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Extension of Density Functional Theory to Nuclear Orbital plus Molecular Orbital Theory: Self-Consistent Field Calculations with the Colle–Salvetti Electron–Nucleus Correlation Functional

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Non Born–Oppenheimer self-consistent field calculations including not only electron–electron (e–e) exchange correlation but also electron–nucleus (e–n) correlation energies have been carried out. In this study, Colle–Salvetti and B3LYP functionals for the e–n correlation and e–e exchange-correlation energies are adopted. Numerical assessments confirm that the standard enthalpies of formation are well reproduced for the G2-1 set. We also apply this method to ammoniated ammonium ion ($N_2H_7{}^+$), one of the "vibrational bonding" systems, and discuss nuclear quantum effects such as the isotope effect.

The Born–Oppenheimer (BO) approximation,[1] which divides nuclear and electronic motions, is a fundamental concept in the field of quantum mechanics of atoms and molecules. The BO treatment has succeeded in accurately describing various chemical and physical phenomena. On the other hand, several attempts to construct a non-BO molecular theory have been performed since the end of 1960s.[2–12] Since the earliest non-BO treatments adopted special formulae to express nuclear wave functions, it is difficult to apply them to large systems in which nuclear quantum effects are of great importance. For example, Thomas defined the Slater protonic wave functions centered on heavier nuclei, namely, N, C, O, and F for ammonia, methane, water, and hydrogen fluoride molecules, respectively.[2–5]

Recent extensive development based on the idea of nuclear orbital (NO) in analogy to molecular orbital (MO) as the one electron wave function paves a way to widen the feasibility of non-BO theory.[13–23] The NOs and MOs, which construct the nuclear and electronic wave functions, can be simultaneously determined with comparatively less computational costs in the mean-field approximation, i.e., Hartree–Fock (HF) approximation. However, this approach has brought in a new problem: namely, not only the electron–electron (e–e) but also electron–nucleus (e–n) and nucleus–nucleus (n–n) correlation effects should be taken into account in order to achieve a highly accurate description. While state-of-the-art correlation theories have been applied to this problem,[16,19] the numerical results exhibit a slow convergence in describing the e–n correlation effect. Consequently, accurate and/or reliable descriptions of the nuclear wave function require high computational costs.

An alternative non-BO treatment is based on the Hohenberg–Kohn–Sham (HKS) density functional theory (DFT) framework.[24,25] The foundation of the non-BO DFT approach has been established by Kalia and Vashishta,[26] Capitani et al.,[27] and other researchers,[28,29] and studied from several points of view.[30–36] However, to the best of our knowledge, self-consistent field (SCF) calculations including an e–n correlation functional in the KS scheme are very limited.[34–36] Recently, the explicit formula of e–n correlation functional, which is based on the Colle–Salvetti (CS) correlation functional,[37–42] has been derived by the authors[22] and Tachikawa's group[33] independently. The main purpose of the present study is an implementation of the SCF scheme of the KS-DFT for non-BO treatment, which adopted the CS e–n correlation functional. The procedure developed in this study is called NOMO/DFT.

The organization of this paper is as follows: The next section describes the theoretical aspects of the NOMO/DFT method. Then, we assess NOMO/DFT incorporating e–e exchange-correlation and e–n correlation energies by estimating the standard enthalpies of formation for molecules and studying nuclear quantum effects in the ammoniated ammonium ion. Finally, concluding remarks are given.

Theoretical Aspects

Non-BO DFT Procedure. This section briefly explains the DFT theory in the framework of the non-BO treatment.[27,29] The total Hamiltonian in the NOMO method is given as:

$$\hat{H} = \hat{T}_{\mathrm{e}} + \hat{T}_{\mathrm{n}} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{en}} + \hat{V}_{\mathrm{nn}} \tag{1}$$

where

$$\hat{T}_{\mathrm{e}} = -\sum_{p} \frac{1}{2} \nabla(\mathbf{r}_p)^2 \equiv \sum_{p} \hat{t}_{\mathrm{e}}(\mathbf{r}_p) \tag{2}$$

$$\hat{T}_{\mathrm{n}} = -\sum_{P} \frac{1}{2m_P} \nabla(\mathbf{r}_P)^2 \equiv \sum_{P} \hat{t}_{\mathrm{n}}(\mathbf{r}_P) \tag{3}$$

