

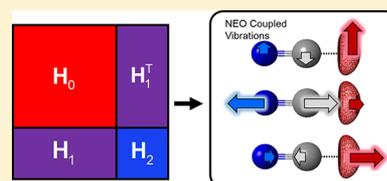
Molecular Vibrational Frequencies within the Nuclear–Electronic Orbital Framework

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Supporting Information

ABSTRACT: A significant challenge for multicomponent quantum chemistry methods is the calculation of vibrational frequencies for comparison to experiment. The nuclear–electronic orbital (NEO) approach treats specified nuclei, typically key protons, quantum mechanically. The Born–Oppenheimer separation between the quantum and classical nuclei prevents the direct calculation of vibrational frequencies corresponding to modes composed of both types of nuclei. Herein an effective strategy for calculating the vibrational frequencies of the entire molecule within the NEO framework is devised and implemented. This strategy requires diagonalization of an extended NEO Hessian that depends on the expectation values of the quantum nuclei as well as the coordinates of the classical nuclei and is constructed with input from multicomponent time-dependent density functional theory (NEO-TDDFT). Application of this NEO-DFT(V) approach to molecular systems illustrates that it accurately incorporates the most significant anharmonic effects. This general theoretical formulation opens up a broad spectrum of new directions for multicomponent quantum chemistry.



Multicomponent quantum chemistry, in which more than one type of particle is treated quantum mechanically with either wave function methods or density functional theory (DFT), is an emerging research field.^{1–8} A significant advantage of multicomponent quantum chemistry is that electronic and nuclear quantum effects can be described simultaneously while avoiding the Born–Oppenheimer separation between the electrons and the quantum nuclei. The nuclear–electronic orbital (NEO) approach^{3,5,6,9–11} balances chemical accuracy and computational practicality by treating all electrons and one or more nuclei, typically key protons, quantum mechanically, while treating at least two nuclei classically to avoid difficulties with translations and rotations. The NEO potential energy surface depends on only the coordinates of the classical nuclei,¹² predicated on the assumption that the electrons and quantum nuclei respond instantaneously to the motion of the classical nuclei. The characterization of stationary points on the NEO potential energy surface as minima or saddle points requires the computation of the NEO Hessian matrix within the coordinate space.¹² The Hessian matrix is also crucial for obtaining the intrinsic reaction coordinate (IRC) or the minimum energy path within the NEO framework. Thus, an efficient method for computing the NEO Hessian matrix is essential for a wide range of applications.

A significant challenge of multicomponent quantum chemistry methods is the calculation of meaningful vibrational frequencies. Molecular geometries can be described by representing the positions of the quantum nuclei by the expectation values of their coordinates. The Born–Oppenheimer separation between the quantum and classical nuclei, reflected by the instantaneous response of the former to the latter, prevents the direct calculation of vibrational frequencies corresponding to modes composed of both types of nuclei. As

a result, the vibrational modes obtained from diagonalizing the NEO Hessian matrix at a minimum on the NEO potential energy surface are not directly connected to those obtained from experimental infrared or Raman spectroscopy. In order to build this connection and enable the calculation of meaningful vibrational frequencies within the NEO framework, the quantum and classical nuclei must be coupled in a rigorous manner.

In this Letter, we derive the equations to efficiently calculate the NEO Hessian matrix and devise an effective strategy to enable the calculation of meaningful vibrational frequencies. The NEO Hessian is composed of second derivatives of the NEO energy with respect to only the classical nuclei, invoking the Born–Oppenheimer separation between the quantum and classical nuclei. The vibrational frequencies are calculated by diagonalizing an extended NEO Hessian that includes second derivatives of the NEO energy with respect to the expectation values of the quantum nuclei as well as the classical nuclei, thereby coupling these two types of nuclei. Diagonalization of this extended NEO Hessian produces vibrational modes that are composed of both types of nuclei and therefore can be directly connected to the vibrational modes measured spectroscopically. This strategy, denoted NEO-DFT(V), differs from conventional quantum chemistry calculations of vibrational frequencies because the delocalization and zero point energy effects of the quantum nuclei are included in the geometry optimizations, and anharmonic effects are included in the expectation values of the quantum nuclei used in the extended NEO Hessian. These differences are expected to

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improve the quantitative accuracy of the vibrational frequencies, particularly those involving the quantum nuclei. After deriving the key equations, we apply this strategy to a set of molecular systems and compare the calculated vibrational frequencies to experimental data.

