Theoretical Investigation of Isotope Effects: The Any-Particle Molecular Orbital Code

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ABSTRACT: To study the hydrogen isotope effects in a series of diatomic molecules and water dimers we have created the any particle molecular orbital computer package (APMO). The current version of the APMO code is an implementation of the nuclear orbital and molecular orbital approaches (NMO) at the Hartree-Fock level of theory. We have applied the APMO code to a variety of systems to elucidate the isotope effects on electronic wave functions, geometries and hydrogen bonds. We have studied the isotope effect on the dipole moments, electron densities and geometries of hydrogen molecule, lithium hydride and hydrogen fluoride and we have observed a reduction in the bond distance as the mass of the hydrogen isotopes is increased. This observation is in agreement with experimental data. We have also studied the primary and secondary isotope effects on the hydrogen bond of water dimers and we have observed that the hydrogen-bond becomes weaker as the mass of the bonded hydrogen is increased. This trend has been observed by other authors. In contrast, the hydrogen bond becomes stronger when the mass of secondary hydrogens is increased. Our trends for secondary effects are in agreement with other theoretical and experimental studies. To our knowledge these are the first reported results on the secondary isotope effect on the hydrogen bond of water dimers using a NMO method. The applications presented in this paper demonstrate that the APMO code is highly suitable for the investigation of isotope effects in molecular systems containing a variety of quantum nuclei. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 108: 1742–1749, 2008

Key words: primary and secondary isotope effects; hydrogen bond; born-oppenheimer approximation; nuclear orbital and molecular orbital; any particle molecular orbital

1. Introduction

The Born-Oppenheimer (BO) approximation is perhaps the most fundamental approximation in quantum chemistry. The application of this approximation has made possible the study of systems containing thousands of electrons and nuclei. Despite the success in many research areas of the quantum chemistry methods based on the BO approximation, they still fail to provide a correct description of isotope effects. To describe the H/D/T isotope effect one must include the nuclear kinetic energy as the zero-point energy (ZPE) correction. For most chemical systems the nonadiabatic effects beyond the BO approximation are very small, and the adiabatic approximation suffices. In the case of systems containing hydrogen atoms, however, the nonadiabatic effect and the coupling effect between electronic and nuclear motion, which are not included in the framework of the BO approximation, may be very important. Therefore, the lightest nuclei, such as the proton, deuteron and triton should be treated as quantum particles as a better approximation.

In this regard, several authors have proposed alternative approaches that go beyond the BO approximation, to include nuclear effects in electronic structure calculations. Back in 1969–1970 Thomas [1, 2] proposed to use a mixed nuclear-electronic Schrödinger equation to calculate a mixed nuclear-electronic wave function. The protons of CH_4, NH_3, H_2O, and HF were treated using molecular orbitals (MO) constructed in terms of Slater type functions centered on the heavier central atom. More recent non-BO approaches have been summarized in [3]. Most of the methods within Ref. 3 have the use of gaussian type functions (GTF) to construct nuclear molecular orbitals in common.

Adamowicz and Kozlowski [4] proposed a non-BO theory based on explicitly correlated GTFs for nuclear and electronic coordinates. Although their calculations have reached spectroscopic accuracy for diatomic and triatomic systems, the problem of their approach is that the complexity of the formulas increase with the number of identical particles (N) and computational costs increases very rapidly (N factorial).

Tachikawa et al. have proposed the Full variational molecular orbital method (FVMO) [5], the Dynamic extended molecular orbital method (DEMO) [6, 7], and the multi-component molecular orbital method (MCMO) [8]. In these, both nuclear and electronic wave functions are constructed with molecular orbitals written in terms of GTFs which are optimized variationally.

Nakai and coworkers have developed a rigorous non-BO method called nuclear orbital molecular orbital (NOMO) [9]. This method is in principle capable of giving the exact solution for the non-BO problem. In practice, several hierarchies appear in an actual NOMO treatment where usually vibrations and rotations are not described accurately.

