Diagonal Born-Oppenheimer Corrections within the Nuclear-Electronic Orbital Framework

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Abstract

The nuclear-electronic orbital (NEO) method treats specified nuclei, typically protons, quantum mechanically on the same level as the electrons. This approach invokes the Born-Oppenheimer separation between the quantum and classical nuclei, as well as the conventional separation between the electrons and classical nuclei. To test the validity of this additional adiabatic approximation, herein the diagonal Born-Oppenheimer correction (DBOC) within the NEO framework is derived, analyzed, and calculated numerically for a set of eight molecules. Inclusion of the NEO DBOC is found to change the equilibrium bond lengths by only 10^{-4} Å and the heavy atom vibrational stretching frequencies by ~1 – 2 cm^{-1} per quantum proton bonded to an atom participating in the vibrational mode. These results imply that the DBOC does not significantly impact molecular properties computed with the NEO approach. Understanding the physical characteristics and quantitative contributions of the DBOC has broad implications for applications of multicomponent density functional theory and wavefunction methods.

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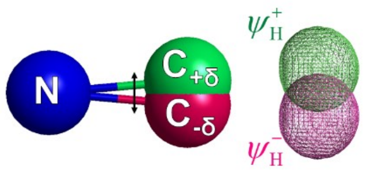

Nuclear quantum effects are manifested by phenomena such as zero-point energy, vibrational excitations, and hydrogen tunneling. Moreover, non-Born-Oppenheimer effects are significant in a wide range of chemical and biological processes, including those involving proton-coupled electron transfer.[1] Multicomponent methods, where more than one type of particle is treated quantum mechanically, have been developed to include nuclear quantum effects as well as some non-Born-Oppenheimer effects in quantum chemistry calculations.[2-5] A computationally tractable multicomponent method is the nuclear-electronic orbital (NEO) method.[5] The NEO method differs from conventional electronic structure methods in that specified nuclei, typically key protons, are treated quantum mechanically on the same level as the electrons, avoiding the Born-Oppenheimer separation between the specified nuclei and the electrons. Popular conventional electronic methods such as Hartree-Fock theory, density functional theory (DFT), or coupled cluster theory with single and double excitations (CCSD) have been adapted to the NEO framework in the form of NEO-HF, NEO-DFT, and NEO-CCSD, respectively.[5-9]

In the NEO approach, the system is divided into electrons, quantum nuclei, and other nuclei, which are typically denoted classical nuclei for simplicity, although they may be treated quantum mechanically in a different manner. The electrons and quantum nuclei are treated on the same level using molecular orbital techniques, and at least two classical nuclei are required to avoid difficulties with translations and rotations. The NEO potential energy surface depends on only the coordinates of the classical nuclei, and each point on this potential energy surface is determined by solving the time-independent Schrödinger equation for the electrons and quantum nuclei with fixed classical nuclei. Thus, at the core of the NEO method is the Born-Oppenheimer separation between the classical nuclei and the subsystem consisting of the electrons and quantum nuclei. In other words, the electrons and quantum nuclei are assumed to respond instantaneously to the motion of the classical nuclei. Analogous to conventional electronic structure calculations,[10-13] the diagonal Born-Oppenheimer corrections (DBOCs) can be computed within the NEO framework and added to the NEO potential energy surface to account for the most significant non-Born-Oppenheimer effects. The magnitudes of these terms are related to the ratio of the masses of the two types of particles, leading to the expectation that the DBOCs are significantly larger for protons relative to other nuclei than for electrons relative to protons. The objective of this Letter is to derive the equations for the NEO DBOCs and to compute them for a set of eight molecules with varying numbers of quantum protons, analyzing their magnitudes and impact on the NEO potential energy surfaces.

The adiabatic approximation for the total wavefunction within the NEO-HF and NEO-DFT frameworks is

$$\begin{aligned}\Psi &= \psi_{\mathrm{c}}(\mathbf{R})\psi_{\mathrm{NEO}}(\mathbf{r}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}};\mathbf{R}) \\ &= \psi_{\mathrm{c}}(\mathbf{R})\psi_{\mathrm{e}}(\mathbf{r}_{\mathrm{e}};\mathbf{R})\psi_{\mathrm{p}}(\mathbf{r}_{\mathrm{p}};\mathbf{R})\end{aligned} \tag{1}$$