$$\hat{V}_{\mathrm{ee}} = \sum_{p<q} \frac{1}{r_{pq}} \tag{4}$$

$$\hat{V}_{\mathrm{en}} = -\sum_{p,P} \frac{Z_P}{r_{pP}} \tag{5}$$

$$\hat{V}_{\mathrm{nn}} = \sum_{P<Q} \frac{Z_P Z_Q}{r_{PQ}} \tag{6}$$

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$\hat{T}_{\mathrm{e}}$ and $\hat{T}_{\mathrm{n}}$ represent the electronic and nuclear kinetic operators, respectively. $\hat{V}_{\mathrm{ee}}$, $\hat{V}_{\mathrm{en}}$, and $\hat{V}_{\mathrm{nn}}$ represent the e–e, e–n, and n–n two-particle interaction operators, respectively. Capital characters P, Q and small characters p, q indicate nuclei and electrons, respectively. m_P, Z_P, and $\{r_{pq}, r_{pP}$, and $r_{PQ}\}$ indicate the nuclear mass, nuclear charge, distances of two particles, i.e., e–e, e–n, and n–n distances, respectively. For simplicity, the discussion below is limited to the case of a single species of nucleus such as a proton or deuteron. The extension to the general case is straightforward. Thus, the nuclear mass and nuclear charge are simply denoted by m and Z, respectively. The wave function Ψ in the NOMO method is given by

$$\Psi(\{\mathbf{r}_p, \sigma_p\}, \{\mathbf{R}_P, \lambda_P\}) = \Phi^{\mathrm{e}}(\{\mathbf{r}_p, \sigma_p\}) \cdot \Phi^{\mathrm{n}}(\{\mathbf{R}_P, \lambda_P\}) \tag{7}$$

where $\{\mathbf{r}_p, \sigma_p\}$ and $\{\mathbf{R}_P, \lambda_P\}$ indicate the electronic coordinates and their spin functions and the corresponding ones of the nucleus, respectively. The electron and nucleus densities ($\rho_{\mathrm{e}}^{\sigma}$ and $\rho_{\mathrm{n}}^{\lambda}$) in the DFT approach of the NOMO method are given as:

$$\begin{aligned}\rho_{\mathrm{e}}^{\sigma}(\mathbf{r}_1) = \int &|\Psi(\{\mathbf{r}_p, \sigma_p\}, \{\mathbf{R}_P, \lambda_P\})|^2 \\ &\times \mathrm{d}\mathbf{r}_2\mathrm{d}\sigma_2\mathrm{d}\mathbf{r}_3\mathrm{d}\sigma_3 \ldots \mathrm{d}\mathbf{R}_1\mathrm{d}\lambda_1\mathrm{d}\mathbf{R}_2\mathrm{d}\lambda_2 \ldots\end{aligned} \tag{8}$$

$$\begin{aligned}\rho_{\mathrm{n}}^{\lambda}(\mathbf{R}_1) = \int &|\Psi(\{\mathbf{r}_p, \sigma_p\}, \{\mathbf{R}_P, \lambda_P\})|^2 \\ &\times \mathrm{d}\mathbf{r}_1\mathrm{d}\sigma_1\mathrm{d}\mathbf{r}_2\mathrm{d}\sigma_2 \ldots \mathrm{d}\mathbf{R}_2\mathrm{d}\lambda_2\mathrm{d}\mathbf{R}_3\mathrm{d}\lambda_3 \ldots\end{aligned} \tag{9}$$

The ground-state energy in the NOMO/DFT approach is defined as:

$$E[\{\rho_{\mathrm{e}}^{\sigma}\}, \{\rho_{\mathrm{n}}^{\lambda}\}] = \min\langle\Psi_{\{\rho_{\mathrm{e}}^{\sigma}\},\{\rho_{\mathrm{n}}^{\lambda}\}}|\hat{H}|\Psi_{\{\rho_{\mathrm{e}}^{\sigma}\},\{\rho_{\mathrm{n}}^{\lambda}\}}\rangle \tag{10}$$

Equation 10 searches all wave functions in the domain of the NOMO Hamiltonian $\hat{H}$ defined in eq 1 under an appropriate constraint such as symmetries.

Kohn–Sham equations in the NOMO/DFT approach can be derived by using one-particle wave functions, $\{\varphi_p^{\sigma}\}$ and $\{\varphi_P^{\lambda}\}$:

$$(\hat{t}_{\mathrm{e}}(\mathbf{r}) + \hat{\nu}_{\mathrm{e}}^{\mathrm{eff},\sigma}(\mathbf{r}, \mathbf{R}))\phi_p^{\sigma}(\mathbf{r}) = \varepsilon_p\phi_p^{\sigma}(\mathbf{r}) \tag{11}$$

$$(\hat{t}_{\mathrm{n}}(\mathbf{R}) + \hat{\nu}_{\mathrm{n}}^{\mathrm{eff},\lambda}(\mathbf{r}, \mathbf{R}))\phi_P^{\lambda}(\mathbf{R}) = \varepsilon_P\phi_P^{\lambda}(\mathbf{R}) \tag{12}$$