Both Nakai and Tachikawa have constructed computational implementations of their methods and have applied those with relative success to investigate isotope an nuclear quantum effects in a variety of molecular systems. However, their codes are not currently available to other researchers.

Hammes-Schiffer and coworkers have developed the nuclear-electronic orbital approach (NEO) [10], where both the nuclear and electronic orbitals are written in terms of GTFs. The method has been extended to different levels of theory and has been applied to a small number of molecular systems. In their studies they have been more concentrated on the nuclear quantum effects (i.e., vibrational frequencies, tunneling) than on the study of isotope effects. Although their NEO/HF and NEO/MP2 methods have been implemented in the latest version of Gamess [11], these implementations are not yet suitable for studying isotope effects. This is because the program does not support systems containing isotope mixtures.

Given the limited availability of computer codes, based on non-BO methods (such as those described above), to study isotope effects, we have created the any particle molecular orbital code (APMO). Although our current version of the code is slower than regular electronic structure packages, it is robust enough to treat systems containing any combination of quantum particles (i.e., electrons, nuclei, positrons, muons, etc.) within a Hartree-Fock framework. Once we correct some procedural bugs and optimize some numerical procedures the APMO code will be available to the scientific community.

To illustrate some of the applications of the APMO code, we present some results on the hydrogen isotope effect on the dipole moments, electronic populations and geometries of the H_2, LiH and HF hydrogen isotopologues. We also report the hydrogen primary and secondary isotope effects on the hydrogen bond distances of some water dimer isotopologues.

Although we are only presenting a Hartree-Fock study, the trends we have observed for the diatomic systems follow experimental trends [12]. The primary isotope effects on the hydrogen bond of water dimers follow the trends found by other non-BO studies [13, 14]. New theoretical non-BO studies of secondary isotope effects on the hydrogen bond of water dimers are reported and our trends follow those observed experimentally [15, 16] and theoretically (BO based) [17].

An outline of the paper is as follows. In section 2 we summarize the equations of the non-BO methods [8, 10, 13] we have implemented at the Hartree-Fock level of theory. From now on we will refer to them as nuclear molecular orbital methods (NMO). In this section, some computational details are also discussed. In section 3 we present an application of the APMO code to the study of isotope effects on a range of different chemical systems and compare the results to other theoretical and experimental data. Section 4 summarizes the results and provides concluding remarks.

2. Theory

We present generalized expressions for the current implementation of the NMO method, the reader is referred to the original articles for more details [8, 10, 13]. We consider a molecular system containing a number of classical nuclei N^C and a number of quantum particles N^Q. The equations presented in this article are general and consider both fermionic and bosonic particles [13, 18].

The Hamiltonian for a molecular system is written in terms of kinetic energy and potential operators.

$$H_{\text{tot}} = -\sum_{i=1}^{N^Q}\frac{1}{2M_i}\nabla_i^2 + \sum_{i}^{N^Q}\sum_{j>i}^{N^Q}\frac{Z_i^Q \cdot Z_j^Q}{r_{ij}} + \sum_{i}^{N^Q}\sum_{j}^{N^C}\frac{Z_i^Q \cdot Z_j^C}{r_{ij}}$$
$$+ \sum_{i}^{N^C}\sum_{j}^{N^C}\frac{Z_i^C \cdot Z_j^C}{r_{ij}}. \quad (1)$$

At the Hartree-Fock level of theory the total wave function for a molecular system can be approximated as a product of single configurational wave functions for the different types of quantum species α

$$\Psi_0 = \prod_{i}^{\alpha}\Phi^i, \quad (2)$$

here each Φ_i is represented by an antisymmetric product of molecular orbitals in the case of fermionic particles and by a symmetric product of molecular orbitals in the case of bosonic particles.