where $\mathbf{r}_{\mathrm{e}}$, $\mathbf{r}_{\mathrm{p}}$, and $\mathbf{R}$ denote the collective coordinates of the electrons, quantum protons, and classical nuclei, respectively, and $\psi_{\mathrm{e}}(\mathbf{r}_{\mathrm{e}};\mathbf{R})$, $\psi_{\mathrm{p}}(\mathbf{r}_{\mathrm{p}};\mathbf{R})$, and $\psi_{\mathrm{c}}(\mathbf{R})$ denote the wavefunctions associated with the electrons, quantum protons, and “classical” nuclei, respectively. Here $\psi_{\mathrm{NEO}}(\mathbf{r}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}};\mathbf{R})$ is the NEO wavefunction satisfying

$$H_{\mathrm{NEO}}\psi_{\mathrm{NEO}}(\mathbf{r}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}};\mathbf{R}) = E_{\mathrm{NEO}}(\mathbf{R})\psi_{\mathrm{NEO}}(\mathbf{r}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}};\mathbf{R}) \tag{2}$$

where the NEO Hamiltonian includes the kinetic energies of the electrons and quantum protons but not the kinetic energy of the classical nuclei. The second equality in Eq. (1) is valid only for

NEO wavefunctions of the form $\psi_{\mathrm{NEO}}\left(\mathbf{r}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}};\mathbf{R}\right)=\psi_{\mathrm{e}}\left(\mathbf{r}_{\mathrm{e}};\mathbf{R}\right)\psi_{\mathrm{p}}\left(\mathbf{r}_{\mathrm{p}};\mathbf{R}\right)$, as for NEO-HF and NEO-DFT. Furthermore, although the quantum nuclei are assumed to be protons, the expressions derived herein are valid for other types of quantum nuclei as well.

The variational optimization of $\psi_{\mathrm{c}}\left(\mathbf{R}\right)$ leads to the following equation for the "classical" nuclei

$$\left[-\frac{1}{2}\sum_{I}\frac{1}{M_I}\nabla_I^2-\left\langle\psi_{\mathrm{e}}\psi_{\mathrm{p}}\left|\frac{1}{2}\sum_{I}\frac{1}{M_I}\nabla_I^2(\psi_{\mathrm{e}}\psi_{\mathrm{p}})\right.\right\rangle+E_{\mathrm{NEO}}\left(\mathbf{R}\right)\right]\psi_{\mathrm{c}}=E\psi_{\mathrm{c}} \tag{3}$$

where the summations are over all "classical" nuclei, which have masses M_I. The Born-Oppenheimer NEO potential energy surface is $E_{\mathrm{NEO}}\left(\mathbf{R}\right)$, and the NEO DBOC is the second term on the left side of Eq. (3). The NEO DBOC can be expressed as

$$\begin{aligned}E_{\mathrm{DBOC}}&=-\sum_{I}\frac{1}{2M_I}\left\langle\psi_{\mathrm{e}}\psi_{\mathrm{p}}\,|\,\nabla_I^2(\psi_{\mathrm{e}}\psi_{\mathrm{p}})\right\rangle\\&=-\sum_{I}\frac{1}{2M_I}\left[\left\langle\psi_{\mathrm{e}}\,|\,\nabla_I^2\psi_{\mathrm{e}}\right\rangle+\left\langle\psi_{\mathrm{p}}\,|\,\nabla_I^2\psi_{\mathrm{p}}\right\rangle\right]\\&=\sum_{I}\frac{1}{2M_I}\left[\left\langle\nabla_I\psi_{\mathrm{e}}\,|\,\nabla_I\psi_{\mathrm{e}}\right\rangle+\left\langle\nabla_I\psi_{\mathrm{p}}\,|\,\nabla_I\psi_{\mathrm{p}}\right\rangle\right]\end{aligned} \tag{4}$$

The electronic term has the identical form as the DBOC in conventional electronic structure theory.[10-13] Note that the DBOC would have a more complicated form if the NEO wavefunction were not simply the product of electronic and protonic wavefunctions. Extensions of this NEO DBOC derivation to correlated wavefunction NEO methods, such as NEO-CCSD[9] and configuration interaction methods, may be implemented following the analogous derivations for conventional electronic structure theory.[13-17] Note also that the DBOC is rigorously derived for wave function theories but in practice can be computed for the Kohn-Sham determinant within the framework of DFT, as discussed further below.