$\hat{\nu}_{\mathrm{e}}^{\mathrm{eff},\sigma}(\mathbf{r}, \mathbf{R})$ and $\hat{\nu}_{\mathrm{n}}^{\mathrm{eff},\lambda}(\mathbf{r}, \mathbf{R})$ are the effective potential operators of electrons and nuclei:

$$\hat{\nu}_{\mathrm{e}}^{\mathrm{eff},\sigma}(\mathbf{r}) = \hat{\nu}(\mathbf{r}, \mathbf{R}) + \hat{\nu}_{\mathrm{e}}^{\mathrm{xc},\sigma}(\mathbf{r}) \tag{13}$$

$$\hat{\nu}_{\mathrm{n}}^{\mathrm{eff},\lambda}(\mathbf{R}) = -Z\hat{\nu}(\mathbf{r}, \mathbf{R}) + \hat{\nu}_{\mathrm{n}}^{\mathrm{xc},\lambda}(\mathbf{R}) \tag{14}$$

where $\hat{\nu}(\mathbf{r}, \mathbf{R})$ is the classical Coulomb potential independent of spins indices and is given as:

$$\hat{\nu}(\mathbf{r}, \mathbf{R}) = \sum_{\sigma}\int \mathrm{d}\mathbf{r}' \frac{\rho_{\mathrm{e}}^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{\lambda}\int \mathrm{d}\mathbf{R}' \frac{Z\rho_{\mathrm{n}}^{\lambda}(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} \tag{15}$$

The exchange-correlation energy E^{xc} is given as:

$$\begin{aligned}E^{\mathrm{xc}}[\{\rho_{\mathrm{e}}^{\sigma}\}, \{\rho_{\mathrm{n}}^{\lambda}\}] = {}& E_{\mathrm{ee}}^{\mathrm{xc}}[\{\rho_{\mathrm{e}}^{\sigma}\}] + E_{\mathrm{nn}}^{\mathrm{xc}}[\{\rho_{\mathrm{n}}^{\lambda}\}] \\ &+ E_{\mathrm{en}}^{\mathrm{c}}[\{\rho_{\mathrm{e}}^{\sigma}\}, \{\rho_{\mathrm{n}}^{\lambda}\}]\end{aligned} \tag{16}$$

The first, second, and third terms on the right-hand side in eq 16 are the e–e and n–n exchange correlation, and e–n correlation energies, respectively. The third term of eq 16 is independent of the electron and nucleus spins and is given as:

$$E_{\mathrm{en}}^{\mathrm{c}}[\{\rho_{\mathrm{e}}^{\sigma}\}, \{\rho_{\alpha}^{\lambda}\}] = E_{\mathrm{en}}^{\mathrm{c}}[\rho_{\mathrm{e}}, \rho_{\mathrm{n}}] \tag{17}$$

where

$$\rho_{\mathrm{e}} = \sum_{\sigma}\rho_{\mathrm{e}}^{\sigma} \tag{18}$$

$$\rho_{\mathrm{n}} = \sum_{\lambda}\rho_{\mathrm{n}}^{\lambda} \tag{19}$$

$\hat{\nu}_{\mathrm{e}}^{\mathrm{xc}}(\mathbf{r})$ and $\hat{\nu}_{\mathrm{n}}^{\mathrm{xc},\lambda}(\mathbf{r})$ are the exchange-correlation potentials given by differentiating the exchange-correlation energy E^{xc} with respect to electron and nucleus densities:

$$\hat{\nu}_{\mathrm{e}}^{\mathrm{xc},\sigma}(\mathbf{r}) = \frac{\mathrm{d}E_{\mathrm{ee}}^{\mathrm{xc}}[\{\rho_{\mathrm{e}}^{\sigma'}\}]}{\mathrm{d}\rho_{\mathrm{e}}^{\sigma}} + \frac{\mathrm{d}E_{\mathrm{en}}^{\mathrm{c}}[\rho_{\mathrm{e}}, \rho_{\mathrm{n}}]}{\mathrm{d}\rho_{\mathrm{e}}^{\sigma}} = \hat{\nu}_{\mathrm{ee}}^{\mathrm{xc},\sigma} + \hat{\nu}_{\mathrm{en}}^{\mathrm{c},\sigma} \tag{20}$$

$$\hat{\nu}_{\mathrm{n}}^{\mathrm{xc},\lambda}(\mathbf{r}) = \frac{\mathrm{d}E_{\mathrm{nn}}^{\mathrm{xc}}[\{\rho_{\mathrm{n}}^{\lambda}\}]}{\mathrm{d}\rho_{\mathrm{n}}^{\lambda}} + \frac{\mathrm{d}E_{\mathrm{en}}^{\mathrm{c}}[\rho_{\mathrm{e}}, \rho_{\mathrm{n}}]}{\mathrm{d}\rho_{\mathrm{n}}^{\lambda}} = \hat{\nu}_{\mathrm{nn}}^{\mathrm{xc},\lambda} + \hat{\nu}_{\mathrm{ne}}^{\mathrm{c},\lambda} \tag{21}$$

In eqs 20 and 21, the first term on the right-hand side is the e–e and n–n exchange-correlation potentials, respectively, and the second term e–n correlation potential operator.