The Hartree-Fock equations are written in terms of the effective one-particle operator for a quantum species α

$$f^\alpha\psi_i^\alpha = \epsilon_i^\alpha\psi_i^\alpha, \qquad i = 1, \ldots, N^\alpha \quad (3)$$

where N^α is the number of particles of type α. f^α can be written as

$$f^\alpha(i) = -\frac{\nabla_i^2}{2M^\alpha} + \sum_{I}^{N^C}\frac{Z_I^C Z_i^\alpha}{r_{Ii}} + \sum_{j}^{N^\alpha}[J_j^\alpha \mp K_j^\alpha]$$
$$+ \sum_{\beta \neq \alpha}^{N^{\text{types}}}\sum_{j=1}^{N^\beta}\lambda J_j^\beta \quad (4)$$

here α and β are different labels for the quantum species. N^{types} is the number of types of quantum species. N^C is the number of classical nuclei. $\lambda = \text{sign}(\alpha) \times \text{sign}(\beta)$ is the product of the signs of the charges of species α and β. The $\pm$ signs are chosen for fermionic and bosonic species respectively. The J and K are Coulomb and exchange operators

$$J_j^\alpha(1) = \int d\mathbf{r}_2\psi_j^{\alpha*}(2)\frac{1}{r_{12}}\psi_j^\alpha(2) \quad (5)$$

$$K_j^\alpha(1)\psi_i^\alpha(1) = \left[\int d\mathbf{r}_2\psi_j^{\alpha*}(2)\frac{1}{r_{12}}\psi_i^\alpha(2)\right]\psi_j^\alpha(1). \quad (6)$$

Solving Eq. (3) one can obtain the MOs of species α. Equation (4) shows that the effective field experienced by one quantum species depends on the MOs of the remaining species. The MOs for all species can be obtained solving Eq. (3) equation for each species iteratively.

The MOs for species α are constructed as a linear combination of N_{bf}^α GTFs

$$\psi_i^\alpha(1) = \sum_{\mu}^{N_{bf}^\alpha}C_{\mu i}^\alpha\phi_\mu^\alpha(1). \quad (7)$$

TABLE I

Equilibrium distances, partial electronic charges, dipole moments and total energies for H_2 and its Isotopologues calculated at a level of theory NMO-RHF[6-31G**:1s].

Molecule	R_{n-n}/Å	Mulliken	Löwdin	Dipole/a.u.	Energy/Hartree
H_2	0.776519	0.0000(H)	0.0000(H)	0.0000	−1.047241
HD	0.769817	−0.0073(D)	−0.0051(D)	0.0107	−1.058864
HT	0.766830	−0.0106(T)	−0.0074(T)	0.0154	−1.064175
D_2	0.763219	0.0000(D)	0.0000(D)	0.0000	−1.070505
DT	0.760290	−0.0033(T)	−0.0023(T)	0.0047	−1.075822
T_2	0.757383	0.0000(T)	0.0000(T)	0.0000	−1.081141
H_2[a]	0.732583	0.0000(H)	0.0000(H)	0.0000	−1.131334

[a] Conventional MO-RHF.

The average position of the α quantum species (calculated as the expectation value of the coordinates) are longer than the equilibrium distances obtained by the conventional MO method, because of the anharmonicity of the potential.

$$R^\alpha = \langle \mathbf{\Phi}^\alpha | \hat{R} | \mathbf{\Phi}^\alpha \rangle. \tag{8}$$

2.1. COMPUTATIONAL ASPECTS

Here we summarize some of the details of the implementation of the APMO code. A complete description of the implementation is found in [19]. We have followed an object-oriented programming philosophy, so that the code can be reutilized and extended. For instance, we have created a class whose methods implement Eqs. (3) and (4) only once. These methods can be reutilized for any type of quantum species. Some classes have been emulated with Fortran and some others constructed with C++. We utilized the latest Fortran language standard to code the overlap, kinetic energy, nuclear attraction and repulsion integrals routines. These routines were implemented following the recursive formulas proposed by Obara and Saika [20]. The precision of the integral routines was validated with Matlab. We employed the Lapack v3.1.1 [21] library for matrix manipulation. We used the Fletcher-Reeves conjugate gradient algorithm found in the GSL 1.9 library [22] for geometry optimization. The convergence of optimization was reached when the gradient became less than 10^{-6} a.u.

