r}^{e},\mathbf{r}^{p}) - 1]\psi^{p}(\mathbf{r}^{p}) \tag{17}$$

$$\Lambda^{p}(\mathbf{r}^{p}) = \int d\mathbf{r}_{e}\, \psi^{e}(\mathbf{r}^{e})[G^{2}(\mathbf{r}^{e},\mathbf{r}^{p}) - 1]\psi^{e}(\mathbf{r}^{e}) \tag{18}$$

Expansion of the molecular orbitals in Gaussian basis sets using eqs 8 and 9 leads to Hartree−Fock−Roothaan equations that are identical to those in NEO-HF except that the Fock operators are modified to be the expressions in square brackets in eqs 15 and 16. As the GTG factor $G(\mathbf{r}^{e},\mathbf{r}^{p})$ approaches unity, eqs 15 and 16 approach the NEO-HF equations. Note that the molecular orbital energies are different in the two formulations of NEO-XCHF.

We have confirmed that the two formulations of NEO-XCHF give identical ground and excited state energies for the model systems studied in this Letter. We used the first formulation given by eqs 4 and 5 to calculate the vibrational stretching frequencies presented below. The frequencies were calculated as the energy difference between the proton eigenvalues defined in eq 11 for the excited state corresponding to the hydrogen vibrational stretching mode and the ground state. Similar frequencies were obtained by performing a separate NEO-XCHF calculation for the relevant excited state.

This approach can be extended to systems composed of multiple electrons and multiple quantum nuclei by using the following form of the total nuclear−electronic wave function:

$$\Psi_{tot}(\mathbf{r}^{e},\mathbf{r}^{p}) = \Phi^{e}(\mathbf{r}^{e})\,\Phi^{p}(\mathbf{r}^{p})\{1 + \sum_{i=1}^{N_{e}}\sum_{j=1}^{N_{p}}\sum_{k=1}^{N_{gem}} b_{k}\exp[-\gamma_{k}|\mathbf{r}_{i}^{e} - \mathbf{r}_{j}^{p}|^{2}]\} \tag{19}$$

Here, $\Phi^{e}(\mathbf{r}^{e})$ and $\Phi^{p}(\mathbf{r}^{p})$, respectively, are antisymmetrized wave functions (i.e., determinants of spin orbitals) representing the electrons and fermionic nuclei such as protons. The total wave function is antisymmetric with respect to interchange of any two electrons or any two quantum nuclei because the GTG factor is symmetric with respect to these interchanges. The extension to bosonic nuclei is straightforward.[21] Including the GTGs as a summation of Gaussians multiplied by the NEO-HF wave function is more computationally practical than including them as a product of Gaussians or at the basis function level because this form requires only four-particle and simpler integrals. Since the geminal expansion parameters, $b_k$ and $\gamma_k$, represent the fundamental properties of an electron and a proton, these parameters can remain fixed at values predetermined from variational calculations on small systems. We expect that a relatively small number of GTGs (i.e., $N_{gem} \leq 4$) will be required to obtain the desired accuracy of the nuclear−electronic wave function. For the case of multiple electrons and quantum nuclei, modified Hartree−Fock equations analogous to those in eqs 15 and 16 can be solved iteratively to self-consistency. For large systems, the computational efficiency can be enhanced by avoiding the calculation of many of the demanding three- and four-particle integrals with a distance cutoff.

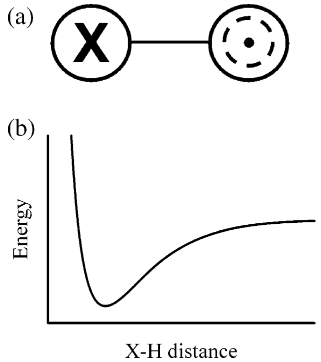

**Figure 1.** (a) Schematic picture of the $X^{+}$[H] model system. The solid circles represent the electronic basis functions, and the dashed circle represents the nuclear basis functions. (b) The ROHF potential energy as a function of the X−H distance for the model system.