For a system with N_c classical nuclei and N_q quantum nuclei, the NEO potential energy surface depends on only the coordinates of the classical nuclei and therefore is $3N_c$ -dimensional.¹² In practice, a single-point energy calculation within the NEO framework also depends on the positions of the electronic and nuclear basis function centers associated with the quantum nuclei. Here we assume that the quantum nuclei are described by a total of N_b basis function centers. Although often each quantum nucleus is represented by a set of basis functions with a single basis function center that is the same for both electronic and nuclear basis functions, leading to $N_b = N_q$, this assumption is not necessary. For a finite basis set, the positions of the basis function centers associated with the quantum nuclei must be optimized variationally to compute each point on the NEO potential energy surface (i.e., for each configuration of the classical nuclei). Mathematically, the NEO potential energy surface is defined by

$$E = E(\mathbf{r}_c, \mathbf{r}_b(\mathbf{r}_c)) \quad (1)$$

where \mathbf{r}_c is a $3N_c$ -dimensional vector denoting the combined coordinates of the classical nuclei and \mathbf{r}_b is a $3N_b$ -dimensional vector denoting the combined coordinates of the basis function centers associated with the quantum nuclei. According to the definition of the NEO potential energy surface, the coordinates \mathbf{r}_b depend on the classical nuclear coordinates \mathbf{r}_c and satisfy the condition

$$\frac{\partial E}{\partial \mathbf{r}_b} = 0 \quad (2)$$

Using the chain rule, the gradient of the NEO energy, which is a $3N_c$ -dimensional vector, is

$$\frac{dE}{d\mathbf{r}_c} = \frac{\partial E}{\partial \mathbf{r}_c} + \frac{\partial E}{\partial \mathbf{r}_b} \frac{d\mathbf{r}_b}{d\mathbf{r}_c} = \frac{\partial E}{\partial \mathbf{r}_c} \quad (3)$$

where the second equality arises because eq 2 is satisfied.

The NEO Hessian matrix, a $3N_c \times 3N_c$ square matrix, can be obtained as

$$\frac{d^2E}{d\mathbf{r}_c^2} = \left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2} \right)_{\mathbf{r}_b} + 2 \frac{\partial^2 E}{\partial \mathbf{r}_b \partial \mathbf{r}_c} \frac{d\mathbf{r}_b}{d\mathbf{r}_c} + \frac{\partial^2 E}{\partial \mathbf{r}_b^2} \left(\frac{d\mathbf{r}_b}{d\mathbf{r}_c} \right)^2 + \frac{\partial E}{\partial \mathbf{r}_b} \frac{d^2 \mathbf{r}_b}{d\mathbf{r}_c^2} \quad (4)$$

where this compact notation does not explicitly indicate the order of matrix operations and transpose of certain matrices for practical implementation. The subscript \mathbf{r}_b in the first term on the right side of eq 4 indicates that \mathbf{r}_b is fixed for this partial derivative. The direct evaluation of this form is not straightforward because the function $\mathbf{r}_b = \mathbf{r}_b(\mathbf{r}_c)$ is not explicitly known. However, this expression can be simplified by taking the derivative of eq 2 with respect to \mathbf{r}_c , yielding

$$\frac{\partial^2 E}{\partial \mathbf{r}_b \partial \mathbf{r}_c} + \frac{\partial^2 E}{\partial \mathbf{r}_b^2} \frac{d\mathbf{r}_b}{d\mathbf{r}_c} = 0 \quad (5)$$

and solving for $\frac{d\mathbf{r}_b}{d\mathbf{r}_c}$. Equations 2 and 5 lead to the simplification of the Hessian matrix in eq 4 as

$$\frac{d^2E}{d\mathbf{r}_c^2} = \left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2} \right)_{\mathbf{r}_b} - \frac{\partial^2 E}{\partial \mathbf{r}_b \partial \mathbf{r}_c} \left(\frac{\partial^2 E}{\partial \mathbf{r}_b^2} \right)^{-1} \frac{\partial^2 E}{\partial \mathbf{r}_b \partial \mathbf{r}_c} \quad (6)$$