3. Results and Discussion

In this section, we apply the APMO code to a variety of isotopologues of the hydrogen molecule,

lithium hydride, hydrogen fluoride and water dimer. We have employed a 6-31G(d, p) electronic basis set [23–25] for all the calculations reported in this article. A 1s GTF has been used for each proton, deuteron and triton with exponents 22.3, 32.8, and 41.0, respectively [26]. Lithium, oxygen and flourine nuclei were treated as +3, +8, and +9 point charges. All hydrogen nuclei were treated as quantum particles.

Our implementation of the NMO method (at the Hartree-Fock level of theory) within the APMO code was used to investigate the isotope effect on the electronic structure and geometries of H_2, HD, HT, D_2, DT, T_2. Table I presents the bond lengths, the Mulliken and Löwdin charges, the dipole moments and the Hartree-Fock energies of the hydrogen molecule isotopologues. Bond lengths are calculated as the expectation values of <R> after optimizing the centers of the nuclear basis. Mulliken and Löwdin charges are calculated following their expressions in terms of electronic overlap and density matrix. Dipole moments are calculated taking into account the nuclear and electronic charge densities. As shown in Table I, there is a progressive reduction in the total energy of H_2 as the mass of the hydrogen isotopes is increased, which is a result of the reduction in the ZPE. The energy determined with the conventional MO is always lower than that of any of the energies calculated considering quantum nuclei, because the conventional MO method (based on the BO approximation) assumes infinite nuclear masses (no ZPE). Equilibrium internuclear distances $\langle R \rangle$ are calculated as the expectation values of the quantum nuclei. The calculated internuclear distances are 0.7765, 0.7698, 0.7668, 0.7632, 0.7602, 0.7574 for H_2, HD, HT, D_2, DT, T_2, respectively. Considering the
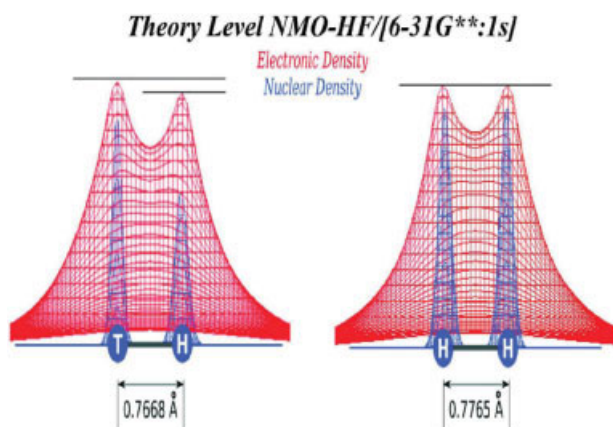
FIGURE 1. An schematic illustration of the electronic and nuclear densities and the internuclear distance R for hydrogen molecule isotopologues H_2 and HT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

anharmonic nature of the potential, the average internuclear distance grows as the ZPE increases. The experimental average internuclear distances [12] for the series above are 0.7511, 0.7498, 0.7493, 0.7484, 0.7476, and 0.7469. This trend agrees well with our results.

Isotope effects on the electronic wave function are also analyzed through the calculated partial charges and dipole moments. Homonuclear molecules do not present a net dipole moment and charge. On the other hand, heteronuclear molecules present a net dipole and a net charge. The data shows that the more massive hydrogen isotope will bear a negative electronic partial charge. Figure 1 illustrates this behavior. Although the calculated

dipole moment of HD of 0.0107 a.u. is greater than the experimental value of 0.00023 a.u. [12], we would expect an improvement of this number using methods with higher levels of electron-electron and nuclear-electron correlation. We are currently implementing the MP2 method in the APMO code.