The programmable equations for the numerical calculation of the electronic and protonic DBOCs, respectively, are as follows:

$$E_{\mathrm{DBOC}}^{\mathrm{e}} = \sum_I \frac{1}{2M_I} \left\langle \nabla_I \psi_{\mathrm{e}} \,|\, \nabla_I \psi_{\mathrm{e}} \right\rangle = \sum_I \frac{1 - S_{\pm I}^{\mathrm{e}}}{4\delta^2 M_I} \tag{5}$$

$$E_{\mathrm{DBOC}}^{\mathrm{p}} = \sum_I \frac{1}{2M_I} \left\langle \nabla_I \psi_{\mathrm{p}} \,|\, \nabla_I \psi_{\mathrm{p}} \right\rangle = \sum_I \frac{1 - S_{\pm I}^{\mathrm{p}}}{4\delta^2 M_I} \tag{6}$$

$$S_{\pm I}^{j} = \left\langle \psi_j(\mathbf{R} + \delta_I) \,|\, \psi_j(\mathbf{R} - \delta_I) \right\rangle, \;\; j = \mathrm{e, p} \tag{7}$$

where δ is the step size in the numerical differentiation, and $S_{\pm I}^{\mathrm{e}}$ and $S_{\pm I}^{\mathrm{p}}$ are electronic and protonic wavefunction overlaps of perturbed geometries, respectively.[13] Typically the quantum subsystem includes both α- and β-spin electrons but only high-spin quantum protons (i.e., the protons are localized with only a single proton occupying each molecular orbital).

To provide a qualitative comparison of the electronic and protonic DBOCs, we examine two simple model systems. The electronic DBOC for the hydrogen atom in units of Hartree is $E_{\mathrm{DBOC}}^{\mathrm{e}} = \frac{m_{\mathrm{e}}}{2m_{\mathrm{p}}}$, which is 0.27 mH or 60 cm^{-1}.[18] The analog for the protonic DBOC is a diatomic molecule, in which the heavy atom has mass M_{C} and the hydrogen atom has mass m_{p}, with a single vibrational mode of frequency v that can be described by a one-dimensional harmonic oscillator model. The protonic DBOC for this model system is $E_{\mathrm{DBOC}}^{\mathrm{p}} = \frac{m_{\mathrm{p}}}{2M_{\mathrm{C}}} \frac{hv}{2}$, where the second factor is the zero-point energy associated with the vibrational mode (see SI for details). To provide a qualitative estimate, if v = 2000 cm^{-1} and M_{C} = 10m_{p}, then $E_{\mathrm{DBOC}}^{\mathrm{p}}$ = 50 cm^{-1}, which is of similar magnitude as $E_{\mathrm{DBOC}}^{\mathrm{e}}$ for the hydrogen atom. Moreover, $E_{\mathrm{DBOC}}^{\mathrm{e}}$ and $E_{\mathrm{DBOC}}^{\mathrm{p}}$ for these model systems are each expressed as the product of a ratio of masses and an intrinsic energy (i.e., the Hartree for the hydrogen atom and the zero-point energy associated with the vibrational mode for the diatomic molecule). We emphasize that these model systems do not account for the complexities of molecules, which involve many heavy nuclei of varying masses and nuclear charges, multiple types of electrons (i.e., core and valence), and proton vibrational modes of different types and frequencies. Nevertheless, these model systems illustrate the common form of the electronic and protonic DBOCs, as well as the dependence of the protonic DBOC on the frequencies associated with the quantum protons.

We computed the DBOCs for a diverse set of molecules with varying numbers of quantum protons. For each molecule, all electrons and all protons were treated quantum mechanically, as depicted for two molecules in Figure 1. The geometry of each system was optimized at the NEO-DFT level using the B3LYP electronic exchange-correlation functional[19-21] and the epc17-2 electron-proton correlation functional[8] unless otherwise specified. Note that the choice of electronic exchange-correlation functional is not expected to impact the conclusions based on the analysis herein.[22] The cc-pVTZ electronic basis set[23] was used in conjunction with an even-tempered 8*s*8*p*8*d*8*f* nuclear basis set with $\alpha = 2\sqrt{2}$ and $\beta = \sqrt{2}$.[24] The electronic and nuclear basis function centers for each quantum hydrogen were chosen to be the same and were optimized variationally as part of the single-point NEO energy calculations. All of the conventional electronic DFT calculations were performed at the B3LYP/cc-pVTZ level. An in-house developmental version of the GAMESS quantum chemistry package[25] was used for the NEO calculations. The convergence criteria for both the electronic and nuclear densities in the self-consistent-field (SCF) procedure were 10^{-8}, which is tighter than the default values because the numerical DBOC is highly sensitive to slight changes in the wavefunction between perturbed geometries. Equations (5)–(7) were used to compute the total NEO DBOC, as well as the electronic and protonic components, by perturbing each classical coordinate by $\delta = 10^{-3}$ Bohr, which was found to be sufficient for the desired level of accuracy (Tables S2 and S3). For comparison, the DBOC computed with conventional electronic DFT was also calculated.