Exchange-Correlation Functionals. This study adopts the CS functional for the e–n correlation energy $E_{\mathrm{en}}^{\mathrm{c}}$, which was developed previously.[22] In the CS e–n correlation energy, the denominator is approximated by the exponential form in order to eliminate the singularity. The final expression of $E_{\mathrm{en}}^{\mathrm{c}}$ is given as:

$$\begin{aligned}E_{\mathrm{en}}^{\mathrm{c}} = \sum_{\alpha'}\int &\mathrm{d}\mathbf{R}\rho_{\mathrm{e}}(\mathbf{R})\rho_{\alpha'}(\mathbf{R}) \\ &\times \frac{\pi Z_{\alpha'}^2[(24 + (-9 + 2\sqrt{2})\pi)Z_{\alpha'} + 4(-4 + \pi)\sqrt{\pi}\beta]}{2\pi\beta^4 \exp\left[\dfrac{4Z_{\alpha'}(Z_{\alpha'} - \sqrt{\pi}\beta)}{\pi\beta^2}\right]}\end{aligned} \tag{22}$$

where

$$\rho_{\mathrm{e}}(\mathbf{R}) = \sum_{\sigma}\rho_{\mathrm{e}}^{\sigma}(\mathbf{R}) \tag{23}$$

$$\beta(\mathbf{R}) = q\rho_{\mathrm{e}}(\mathbf{R})^{1/3} \tag{24}$$

In eq 24, a parameter q needs to be determined. Since the e–n correlation lengths seem to depend on atomic numbers, an atom dependent parameter q for the CS correction is adopted in this study.

The potential $\hat{\nu}_{\mathrm{en}}^{\mathrm{c},\sigma}$ in eq 1 is obtained by differentiating eq 4 with respect to the electron density $\rho_{\mathrm{e}}^{\sigma}(\mathbf{r})$:

$$\begin{aligned}\hat{\nu}_{\mathrm{en}}^{\mathrm{c},\sigma} &= \frac{\mathrm{d}E_{\mathrm{en}}^{\mathrm{c}}}{\mathrm{d}\rho_{\mathrm{e}}^{\sigma}} = \frac{\partial E_{\mathrm{en}}^{\mathrm{c}}}{\partial\rho_{\mathrm{e}}} \cdot \frac{\partial\rho_{\mathrm{e}}}{\partial\rho_{\mathrm{e}}^{\sigma}} \\ &= \sum_{\alpha'}\rho_{\alpha'}(\mathbf{R}) \\ &\quad \times \frac{\pi Z_{\alpha'}^2[(24 + (-9 + 2\sqrt{2})\pi)Z_{\alpha'} + 4(-4 + \pi)\sqrt{\pi}\beta]}{2\pi\beta^4 \exp\left[\dfrac{4Z_{\alpha'}(Z_{\alpha'} - \sqrt{\pi}\beta)}{\pi\beta^2}\right]} \\ &\quad + \frac{\partial E_{\mathrm{en}}^{\mathrm{c}}}{\partial\beta} \cdot \frac{\partial\beta}{\partial\rho_{\mathrm{e}}} \cdot \frac{\partial\rho_{\mathrm{e}}}{\partial\rho_{\mathrm{e}}^{\sigma}}\end{aligned} \tag{25}$$

where

$$\begin{aligned}\frac{\partial E_{\mathrm{en}}^{\mathrm{c}}}{\partial\beta} = {}&\sum_{\alpha'}2\rho_{\mathrm{e}}(\mathbf{R})\rho_{\alpha'}(\mathbf{R}) \Bigg/ \left(2\pi\beta^7 \exp\left[\frac{4Z_{\alpha'}(Z_{\alpha'} - \sqrt{\pi}\beta)}{\pi\beta^2}\right]\right) \\ &\times \{\pi Z_{\alpha'}^2[2(24 + (-9 + 2\sqrt{2})\pi)Z_{\alpha'}^3 \\ &+ (-56 + (17 - 2\sqrt{2})\pi)\sqrt{\pi}\beta Z_{\alpha'}^2 \\ &+ (-8 + (5 - 2\sqrt{2})\pi)\sqrt{\pi}\beta^2 - 3(-4 + \pi)\pi^{3/2}\beta^3]\}\end{aligned} \tag{26}$$

$$\frac{\partial\beta}{\partial\rho_{\mathrm{e}}} \cdot \frac{\partial\rho_{\mathrm{e}}}{\partial\rho_{\mathrm{e}}^{\sigma}} = \frac{1}{3}q\rho_{\mathrm{e}}(\mathbf{R})^{-2/3} \tag{27}$$