In addition, we have studied the hydrogen isotope effect on the LiH and HF isotopologues. Table II reports optimized bond lengths, Mulliken and Löwdin partial charges, dipole moments and energies. The calculated internuclear distances for LiH, LiD, LiT are 1.6614, 1.6523, 1.6482 Å whereas the experimental values [12] for LiH and LiD are 1.5957, 1.5494 Å. Our trends are in agreement with the experimental data. The trends for partial charges on hydrogen, dipole moments and energies also agree well with other theoretical data [7]. For HF, the calculated internuclear distances follow the experimental trends [12] and those observed in H_2 and LiH. The dipole moment trend can be understood considering the reduction in the electronic partial charge on flourine atom as the mass of the hydrogen isotope increases.

We have investigated primary isotope effects on the hydrogen bond of some water dimer isotopologues. Figure 2 shows an schematic illustration of the water dimer and the isotope being substituted (in green). Table III summarizes the results for the calculated donor-acceptor R_{DA} and acceptor-bonded-hydrogen R_{AX} distances, here subscripts D, A, and X indicate donor, acceptor and bonded-hydrogen respectively.

The H/D/T primary isotope effects on the hydrogen bond are demonstrated clearly in these dimers. We observe in all systems that as the mass

TABLE II

Equilibrium internuclear distances, partial electronic charges, dipole moments and energies for LiH, HF and their isotopologues calculated at a level theory NMO-RHF[6-31G**:1s].

Molecule[a]	R_{n-n}/Å	Mulliken	Löwdin	Dipole/a.u.	Energy/Hartree
LiH	1.661388	0.1827 (Li)	0.0072 (Li)	2.3419	−7.943768
LiD	1.652289	0.1862 (Li)	0.0134 (Li)	2.3427	−7.954136
LiT	1.648204	0.1877 (Li)	0.0162 (Li)	2.3429	−7.958875
LiH[b]	1.629788	0.1935 (Li)	0.0286 (Li)	2.3423	−7.981340
HF	0.921832	−0.4500 (F)	−0.2965 (F)	0.8195	−99.970489
DF	0.915526	−0.4329 (F)	−0.2860 (F)	0.8035	−99.981871
TF	0.912890	−0.4250 (F)	−0.2813 (F)	0.7964	−99.987075
HF[b]	0.900524	−0.3866 (F)	−0.2594 (F)	0.7648	−100.01169

[a] Li and F nuclei treated as point charges.
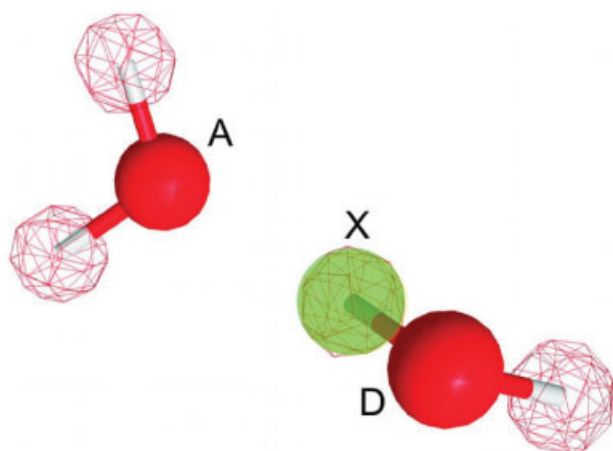[b] Conventional MO-RHF.

FIGURE 2. Schematic picture of primary isotope effect on a water dimer. The hydrogen isotopes are treated quantum mechanically as nuclear orbitals. Shaded hydrogen corresponds to the isotope being substituted. Oxygen nuclei in red are treated classically as point charges. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

of bonded hydrogen X increases the distances R_{AX} and R_{DA} increase as well. These results clearly indicate that there is a weakening of the hydrogen bond as the mass of H increases. These trends are in agreement to those reported by Tachikawa [13, 14], who suggested that the weakening of the hydrogen bond upon deuteration is a manifestation of the Ubbelohde effect that occurs in crystal structures.

TABLE III

Primary isotope effect on the hydrogen bond of water dimer isotopologues.