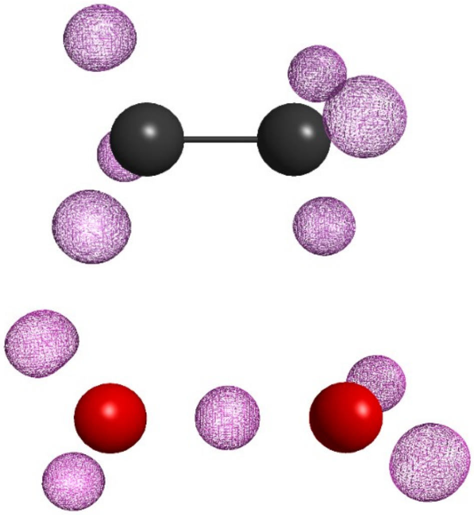

Figure 1: Proton orbitals (pink mesh) obtained from NEO-DFT/B3LYP/epc17-2 calculations of ethane (top) and $H_5O_2^+$ (bottom).

Table 1 presents the total NEO DBOC, the corresponding electronic and protonic components, and the conventional electronic DBOC, denoted $E_{\mathrm{DBOC}}^{\mathrm{e,conv}}$, for eight molecules. The numerical precision of the calculated values of the DBOC is ~0.1 cm^{-1} (Table S1). For each of these molecules, the electronic component of the NEO DBOC is 30–45 cm^{-1} lower per quantum proton than the DBOC computed with conventional electronic DFT. This trend is a direct consequence of the quantization of the protons in the NEO-DFT framework, leading to a reduced number of “classical” nuclear coordinates and a smaller number of terms in the NEO-DBOC compared to the conventional electronic DBOC. As further validation of our calculations, the conventional DFT DBOC values for HCN and HCC^- are in agreement with literature values of 838 and 769 cm^{-1}, respectively, using Hartree-Fock theory with the aug-cc-pVTZ basis set.[26]

Table 1: Total NEO DBOC, the Electronic and Protonic Components, and the Conventional Electronic DBOC.[a]

	HCN	HNC	HCC^-	HCCH	H_2CCH_2	H_3CCH_3	FHF^-	$H_5O_2^+$
$E_{\mathrm{DBOC}}^{\mathrm{tot}}$	1335	1210	1250	1790	2187	2502	1173	1745
$E_{\mathrm{DBOC}}^{\mathrm{e}}$	805	802	728	742	751	760	1130	1043
$E_{\mathrm{DBOC}}^{\mathrm{p}}$	530	407	522	1048	1435	1742	43	702
$E_{\mathrm{DBOC}}^{\mathrm{e,conv}}$	839	833	770	808	928	1035	1159	1193

[a]All NEO calculations were performed at the DFT/B3LYP/epc17-2 level of theory with the basis sets given in the text. The conventional electronic calculations were performed at the DFT/B3LYP/cc-pVTZ level of theory. All energies are given in units of cm^{-1}.

The protonic components of the NEO DBOC exhibit more widely varying behavior in Table 1. The three terminal single-proton systems all yield comparable values for the protonic contribution to the NEO DBOC. The magnitude of $E_{\mathrm{DBOC}}^{\mathrm{p}}$ is somewhat smaller than the magnitude of $E_{\mathrm{DBOC}}^{\mathrm{e}}$, an apparent contradiction given the significantly larger mass of a proton compared to an electron, which would be expected to lead to larger non-Born-Oppenheimer effects. However, accounting for the significantly larger number of electrons than quantum protons, a single proton is found to contribute more to the DBOC than does a single electron for most systems studied. Moreover, as discussed above in the context of simple model systems, the DBOC is expected to depend qualitatively on an intrinsic energy, which is related to the proton vibrational frequencies for $E_{\mathrm{DBOC}}^{\mathrm{p}}$, as well as the masses.