Similarly, the potential $\hat{\nu}_{\mathrm{ne},\alpha}^{\mathrm{c}}$ in eq 2 is obtained by differentiating eq 4 with respect to the nucleus density $\rho_{\alpha}(\mathbf{R})$:

$$\begin{aligned}\hat{v}^{\mathrm{c}}_{\mathrm{ne},\alpha} &= \frac{dE^{\mathrm{c}}_{\mathrm{en}}}{d\rho_\alpha} \\ &= \rho_{\mathrm{e}}(\mathbf{R})\frac{\pi Z_\alpha^2[(24+(-9+2\sqrt{2})\pi)Z_\alpha+4(-4+\pi)\sqrt{\pi}\beta]}{2\pi\beta^4\exp\left[\dfrac{4Z_\alpha(Z_\alpha-\sqrt{\pi}\beta)}{\pi\beta^2}\right]}\end{aligned} \tag{28}$$

In this study, the conventional B3LYP[43] used in the BO calculations is adopted for the e–e exchange-correlation potential. The n–n exchange-correlation energy is not considered in this study because it is in general, negligibly small as shown in the NOMO/MP2 method in comparison with the e–e and e–n correlation energies.[19] Since the n–n exchange-correlation might be important for specific systems, it will be incorporated and assessed in the near future.

Results and Discussion

Numerical Applications. We determine values of parameters q in the CS e–n functional and assess them for the G2-1 set[44] and the ammoniated ammonium ion ($N_2X_7{}^+$) for X = H, D, and T. The cc-pVTZ[45] electronic basis set is used for the parameter determination and the G2-1 set, and the aug-cc-pVTZ[46] electronic basis set is used for $N_2X_7{}^+$. For nuclei, we adopt primitive (7s7p7d) basis functions of which orbital exponents are determined by means of the even-tempered scheme.[14,47] The Euler–Maclaurin and Gauss–Legendre schemes are adopted for radial and angular integrations for the e–e and e–n functionals. The numbers of radial (r) and angular (θ, φ) grid points in the polar coordinate are 96, 12, and 24, respectively. The orbital centers of the nuclear basis functions are set to be the location of the classical nuclei. The experimental distances of diatomic molecules for the parameter determination are used.[48] The geometrical parameters for the G2-1 set are fully optimized at the B3LYP/6-31G(2df,p) level and the geometrical parameters for $N_2H_7{}^+$ are fully optimized at the B3LYP/aug-cc-pVTZ level. All calculations are carried out by a modified version of the GAMESS program.[49]

Determination of e–n Correlation Length Parameter *q*. This subsection explains a procedure for determining the parameter q included in the CS functional as formulated in the previous subsection. The B3LYP functional is adopted for the e–e correlation in both BO and NOMO calculations. The parameter q of He, Be, Ne, and Ar are determined to reproduce BO energies of the corresponding atoms. The parameters q of the first-, second-, and third-row elements except for He, Be, Ne, and Ar are determined so that the total energies for homonuclear diatomic molecules in the NOMO treatment coincide with those of the conventional BO results, which contains the zero-point energies up to the third term:[48]

$$G(\nu) = \omega_e\left(\nu+\frac{1}{2}\right) - \omega_e\chi_e\left(\nu+\frac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\frac{1}{2}\right)^3 \tag{29}$$

Table 1 shows the determined parameters q. For reference, values q^{atom} optimized for atoms in Ref. 22 are also shown. The differences from q^{mol} are shown in parentheses. The values of the parameters q^{mol} as well as q^{atom} gradually increase with respect to atomic numbers from 4.8330 to 7.4727. Since the parameter q corresponds to the inverse of correlation length, the lighter atoms possess a longer correlation length. The values of q^{mol} for H, D, and T are slightly smaller than those of q^{atom}, while those for Li–Ar except for He, Be, Ne, and Ar are slightly larger.

Table 1. Parameters q in the Colle–Salvetti Electron–Nucleus Correlation Functional in the NOMO Treatment

	q^{atom}	q^{mol}
H	4.9448 (0.1119)	4.8330
D	5.4618 (0.1255)	5.3363
T	5.7911 (0.1346)	5.6565
^{4}He	5.6499 (0.0000)	5.6499
^{7}Li	6.0058 (−0.0039)	6.0097
^{9}Be	6.1507 (0.0000)	6.1507
^{11}B	6.2945 (−0.0114)	6.3059
^{12}C	6.3504 (−0.0134)	6.3639
^{14}N	6.4816 (−0.0123)	6.4938
^{16}O	6.5981 (−0.0069)	6.6050
^{19}F	6.7613 (−0.0022)	6.7636
^{20}Ne	6.8035 (0.0000)	6.8035
^{23}Na	6.9299 (−0.0002)	6.9301
^{24}Mg	6.9528 (−0.0001)	6.9529
^{27}Al	7.0679 (−0.0007)	7.0686
^{28}Si	7.0997 (−0.0010)	7.1007
^{31}P	7.2043 (−0.0014)	7.2057
^{32}S	7.2329 (−0.0011)	7.2339
^{35}Cl	7.3277 (−0.0007)	7.3284
^{40}Ar	7.4727 (0.0000)	7.4727