Dimer[a]	R_{DA}/Å	R_{AX}/Å
$H_2O \cdot \cdot \cdot HOH$	2.950358	1.982522
$H_2O \cdot \cdot \cdot DOH$	2.951926	1.990658
$H_2O \cdot \cdot \cdot TOH$	2.958550	2.000768
$D_2O \cdot \cdot \cdot HOD$	2.944809	1.977248
$D_2O \cdot \cdot \cdot DOD$	2.952303	1.994296
$D_2O \cdot \cdot \cdot TOD$	2.962203	2.004127
$T_2O \cdot \cdot \cdot HOT$	2.952305	1.985121
$T_2O \cdot \cdot \cdot DOT$	2.952990	1.993569
$T_2O \cdot \cdot \cdot TOT$	2.962715	2.008907
$H_2O \cdot \cdot \cdot HOH$[b]	2.980331	2.038823

Calculated internuclear distances R_{AD} and R_{AX} at a level theory NMO-RHF [6-31G**: 1s].
[a] Oxigen nuclei treated as point charges.
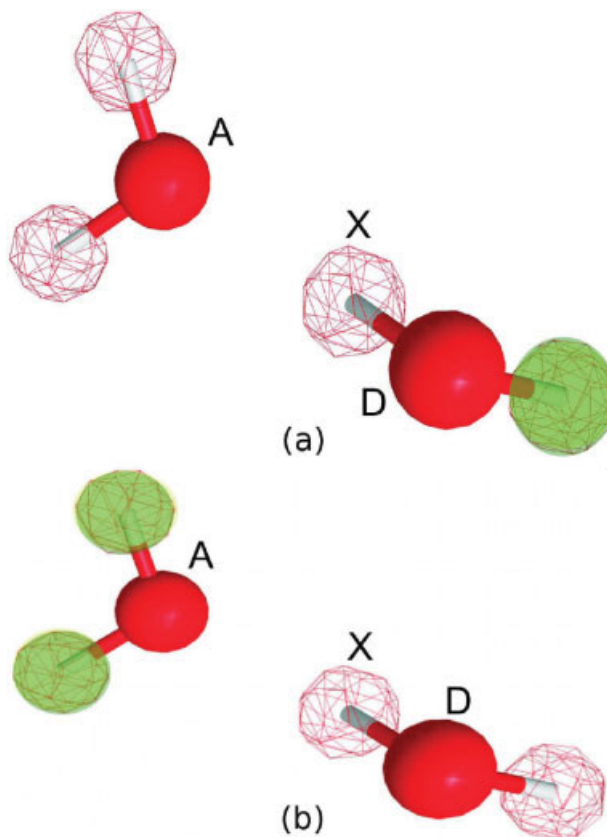[b] Conventional MO-RHF.

FIGURE 3. Schematic picture of secondary isotope effect on a water dimer. Oxygen nuclei in red are treated classically as point charges, hydrogen isotopes are treated quantum mechanically as nuclear orbitals. Colored hydrogens represent the isotopes being substituted. Figures (a) and (b) sketch the donor and acceptor secondary isotopes being substituted. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

We have investigated the donor secondary isotope effect on the hydrogen bond of a number of water dimer isotopologues. Figure 3(a) illustrates the system and the isotope being replaced (in green). R_{DA} and R_{AX} distances are summarized in Table IV These results indicate that there is a reduction in the R_{DA} and R_{AX} distances as the mass of the substituted isotope increases, which is a clear manifestation of the strengthening of the hydrogen bond. To our knowledge, these are the first NMO results of donor secondary isotope effects on water dimers. Our trends agree well with experimental [15, 16] and theoretical (BO based)[17] results.

For a final application, we have investigated the acceptor secondary isotope effect on a number of

TABLE IV

Donor secondary isotope effect on the hydrogen bond of water dimer isotopologues.