Although $E_{\mathrm{DBOC}}^{\mathrm{e,conv}}$ per electron in analogous conventional electronic structure calculations has been suggested to be approximately constant,[27] $E_{\mathrm{DBOC}}^{\mathrm{p}}$ per quantum proton is not generally constant. In particular, the value of $E_{\mathrm{DBOC}}^{\mathrm{p}}$ for the internal single-proton system of FHF^- is nearly an order of magnitude smaller than the values for the terminal single-proton systems, most likely due to the significantly lower vibrational frequency associated with the internal hydrogen. On the other hand, comparison of $E_{\mathrm{DBOC}}^{\mathrm{p}}$ for HCC⁻ and HCCH demonstrates an additive effect for the terminal protons in these systems. Specifically, $E_{\mathrm{DBOC}}^{\mathrm{p}}$ almost exactly doubles for HCCH compared to HCC⁻, indicating a constant $E_{\mathrm{DBOC}}^{\mathrm{p}}$ per quantum proton in this case, which is consistent with the nearly identical vibrational frequencies associated with these two hydrogens. In contrast, further increasing the number of protons to generate H_2CCH_2 and H_3CCH_3 does not add a constant amount per proton, but rather adds a smaller amount per proton as the total number of protons increases, reflecting the lower vibrational frequencies associated with the hydrogens in these molecules.

The effect of electron-proton correlation on the NEO DBOC and its components was also investigated. As shown in Table 2, the electronic contribution to the NEO DBOC, $E_{\mathrm{DBOC}}^{\mathrm{e}}$, is not significantly influenced by electron-proton correlation. In contrast, the protonic contribution, $E_{\mathrm{DBOC}}^{\mathrm{p}}$, is strongly influenced by electron-proton correlation. Specifically, the $E_{\mathrm{DBOC}}^{\mathrm{p}}$ values obtained with NEO-HF and NEO-DFT/no-epc, which do not include any electron-proton correlation, are over twice the values obtained with NEO-DFT/epc17-1 and NEO-DFT/epc17-2, which include electron-proton correlation. This difference can be attributed to the highly localized proton densities produced by the methods neglecting electron-proton correlation,[7] manifesting in smaller overlaps between the perturbed geometries in Eq (6) and thus leading to larger values of $E_{\mathrm{DBOC}}^{\mathrm{p}}$. Electron correlation does not impact either the electronic[13] or the protonic contributions to the DBOC, as indicated by the nearly identical results obtained from NEO-HF and NEO-DFT/no-epc. Although the DBOC is rigorously derived for wave function theories, the similar values of the DBOC obtained with Hartree-Fock and DFT (Table 1 compared to Ref. [26] and Table 2) provides some justification for computing the DBOC within the DFT framework as an estimate of non-Born-Oppenheimer effects.

Table 2: Effect of Electron-Proton Correlation on NEO DBOC and its Components for HCN.[a]

	NEO-HF	NEO-DFT		
		no-epc	epc17-1	epc17-2
$E_{\mathrm{DBOC}}^{\mathrm{tot}}$	1928	1928	1237	1335
$E_{\mathrm{DBOC}}^{\mathrm{e}}$	807	806	804	805
$E_{\mathrm{DBOC}}^{\mathrm{p}}$	1121	1122	433	530

[a] All NEO-DFT calculations were performed with the B3LYP electronic functional and with no electron-proton correlation, denoted no-epc, or the epc17-1 or epc17-2 electron-proton correlation functional. The geometry was optimized at each level of theory. All energies are given in units of cm^{-1}.

Despite the relatively large magnitudes of the NEO DBOC values, the impact of the DBOC on the NEO potential energy surface is more important for determining its practical significance. In the context of conventional electronic Hartree-Fock calculations, Handy and Lee examined the impact of the electronic DBOC on the potential energy surface for a set of diatomic molecules.[18] Although the conventional electronic DBOC can be on the order of ~1000 cm^{-1} for these diatomics, the equilibrium bond length was found to change by less than 10^{-3} Bohr for H_2 and less than 10^{-4} Bohr for the other diatomics, and the frequencies were found to change by only ~3 cm^{-1} for H_2 and by less than 0.1 cm^{-1} for the diatomics that do not contain hydrogen.