### III. Application to Model System

To validate the NEO-XCHF approach, we apply it to a model system containing one electron and one proton. The model system, $X^{+}$[H], is depicted in Figure 1. This model consists of a hydrogen atom moving in the field of an infinitely massive positive point charge. The electron and the proton of the hydrogen atom are treated quantum mechanically, and the positive point charge $X^{+}$ is treated classically. We emphasize that the NEO approach is designed for systems in which at least two nuclei are treated classically, thereby eliminating the difficulties associated with translations and rotations.[31] In this model system, however, only a single nucleus is treated classically, so the ground state should be a rotational state that is spherically symmetric about the classical nucleus. We are able to describe the vibrational states along the X−H axis by placing the basis function centers for the nucleus and the electron at a single point. The same basis function center is used for both the electronic and the nuclear basis functions.

The frequencies corresponding to the stretching motion of hydrogen, deuterium, and tritium in the $X^{+}$[H] system were calculated using the NEO-HF and NEO-XCHF methods. The cc-pVDZ electronic basis set was used for all calculations.[32] For the NEO calculations, the distance between the classical nucleus and the centers of the electronic and nuclear basis functions was chosen to be the equilibrium distance obtained from a conventional ROHF/cc-pVDZ calculation of $H_2^{+}$. An even-tempered (ET) nuclear basis set including 5s-, 5p-, and 5d-type Gaussian basis functions was constructed for hydrogen, deuterium, and tritium using the method of Bardo and Rueden-

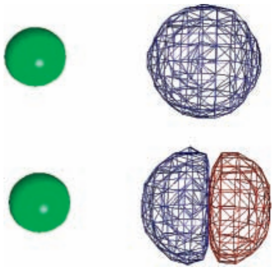

**Figure 2.** Nuclear molecular orbitals corresponding to the ground state and the hydrogen vibrational stretch excited state for the $X^+$[H] model system at the NEO-HF level. The point charge X is represented by a green circle.

**TABLE 1: Exponents for the ET-5s5p5d Nuclear Basis Set for H, D, and T Isotopes**[a]

| $n$ | $\nu_n$ (cm$^{-1}$) | $\zeta_n$ (bohr$^{-2}$) H | $\zeta_n$ (bohr$^{-2}$) D | $\zeta_n$ (bohr$^{-2}$) T |
|---|---|---|---|---|
| 1 | 500 | 2.091 532 | 4.180 988 | 6.274 596 |
| 2 | 866 | 3.622 534 | 7.241 472 | 10.867 601 |
| 3 | 1500 | 6.274 596 | 12.542 965 | 18.823 789 |
| 4 | 2598 | 10.867 601 | 21.724 415 | 32.602 802 |
| 5 | 4500 | 18.823 789 | 37.628 895 | 56.471 366 |

[a] The exponents in the table are related to frequencies using the harmonic approximation. The range of frequencies used for determining the exponents was generated using the even-tempered scheme developed by Bardo and Ruedenberg:[33] $\nu_n = \alpha\beta^n$.

**TABLE 2: Vibrational Stretching Frequencies Calculated from the Energy Level Splittings for the Model System**

| isotope | NEO-HF | NEO-XCHF | NEO-full CI | harmonic ROHF | VSCF ROHF |
|---|---|---|---|---|---|
| H | 3621 | 1649 | 2263 | 1710 | 1645 |
| D | 2729 | 1081 | 1707 | 1210 | 1177 |
| T | 2302 | 963 | 1457 | 988 | 966 |

berg.[33] The exponents for this basis set are given in Table 1. To avoid significant contamination of the vibrational states with rotational character, the d basis functions with the two lowest-frequency exponents were excluded for the calculations on hydrogen and the d basis functions with the lowest-frequency exponent were excluded for the calculations on deuterium and tritium. Four GTGs were included in the NEO-XCHF calculations. The values of $b$ and $\gamma$ in the geminal expansion were variationally optimized simultaneously with the exponent of the nuclear basis function for NEO-XCHF/1s calculations with only a single 1s Gaussian nuclear basis function. The values of these parameters were fixed for the subsequent NEO-XCHF/ET calculations. The NEO-HF nuclear wave functions for the ground state and the excited state corresponding to the hydrogen vibrational stretching mode are depicted in Figure 2.