In this new form, only second-order energy derivatives remain, and all of these terms can be evaluated numerically or analytically. Defining the three submatrices $\mathbf{H}_{cc} = \left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2} \right)_{\mathbf{r}_b}$, $\mathbf{H}_{bc} = \frac{\partial^2 E}{\partial \mathbf{r}_b \partial \mathbf{r}_c}$, and $\mathbf{H}_{bb} = \frac{\partial^2 E}{\partial \mathbf{r}_b^2}$, as well as the NEO Hessian matrix \mathbf{H}_{NEO} , eq 6 can be expressed as

$$\mathbf{H}_{\text{NEO}} = \mathbf{H}_{cc} - \mathbf{H}_{bc}^T \mathbf{H}_{bb}^{-1} \mathbf{H}_{bc} \quad (7)$$

This matrix folding process accounts for the effect of the optimization of the nuclear basis function centers associated with the quantum nuclei. In eqs 2–7, the partial derivatives with respect to \mathbf{r}_c are computed with \mathbf{r}_b fixed, and the partial derivatives with respect to \mathbf{r}_b are computed with \mathbf{r}_c fixed. In the complete basis set limit, \mathbf{H}_{cc} will be equivalent to \mathbf{H}_{NEO} .

Diagonalizing the NEO Hessian given in eq 7 leads to the vibrational modes within the classical coordinate space, assuming that the quantum nuclei respond instantaneously to the motion of classical nuclei. However, because the mass difference between classical and quantum nuclei is not substantial, non-Born–Oppenheimer or nonadiabatic effects between the two types of nuclei may be significant. Moreover, the NEO framework does not provide frequencies that can be compared directly with experimentally measured IR spectra because the normal modes obtained from the NEO Hessian depend on only the classical nuclear coordinates and do not accurately describe the coupling effects between the classical and quantum nuclear motions. To address this issue, we propose and implement a practical strategy to recover the experimentally meaningful vibrational modes by combining NEO Hessian and NEO-TDDFT calculations.¹³

In a NEO calculation, the Hessian matrix is defined in the space of the N_c classical nuclear coordinates, denoted by \mathbf{r}_c , and the normal modes obtained from this Hessian do not depend explicitly on the quantum nuclear coordinates. However, an extended NEO Hessian may be defined to depend on both the classical nuclear coordinates, \mathbf{r}_c , and the expectation values of the quantum nuclear coordinates defined as

$$\mathbf{r}_{q_i} = \int \mathbf{r} \rho_{q_i}(\mathbf{r}) d\mathbf{r} \quad (8)$$

Here $\rho_{q_i}(\mathbf{r})$ and \mathbf{r}_{q_i} denote the density and expectation value (i.e., average position), respectively, of the i th quantum nucleus. This extended NEO Hessian matrix can be divided into three submatrices: $\mathbf{H}_0 = \left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2} \right)_{\mathbf{r}_q}$, $\mathbf{H}_1 = \frac{\partial^2 E}{\partial \mathbf{r}_q \partial \mathbf{r}_c}$, and

$\mathbf{H}_2 = \frac{\partial^2 E}{\partial \mathbf{r}_q^2}$, where \mathbf{r}_q is a $3N_q$ -dimensional vector denoting the combined coordinates of the expectation values of the quantum nuclei. Analogous to conventional quantum chemistry calculations, the nonzero eigenvalues of the mass-weighted extended Hessian matrix correspond to the squares of the frequencies of the vibrational modes, and the associated eigenvectors correspond to the amplitudes of motion along the mass-weighted coordinates for these modes.

The $\frac{\partial^2 E}{\partial \mathbf{r}_q^2}$ term defined as \mathbf{H}_2 is the force constant matrix for the quantum nuclei while all classical nuclei are fixed within the harmonic oscillator approximation. Thus, this term is related to the harmonic vibrational excitation frequencies, which can be approximated by the vibrational excitation frequencies ω obtained from a NEO-TDDFT calculation.¹³ In this case, the Hessian matrix elements can be calculated as

$$\mathbf{H}_2 = \frac{\partial^2 E}{\partial \mathbf{r}_q^2} = \mathbf{U}^\dagger \mathbf{\Omega} \mathbf{M} \mathbf{U} \quad (9)$$