With this previous work as inspiration, we examined the equilibrium bond lengths and vibrational frequencies corresponding to $E_{\mathrm{NEO}}(\mathbf{R})+E_{\mathrm{DBOC}}^{\mathrm{tot}}(\mathbf{R})$ for eight molecules. Each molecule contains only two classical nuclei because all protons are treated quantum mechanically on the same level as the electrons. The frequency for the heavy atom stretching motion for each molecule was calculated via a finite difference second derivative, effectively making the DBOC contribution to the stretching frequency a numerical fourth derivative. As a result, the numerical precision is estimated to be lower for the vibrational frequency than for the magnitude of the DBOC. In particular, the numerical precision for the vibrational frequencies is estimated to be ~1 cm^{-1} or slightly greater in some cases (Tables S2 and S3). When the DBOC is included in the potential energy surface, the equilibrium bond length for the heavy nuclei changes on the order of 10^{-4} Å for a stabilization in energy of less than 1 μHartree. This extremely small change in bond length was not considered when calculating the effect of the DBOC on the vibrational frequencies presented herein. However, the frequencies computed at the DBOC optimized geometries for several of the triatomic molecules are available in the SI (Table S4).

Table 3: Vibrational Stretching Frequencies for the Heavy Atom Mode in the NEO Framework with and without the NEO DBOC and its Components.[a]

	HCN	HNC	HCC^-	HCCH	H_2CCH_2	H_3CCH_3	FHF^-	$H_5O_2^+$
No DBOC	2293	2160	1963	2207	1642	1061	607	642
With $E_{\text{DBOC}}^{\text{e}}$	2293	2160	1963	2208	1642	1062	607	643
With $E_{\text{DBOC}}^{\text{p}}$	2293	2161	1962	2209	1648	1072	606	648
With $E_{\text{DBOC}}^{\text{tot}}$	2293	2161	1962	2209	1648	1073	606	648

[a] For all of these molecules, the NEO potential energy surface is one-dimensional with a single vibrational mode because all protons are treated quantum mechanically and each molecule has only two heavy atoms. All calculations were performed at the NEO-DFT/B3LYP/epc17-2 level of theory with the basis sets given in the text. All energies are given in units of cm^{-1}. The numerical precision of the vibrational frequency calculations including the DBOC was determined to be typically 1 cm^{-1} or slightly greater in some cases (see the SI for details).

Table 3 presents the vibrational stretching frequencies for the heavy atom mode in each molecule computed with and without the NEO DBOC. These data illustrate that inclusion of the electronic component of the DBOC, $E_{\text{DBOC}}^{\text{e}}$, increases the vibrational frequency by no more than 1 cm^{-1}. The protonic component, $E_{\text{DBOC}}^{\text{p}}$, has a similarly small effect of ~1 cm^{-1} for the molecules with one or two quantum protons, but this effect increases for molecules with more quantum protons. The quantum protons are expected to influence only the stretching modes associated with atoms to which they are bonded. Even in the extreme case of ethane, with six quantum protons adjacent to the heavy atom vibrational mode, $E_{\text{DBOC}}^{\text{p}}$ only changes the vibrational frequency by 11 cm^{-1}. Although this effect is expected to be even smaller for typical modes, the DBOC could be included in the NEO potential energy surface routinely by computing it analytically. The analytical computation of the NEO Hessian and the DBOC is a direction of current research.

Furthermore, when the DBOC effects are considered to be significant, they can be included in the calculation of the molecular vibrational frequencies using the NEO methodology developed recently to couple the classical and quantum mechanical vibrational modes.[28] This approach entails diagonalization of an extended NEO Hessian that depends on the expectation values of the quantum protons as well as the coordinates of the classical nuclei. The practical incorporation of the DBOCs within this strategy requires the assumption that the partial second derivatives of the DBOCs with respect to the expectation values of the quantum protons are negligible.

In this Letter, the diagonal Born-Oppenheimer correction within the NEO multicomponent framework was derived, and its magnitude and significance were analyzed for a set of molecules. In terms of the magnitude of the DBOC, the contribution from the quantum protons was found to be of similar order of magnitude as the contribution from the electrons for the molecules studied. The contribution per proton is greater than the contribution per electron, but the molecules contain significantly more electrons than quantum protons. Inclusion of the DBOC was found to change the equilibrium bond lengths on the order of 10^{-4} Å and to change the vibrational frequencies by ~1–2 cm^{-1} per quantum proton bonded to one of the atoms participating in the vibrational mode. These results suggest that the non-Born-Oppenheimer effects arising from the adiabatic separation between the quantum protons and the other nuclei in the NEO framework do not significantly impact molecular properties and may simply shift the energy of the entire potential energy surface by a constant amount. In this case, the DBOC would not need to be considered when generating reaction paths and dynamics on the NEO potential energy surface. If the DBOC becomes important at certain nonequilibrium geometries, it can be incorporated using the formalism described in this work.

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Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Analysis of simple model for protonic DBOC and tests of numerical precision.

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