The results for the $X^+$[H] model system are presented in Table 2. For comparison, we calculated the frequencies at the ROHF level from the Hessian and with the vibrational self-consistent-field (VSCF) method,[2,34] which is a grid-based method that includes anharmonic effects. The VSCF method is expected to be accurate for this model system because the electron is predominantly adiabatic with respect to the proton. The NEO-HF frequencies are greater than the frequencies calculated using the Hessian and VSCF approaches for all three isotopes by approximately a factor of 2, corresponding to an error with a magnitude of ~2000 cm$^{-1}$ for hydrogen. When four GTGs are included in the NEO-XCHF calculation, the frequencies are within 5 cm$^{-1}$ of the VSCF frequencies for H and T and within 100 cm$^{-1}$ of the VSCF frequency for D.[35] Since dynamical electron−proton correlation is responsible for the dramatic improvement in the frequencies, we also computed the frequencies using the NEO-full CI approach. Note that even the NEO-full CI method does not provide frequencies as accurate as the NEO-XCHF approach. In addition, we found that the variationally optimized exponent of the 1s basis function from the NEO-XCHF/1s calculation corresponds to a frequency much lower and closer to the harmonic ROHF frequency than the exponent from an analogous NEO-HF/1s calculation. Thus, the NEO-XCHF method provides a more accurate description of the nuclear wave function than the NEO-HF method.

We emphasize that the goal of the NEO-XCHF approach is not to obtain quantitatively accurate frequencies for spectroscopic purposes but rather to obtain qualitatively reasonable frequencies that enable the calculation of geometries, isotope effects, vibronic couplings, and tunneling splittings for relatively large systems. The improvement observed for this model system suggests that the NEO-XCHF approach will alleviate the qualitative errors observed previously for properties such as the geometric isotope effects.[20]

## IV. Conclusions

We presented a method that includes explicit electron−proton correlation directly into the nuclear−electronic orbital self-consistent-field framework. Our application of the NEO-XCHF method to a model system illustrates that the description of the nuclear wave function is significantly improved by the inclusion of explicit electron−proton correlation. In particular, the nuclear wave function becomes more delocalized, and the hydrogen vibrational frequencies are decreased when explicit electron−proton correlation is included. An accurate description of the nuclear wave function is essential for the calculation of geometries, isotope effects, vibronic couplings, and tunneling splittings.

The NEO-XCHF approach is computationally practical for many-electron systems because only a relatively small number of nuclei are treated quantum mechanically and only electron−proton correlation is treated explicitly. Electron−electron dynamical correlation can be included within the framework of this approach using density functional theory or second-order perturbation theory. Nondynamical correlation can be included with multiconfigurational methods such as MCSCF[4,5] and nonorthogonal CI.[8] This approach will facilitate computational studies of a wide range of chemically and biologically significant hydrogen transfer and hydrogen bonding systems.

**Acknowledgment.** We gratefully acknowledge the support of AFOSR Grant No. FA9550-04-1-0062. We also thank Todd Martinez and John Tully for very helpful discussions. C.S. thanks Dr. Pål Dahle for generously providing a manuscript of his doctoral thesis.

## References and Notes

(1) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.

(2) Bowman, J. M. *Acc. Chem. Res.* **1986**, *19*, 202.

(3) Webb, S. P.; Iordanov, T.; Hammes-Schiffer, S. *J. Chem. Phys.* **2002**, *117*, 4106.

(4) Pak, M. V.; Hammes-Schiffer, S. *Phys. Rev. Lett.* **2004**, *92*, 103002.