where \mathbf{M} is the diagonal mass matrix corresponding to the quantum nuclei, $\mathbf{\Omega}$ is the diagonal matrix with elements ω^2 corresponding to the NEO-TDDFT vibrational frequencies for fixed classical nuclei, and \mathbf{U} is a unitary matrix that transforms the diagonal frequency matrix to the chosen coordinate system. Note that nuclear delocalization and anharmonicity effects of the quantum nuclei are included in the vibrational excitation frequencies ω , as well as in the optimized geometries and expectation values of the quantum nuclear coordinates. Although these anharmonic frequencies are incorporated as second-order harmonic frequency terms in the extended Hessian, this procedure incorporates a portion of these physically significant effects. This point will be discussed further below in the analysis of the applications.

The $\left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2}\right)_{\mathbf{r}_q}$ term defined as \mathbf{H}_0 is the force constant matrix for the classical nuclei with the expectation values of the quantum nuclei fixed. Therefore, it differs from the elements of the NEO Hessian \mathbf{H}_{NEO} defined in eq 7, which requires the quantum nuclei to respond instantaneously to the motion of the classical nuclei. The NEO energy can be expressed as

$$E = E(\mathbf{r}_c, \mathbf{r}_q(\mathbf{r}_c)) \quad (10)$$

where the expectation values of the quantum nuclei depend on the classical nuclear coordinates. Because the NEO energy is computed by variationally optimizing the densities of the quantum nuclei, the energy is stationary with respect to the expectation values of the quantum nuclei (see the SI for details)

$$\frac{\partial E}{\partial \mathbf{r}_q} = 0 \quad (11)$$

Equations 10 and 11 have the same form as eqs 1 and 2, except that the positions of the basis function centers, \mathbf{r}_b , have been substituted with the expectation values of the quantum nuclei, \mathbf{r}_q . Following the same mathematical derivations leads to

$$\frac{d^2 E}{d\mathbf{r}_c^2} = \left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2}\right)_{\mathbf{r}_q} - \frac{\partial^2 E}{\partial \mathbf{r}_q \partial \mathbf{r}_c} \left(\frac{\partial^2 E}{\partial \mathbf{r}_q^2}\right)^{-1} \frac{\partial^2 E}{\partial \mathbf{r}_q \partial \mathbf{r}_c} \quad (12)$$

$$\mathbf{H}_{\text{NEO}} = \mathbf{H}_0 - \mathbf{H}_1^T \mathbf{H}_2^{-1} \mathbf{H}_1 \quad (13)$$

In this case, \mathbf{H}_0 is the target matrix that contains the $\left(\frac{\partial^2 E}{\partial \mathbf{r}_c^2}\right)_{\mathbf{r}_q}$ matrix elements and can be obtained by

$$\mathbf{H}_0 = \mathbf{H}_{\text{NEO}} + \mathbf{H}_1^T \mathbf{H}_2^{-1} \mathbf{H}_1 \quad (14)$$

The NEO Hessian \mathbf{H}_{NEO} is already known from eq 7, \mathbf{H}_2^{-1} can be calculated as described above, and \mathbf{H}_1 will be derived in the

next step. Note that \mathbf{H}_0 is not the same as \mathbf{H}_{cc} in eq 7 because the partial second derivatives are computed with \mathbf{r}_b fixed for \mathbf{H}_{cc} and with \mathbf{r}_q fixed for \mathbf{H}_0 .

The derivation of \mathbf{H}_1 utilizes the analogue of eq 5 with \mathbf{r}_b substituted by \mathbf{r}_q

$$\frac{\partial^2 E}{\partial \mathbf{r}_q \partial \mathbf{r}_c} + \frac{\partial^2 E}{\partial \mathbf{r}_q^2} \frac{d\mathbf{r}_q}{d\mathbf{r}_c} = 0 \quad (15)$$

Rearrangement of this equation provides the matrix elements in \mathbf{H}_1

$$\frac{\partial^2 E}{\partial \mathbf{r}_q \partial \mathbf{r}_c} = -\frac{\partial^2 E}{\partial \mathbf{r}_q^2} \frac{d\mathbf{r}_q}{d\mathbf{r}_c} \quad (16)$$

which can be written in matrix form as $\mathbf{H}_1 = -\mathbf{H}_2 \mathbf{R}$, with the response of \mathbf{r}_q to \mathbf{r}_c defined as

$$\mathbf{R} = \frac{d\mathbf{r}_q}{d\mathbf{r}_c} = \frac{d}{d\mathbf{r}_c} \int \mathbf{r} \rho_{q_i}(\mathbf{r}) d\mathbf{r} = \int \mathbf{r} \frac{d\rho_{q_i}(\mathbf{r})}{d\mathbf{r}_c} d\mathbf{r} \quad (17)$$