Standard Enthalpies of Formation for the G2-1 Set. Using the parameters q^{mol} listed in Table 1, we evaluate standard enthalpies of formation of the molecules in the G2-1 set. The energy deviations of the standard enthalpies of formation by the BO/HF, BO/DFT, NOMO/HF, and NOMO/DFT methods are shown in Table 2. Note that BO/DFT and NOMO/DFT adopt the B3LYP and B3LYP + CS functionals, respectively. The experimental values are taken from Ref. 50. The standard enthalpies of formation for BO/HF and BO/DFT are calculated by summing the total energy and ZPE estimated by BO/DFT with 6-31G(2df,p) using a scaling factor 0.9854,[50,51] while the standard enthalpies of formation can be directly evaluated as the total energy of the NOMO method. The bottom rows of Table 2 list statistical data, i.e., the mean error (ME), root mean square (RMS), mean absolute error (MAE), and positive and negative maximum deviations (Max. (+) and Max. (−)). The values of Max. (+) are 19.15 and 12.76 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) for SO_2 in BO/DFT and NOMO/DFT, while those are 172.70 and 156.20 kcal mol^{-1} for N_2H_4 in BO/HF and NOMO/HF. The values of Max. (−) are −0.34, −7.75, and −0.63 kcal mol^{-1} for BeH in BO/HF, BO/DFT, and NOMO/HF, while that is −17.42 kcal mol^{-1} for N_2H_4 in NOMO/DFT. The values of MAE are 76.48 and 71.18 kcal mol^{-1} for BO/HF and NOMO/HF, which shows that the standard enthalpies of formation of these methods are severely underestimated, probably because these methods lack the correlation effects. This trend is also observed in ME and RMS. On the other hand, NOMO/DFT produces the small MAE 4.77 kcal mol^{-1} for the G2-1 set, which is close to that of BO/DFT (2.91 kcal mol^{-1}). The assessment of the G2-1 set reveals that the consideration of the e–e and e–n correlation effects drastically reduces the deviation in comparison with NOMO/HF.

Table 2. Deviations of Standard Enthalpies of Formation in the G2-1 Set (in kcal mol^{-1})

Molecule	BO/HF	BO/DFT	NOMO/HF	NOMO/DFT	Exptl.
BeH	−0.34	−7.75	−0.63	−7.54	81.7
C_2H_2	112.37	3.26	99.22	−8.74	54.2
C_2H_4	135.78	1.09	119.26	−13.52	12.5
C_2H_6	161.47	1.50	140.87	−16.54	−20.1
CH_2 (singlet)	54.90	0.92	53.09	0.23	102.8
CH_2 (triplet)	35.71	−1.47	31.78	−4.56	93.7
CH_3Cl	98.78	3.11	87.93	−6.55	−19.6
CH_3OH	144.43	3.03	128.92	−10.93	−48.0
CH_3SH	124.53	3.79	111.53	−7.53	−5.5
CH_3	64.98	−1.94	58.88	−6.66	35.0
CH_4	92.36	−0.38	82.09	−8.90	−17.9
CH	27.53	−1.04	27.76	−0.27	142.5
CN	91.82	3.00	85.53	−2.29	104.9
CO_2	143.28	2.24	130.80	−10.04	−94.1
CO	85.46	4.55	80.53	−0.35	−26.4
CS	76.02	7.25	73.06	4.32	66.9
Cl_2	40.42	4.18	39.47	3.23	0.0
ClF	55.23	2.70	53.68	1.17	−13.2
ClO	60.25	1.11	58.52	−0.62	24.2
F_2	73.30	0.67	71.68	−0.94	0.0
H_2CO	117.08	1.42	107.24	−7.65	−26.0
H_2O_2	134.86	3.51	125.05	−5.61	−32.5
H_2O	78.36	4.31	72.30	−1.03	−57.8
H_2S	54.45	2.02	51.03	−0.64	−4.9
HCN	114.30	0.61	104.25	−8.71	31.5
HCO	97.06	−0.80	90.02	−7.49	10.0
HCl	30.18	2.28	28.20	0.69	−22.1
HF	45.10	3.79	41.96	0.83	−65.1
HOCl	87.81	3.76	82.54	−1.16	−17.8
Li_2	20.46	3.68	20.03	3.25	51.6
LiF	47.96	1.81	45.44	−0.81	−80.1
LiH	23.94	−0.25	23.55	0.05	33.3
N_2H_4	172.70	−2.35	156.20	−17.42	22.8
N_2	114.19	0.45	108.82	−4.78	0.0
NH_2	65.41	−4.45	62.01	−6.98	45.1
NH_3	98.75	−0.57	90.13	−8.18	−11.0
NH	33.01	−3.49	32.61	−3.52	85.2
NO	99.76	−1.48	95.28	−5.96	21.6
Na_2	17.94	0.26	17.74	0.10	34.0
NaCl	28.85	6.83	27.76	5.69	−43.6
O_2	87.40	−3.22	83.83	−6.85	0.0
OH	38.92	−0.30	37.18	−1.74	9.4
OS	74.10	2.35	71.51	−0.28	1.2
P_2	81.37	4.02	79.65	2.30	34.3
PH_2	45.64	−4.19	44.15	−4.84	33.1
PH_3	71.53	−0.78	67.20	−3.96	1.3
S_2	53.02	1.05	51.57	−0.41	30.7
SO_2	161.99	19.15	155.61	12.76	−71.0
Si_2H_6	116.42	3.29	106.56	−4.07	19.1
Si_2	48.97	6.27	47.97	5.18	139.9
SiH_2 (singlet)	42.09	−1.09	41.69	−0.46	65.2
SiH_2 (triplet)	25.43	−1.48	23.54	−2.61	86.2
SiH_3	46.73	−1.67	43.55	−3.63	47.9
SiH_4	67.66	0.23	62.75	−2.99	8.2
SiO	84.85	7.99	81.86	4.96	−24.6
ME	76.48	1.50	71.18	−3.15	—
MAE	76.50	2.91	71.20	4.77	—
RMS	86.67	4.14	80.02	6.33	—
Max. (+)	172.70	19.15	156.20	12.76	—
Max. (−)	−0.34	−7.75	−0.63	−17.42	—