(5) Pak, M. V.; Swalina, C.; Webb, S. P.; Hammes-Schiffer, S. *Chem. Phys.* **2004**, *304*, 227.

(6) Swalina, C.; Pak, M. V.; Hammes-Schiffer, S. *Chem. Phys. Lett.* **2005**, *404*, 394.

(7) Swalina, C.; Pak, M. V.; Hammes-Schiffer, S. *J. Chem. Phys.* **2005**, *123*, 014303.

(8) Skone, J. H.; Pak, M. V.; Hammes-Schiffer, S. *J. Chem. Phys.* **2005**, *123*, 134108.

(9) Shigeta, Y.; Takahashi, H.; Yamanaka, S.; Mitani, M.; Nagao, H.; Yamaguchi, K. *Int. J. Quantum Chem.* **1998**, *70*, 659.

(10) Shigeta, Y.; Nagao, H.; Nishikawa, K.; Yamaguchi, K. *J. Chem. Phys.* **1999**, *111*, 6171.

(11) Nakai, H.; Sodeyama, K. *J. Chem. Phys.* **2003**, *118*, 1119.

(12) Tachikawa, M.; Mori, K.; Nakai, H.; Iguchi, K. *Chem. Phys. Lett.* **1998**, *290*, 437.

(13) Shigeta, Y.; Ozaki, Y.; Kodama, K.; Nagao, H.; Kawabe, H.; Nishikawa, K. *Int. J. Quantum Chem.* **1998**, *69*, 629.

(14) Nakai, H.; Sodeyama, K.; Hoshino, M. *Chem. Phys. Lett.* **2001**, *345*, 118.

(15) Kreibich, T.; Gross, E. K. U. *Phys. Rev. Lett.* **2001**, *86*, 2984.

(16) Nakai, H. *Int. J. Quantum Chem.* **2002**, *86*, 511.

(17) Bochevarov, A. D.; Valeev, E. F.; Sherrill, C. D. *Mol. Phys.* **2004**, *102*, 111.

(18) Tachikawa, M. *Mol. Phys.* **2002**, *100*, 881.

(19) Udagawa, T.; Ishimoto, T.; Tokiwa, H.; Tachikawa, M.; Nagashima, U. *Chem. Phys. Lett.* **2004**, *389*, 236.

(20) Swalina, C.; Hammes-Schiffer, S. *J. Phys. Chem. A* **2005**, *109*, 10410.

(21) Reyes, A.; Pak, M. V.; Hammes-Schiffer, S. *J. Chem. Phys.* **2005**, *123*, 064104.

(22) Kutzelnigg, W.; Klopper, W. *J. Chem. Phys.* **1991**, *94*, 1985.

(23) Persson, B. J.; Taylor, P. R. *J. Chem. Phys.* **1996**, *105*, 5915.

(24) Silver, D. M.; Mehler, E. L.; Ruedenberg, K. *J. Chem. Phys.* **1970**, *52*, 1174.

(25) Valeev, E. F.; Schaefer, H. F., III. *J. Chem. Phys.* **2000**, *113*, 3990.

(26) Cafiero, M.; Bubin, S.; Adamowicz, L. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1491.

(27) McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* **1978**, *26*, 218.

(28) Persson, B. J.; Taylor, P. R. *Theor. Chem. Acc.* **1997**, *97*, 240.

(29) Boys, S. F. *Proc. R. Soc. London, Ser. A* **1960**, *258*, 402.

(30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(31) Nakai, H.; Hoshino, M.; Miyamoto, K.; Hyodo, S. *J. Chem. Phys.* **2005**, *122*, 164101.

(32) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(33) Bardo, R. D.; Ruedenberg, K. *J. Chem. Phys.* **1974**, *60*, 918.

(34) Chaban, G. M.; Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1999**, *111*, 1823.

(35) The larger discrepancy for D arises from slight mixing of rotational character into the states for this particular frequency with this nuclear basis set. This problem will not arise for systems with more than a single classical nucleus. We confirmed that the contributions of the rotational states are negligible for H and T.