The matrix \mathbf{R} can be calculated either numerically or analytically. For the applications described below, we compute the numerical gradient of the expectation value of each quantum nucleus with respect to each classical nucleus. Analytically, the density matrix response with respect to changes in the classical nuclear coordinates can be obtained by coupled perturbed NEO-Hartree-Fock/Kohn-Sham equations, which is a direction of current research. In eqs 11–17, the partial derivatives with respect to \mathbf{r}_c are computed with \mathbf{r}_q fixed, and the partial derivatives with respect to \mathbf{r}_q are computed with \mathbf{r}_c fixed.

Combining all of these parts, the extended Hessian matrix can be calculated from the following expressions

$$\mathbf{H}_2 = \mathbf{U}^\dagger \mathbf{\Omega} \mathbf{M} \mathbf{U} \quad (18)$$

$$\mathbf{H}_1 = -\mathbf{H}_2 \mathbf{R} \quad (19)$$

$$\mathbf{H}_0 = \mathbf{H}_{\text{NEO}} + \mathbf{H}_1^T \mathbf{H}_2^{-1} \mathbf{H}_1 = \mathbf{H}_{\text{NEO}} + \mathbf{R}^T \mathbf{H}_2 \mathbf{R} \quad (20)$$

Note that all of these quantities are straightforward to calculate. The two matrices \mathbf{H}_{NEO} and \mathbf{R} can be calculated numerically or analytically within the NEO-DFT method, while \mathbf{H}_2 is constructed from the results of a NEO-TDDFT calculation. These three matrices alone are sufficient for calculating the remaining required pieces for the full vibrational analysis, which is performed on the mass-weighted extended Hessian matrix. The construction of the extended Hessian matrix is depicted in Figure 1, and an example of this NEO-DFT(V) procedure applied to HCN is depicted in Figure 2.

Herein the NEO-DFT(V) method is used to compute the vibrational modes for a set of five molecular systems, each with a single proton. For each system, the geometries were optimized at the NEO-DFT level with the B3LYP electronic exchange–correlation functional^{14–16} and the epc17-2 electron–proton correlation functional.^{9,10} The cc-pVTZ¹⁷ electronic basis set was used for all heavy nuclei, while the cc-pV6Z¹⁸ basis set, excluding the *h*-function (denoted cc-pV6Z* herein), was employed for the protons. An even-tempered 8s8p8d8f proton basis set was used for all calculations with $\alpha = 2\sqrt{2}$ and $\beta = \sqrt{2}$.¹⁹ The NEO Hessian and the derivatives of the expectation value of the quantum proton with respect to the classical nuclei were computed numerically. The NEO-TDDFT calculations were performed at the same

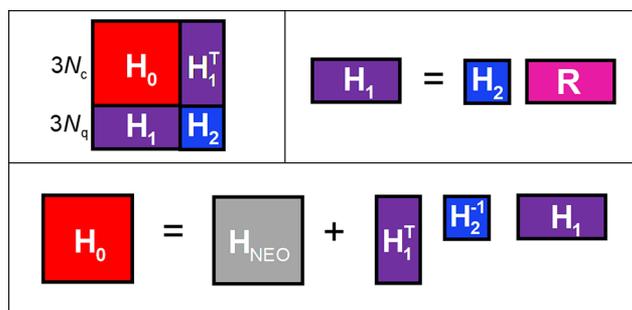


Figure 1. Schematic depiction of the extended Hessian matrix (upper left corner) associated with the coordinates of the classical nuclei and the expectation values of the quantum nuclei. The components H_0 , H_1 , and H_2 are defined in eqs 18–20. H_{NEO} is the $3N_c \times 3N_c$ NEO Hessian matrix defined in eq 7, predicated on the instantaneous response of the quantum nuclei to the classical nuclei. H_2 is the $3N_q \times 3N_q$ matrix computed from a unitary transform of the diagonal matrix composed of the NEO-TDDFT vibrational excitation frequencies associated with the quantum nuclei for fixed classical nuclei. R is the $3N_q \times 3N_c$ matrix defined in eq 17, corresponding to the derivatives of the expectation values of the quantum nuclei with respect to the classical nuclear coordinates.