Vibrational Bonded Systems: Ammoniated Ammonium Ion. Several groups[52–62] have investigated a new type of chemical bonding "vibrational bonding," which is caused by the fact that the potential energy surface has no minima but the bound states are formed because of the zero-point energy and low energy barrier. In this study, we treat an illustrative example of the vibrational bonding: ammoniated ammonium ion $N_2H_7^+$. This system has been investigated extensively.[55–62]

Figure 1 shows a schematic potential energy curve (PEC) with respect to the distance between NH_3 and a proton. The structure of $N_2H_7^+$ observed experimentally is D_{3d},[55] in which the proton is located at the middle of a NH_3 dimer as shown in Figure 1. On the other hand, the optimized structure of $N_2H_7^+$ calculated by BO/DFT is C_{3v} structure, in which the proton is closer to one of the NH_3 in the dimer.

Table 3 shows the total energies of the C_{3v} and D_{3d} structures by the BO/HF and BO/DFT methods. The values of ΔE for BO/HF and BO/DFT are -3.86 and $-0.65\,\mathrm{kcal\,mol^{-1}}$, which indicates that the C_{3v} structure is more stable. This result is not consistent with the experimental results although ΔE for BO/DFT is small.

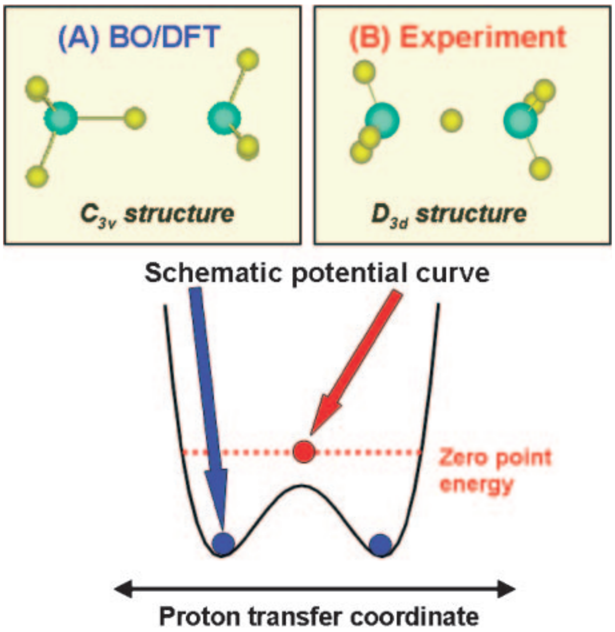

Figure 1. Structures and schematic energy diagram for the vibrational bonding system, $N_2H_7^+$. (A) BO/DFT and (B) NOMO/DFT refer to the structures optimized with and without nuclear quantum effects, respectively.