Dimer[a]	R_{DA}/Å	R_{AX}/Å
$H_2O \cdots HOH$	2.950358	1.982522
$H_2O \cdots HOD$	2.945809	1.978036
$H_2O \cdots HOT$	2.939870	1.973113
$D_2O \cdots DOH$	2.959600	2.000854
$D_2O \cdots DOD$	2.952303	1.994296
$D_2O \cdots DOT$	2.949847	1.988828
$T_2O \cdots TOH$	2.977924	2.019194
$T_2O \cdots TOD$	2.967720	2.010392
$T_2O \cdots TOT$	2.962715	2.008907
$H_2O \cdots HOH$[b]	2.980331	2.038823

Internuclear distances R_{AD} and R_{AX} at a level theory NMO-RHF[6-31G**:1s].
[a] Oxigen nuclei treated as point charges.
[b] Conventional MO-RHF.

water dimer isotopologues. Figure 3(b) illustrates the system and isotope being replaced (in green). Note that both hydrogens on the acceptor are substituted simultaneously. R_{DA} and R_{AX} distances are summarized in Table V. We observe the reduction in the R_{DA} and R_{AX} distances as the mass of the secondary hydrogens increase, this is a clear indication that there is strengthening of the hydrogen bond. To our knowledge, these are the first NMO results on acceptor secondary isotope effects on water dimers. Our trends agree well with experimental [15, 16] and theoretical (BO based)[17] results.

All the trends we presented above are in agreement with other experimental and theoretical results. However, the calculated properties such as dipole moments are still far from experimental values. These deviations are attributed mainly to the lack of electron–electron (e–e), electron–nuclear (e–n) and nuclear–nuclear (n–n) correlations of our Hartree-Fock method. For better results with have to include some kind of correlation. Recently, Nakai [3] calculated e–e, e–n, and n–n correlation energies at a NOMO/MP2 level of theory for H_2, D_2, and T_2. He found for each system that the e–e correlation was at least five times larger than e–n and 40 times larger than the n–n correlations. He concluded that the e–e and e–n correlation energies were more important than the n–n and also that both e–n and n–n correlations decreased as the mass of the isotope increased.

4. Conclusion

In this article, we presented APMO code which is a computational implementation of the NMO method at the Hartree-Fock level of theory.

We applied the APMO package to some diatomic molecules. Observed changes in the dipole moments, partial charges and internuclear distances upon isotopic substitution have demonstrated that there is an effect of the nuclear masses on the electronic structure and geometries. Our trends for diatomic systems are consistent with experimental and theoretical data.

Our studies on the primary isotope effect on hydrogen bonding confirmed the weakening of hydrogen bond with the increases of mass of bonded hydrogen as reported by other authors.

Our results on the secondary effect on hydrogen bond suggested that the hydrogen bond becomes stronger as the mass of the secondary hydrogens are increased, to our knowledge these are the first calculations of this type reported using a NMO method.

These theoretical and computational developments clearly show that the APMO code is highly suitable to study isotope effects. In contrast with other codes available in the literature, our package has been designed to treat systems containing any combination of quantum particles.

The current Hartree-Fock results show that for an accurate description of these systems we require

TABLE V

Acceptor secondary isotope effect on the hydrogen bond of water dimer isotopologues.

Dimer[a]	R_{DA}/Å	R_{AX}/Å
$H_2O \cdots HOH$	2.950358	1.982522
$D_2O \cdots HOH$	2.946483	1.982242
$T_2O \cdots HOH$	2.943447	1.980042
$H_2O \cdots DOD$	2.963213	2.001690
$D_2O \cdots DOD$	2.952303	1.994296
$T_2O \cdots DOD$	2.952067	1.992652
$H_2O \cdots TOT$	2.965376	2.007010
$D_2O \cdots TOT$	2.964583	2.006338
$T_2O \cdots TOT$	2.962715	2.005907
$H_2O \cdots HOH$[b]	2.980331	2.038823

Internuclear distances R_{AD} and R_{AX} at a level theory NMO-RHF[6-31G**:1s].
[a] Oxigen nuclei treated as point charges.
[b] Conventional MO-RHF.

the inclusion of electron–electron and electron–nucleus correlation. Implementation of the MP2 theory is currently in progress.

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