Table 4 lists total energies and symmetries of $N_2X_7^+$ (X = H, D, and T) computed by NOMO methods. All X atoms are treated quantum mechanically. In order to clarify roles of functionals, four different combinations of functionals are adopted: e–e E_x^{B3LYP}, e–e E_{xc}^{B3LYP}, e–e E_x^{B3LYP} + e–n E_{CS}, e–e E_{xc}^{B3LYP} + e–n E_{CS}. Noted that e–e E_x^{B3LYP} and e–e E_{xc}^{B3LYP} represent B3LYP e–e exchange and B3LYP e–e exchange-correlation functionals and E_{CS} is the CS e–n correlation functional. All calculations were carried out self-consistently. The NOMO/HF method is performed for comparison. The symmetries of the most stable $N_2X_7^+$ species are also shown. The differences from values of X = H are represented in parentheses.

Let us discuss the case of X = H. The NOMO/HF and NOMO/DFT with E_x^{B3LYP} and E_{xc}^{B3LYP} provide higher total energies in comparison of the BO/B3LYP energy. However, NOMO/DFT with E_{xc}^{B3LYP} reproduces the experimental symmetry without e–n correlation functional although NOMO/HF and NOMO/DFT with E_x^{B3LYP} do not. This indicates that the e–e correlation functional plays an important role in determining the stable structure. NOMO/DFT with $E_x^{\mathrm{B3LYP}} + E_{\mathrm{CS}}$ and $E_{xc}^{\mathrm{B3LYP}} + E_{\mathrm{CS}}$ provides reasonable total energies closer to the BO/B3LYP energy because of the consideration of e–n correlation energies. The inclusion of E_{CS} permits us a quantitative discussion for non-BO systems. Only the combination of E_{xc}^{B3LYP} and E_{CS} can reproduce the experimental symmetry with the reasonable total energy. Thus, NOMO/DFT needs E_{xc}^{B3LYP} and E_{CS} functionals for quantitative discussion of non-BO effects.

Next, we discuss the isotope effects of X = H, D, and T. NOMO/DFT with E_x^{B3LYP} and $E_x^{\mathrm{B3LYP}} + E_{\mathrm{CS}}$ do not change the stable structure: C_{3v} structure. On the other hand, the stable structure obtained by NOMO/DFT with E_{xc}^{B3LYP} and $E_{xc}^{\mathrm{B3LYP}} + E_{\mathrm{CS}}$ changes D_{3d} to C_{3v} structure as X becomes heavier. This is consistent with the result of BO/DFT with E_{xc}^{B3LYP}. The decline of the zero point energy makes it impossible for the X^+ atom to be located at the center of NX_3 dimer. This result demonstrates that isotope effects possibly change stable structures of $N_2X_7^+$ for X = H, D, and T.

Table 3. Total Energies of C_{3v} and D_{3d} Structures of $N_2H_7^+$

Method	Structure		$\Delta\varepsilon$ a)
	C_{3v}	D_{3d}	
BO/HF	−112.8213	−112.8151	−3.86
BO/DFT(B3LYP)	−113.4861	−113.4851	−0.65

a) $\Delta E = E(C_{3v}) - E(D_{3d})$ in $\mathrm{kcal\,mol^{-1}}$.

Table 4. Total Energies (in hartree) and Structure Symmetries for $N_2X_7^+$ for X = H, D, and T

Method	Functional		X = H		X = D		X = T	
	e–e	e–n	Energy	Symmetry	Energy	Symmetry	Energy	Symmetry
NOMO/HF	E_x^{HF}	—	−111.1656	C_{3v}	−111.2434 (−0.0779)	C_{3v}	−111.2789 (−0.1133)	C_{3v}
NOMO/DFT	E_x^{B3LYP}	—	−111.0701	C_{3v}	−111.1474 (−0.0773)	C_{3v}	−111.1826 (−0.1125)	C_{3v}
	E_{xc}^{B3LYP}	—	−111.8305	D_{3d}	−111.9079 (−0.0774)	D_{3d}	−111.9433 (−0.1128)	C_{3v}
	E_x^{B3LYP}	E_{CS}	−112.7013	C_{3v}	−112.7082 (−0.0069)	C_{3v}	−112.7112 (−0.0099)	C_{3v}
	E_{xc}^{B3LYP}	E_{CS}	−113.4616	D_{3d}	−113.4687 (−0.0071)	D_{3d}	−113.4719 (−0.0103)	C_{3v}

Concluding Remarks

We have performed non-BO SCF calculations including the newly developed CS e–n correlation and e–e exchange-correlation functionals. The NOMO/DFT method succeeds in providing 4.77 kcal mol^{-1} of MAE for the G2-1 set, which is close to chemical accuracy. We have investigated $N_2H_7^+$ by NOMO/DFT and reproduced the vibrational bonding structure with D_{3d} symmetry, which is consistent with the experiment. We have also examined the isotope effects by substituting H with D and T, and demonstrated that C_{3v} structure may be more stable for $N_2T_7^+$. The numerical assessment and application reveal that the NOMO/DFT method is a useful alternative for treating the nuclear quantum effects.

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