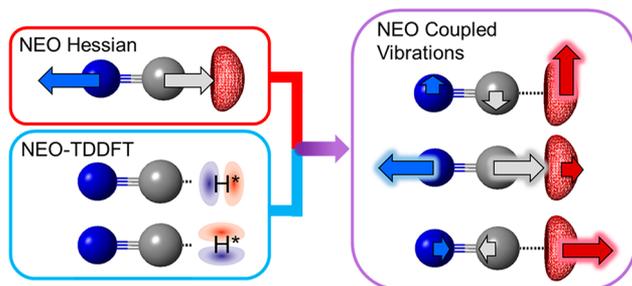


Figure 2. Schematic depiction of the application of the NEO-DFT(V) method to HCN, where the hydrogen nucleus and all electrons are treated quantum mechanically. The quantum proton is depicted in red mesh, and the classical nuclei carbon and nitrogen are depicted in gray and blue, respectively. The NEO Hessian calculation produces the CN vibrational stretch with the hydrogen nucleus responding instantaneously to this motion. The NEO-TDDFT calculation provides the vibrational excitation frequencies associated with the bend (doubly degenerate) and stretch for the hydrogen nucleus with the carbon and nitrogen nuclei fixed. This information is combined to construct the extended Hessian, as shown in Figure 1, to produce the four coupled vibrational motions shown on the right, where the bend is doubly degenerate.

level of theory for these geometries with the exception that the cc-pVDZ¹⁷ basis set was used for the oxygen and fluorine atoms in HCFO and the fluorine atoms in HCF₃. For the NEO-TDDFT calculations, the proton basis function centers were placed at the covalent bond distance determined from conventional DFT; the results with the proton basis function centers placed at the expectation values are similar (Table S1). The unitary matrix U in eq 9 is determined from the normal modes of the quantum proton, as obtained from the conventional DFT Hessian when all classical nuclei are assigned infinite masses. An alternative procedure based on NEO-TDDFT will be explored in future work. All of the NEO calculations and the conventional DFT calculations were performed with an in-house modified version of the GAMESS program.²⁰ For comparison, we also performed conventional DFT calculations including anharmonic corrections perturba-

tively using Gaussian09.²¹ Although these molecules each contain only a single hydrogen nucleus, the extension to multiple protons is straightforward. For multiple protons, the extended Hessian will depend on the expectation value of each proton orbital, and NEO-TDDFT will be used to compute the vibrational frequencies associated with these protons.

The vibrational frequencies obtained from these calculations, as well as experimental data, are given in Table 1. The conventional harmonic DFT and NEO-DFT(V) methods provide similarly accurate vibrational frequencies, with the exception that the hydrogen stretch frequencies for terminal hydrogen nuclei are notably lower and closer to the experimental values when calculated with the NEO-DFT(V) method. This decrease in the frequency of the hydrogen stretch is attributed to the anharmonic effects included directly in the NEO-DFT(V) calculations. Application of anharmonic corrections to the conventional DFT calculations supports this assertion given that the hydrogen stretch frequencies decrease by a similar amount. The hydrogen bending modes are more challenging to compute for linear molecules, as indicated by overestimates of these frequencies by vibrational self-consistent-field calculations (Table S2). Thus, the NEO-DFT(V) method accurately incorporates the most significant anharmonic effects that lead to a substantial decrease in the hydrogen stretch frequencies. These anharmonic effects are included via the quantum treatment of the protons and the use of the NEO-TDDFT excitation energies in the extended NEO Hessian.

A different trend is observed for the FHF⁻ system, where inclusion of anharmonic effects via NEO-DFT(V) or conventional DFT increases the hydrogen stretch frequency. This phenomenon of anharmonicity increasing the hydrogen stretch frequency for FHF⁻ is not uncommon for an internal hydrogen nucleus moving in a single well potential between two other nuclei, in contrast to the terminal hydrogen nuclei in the other molecules studied here. In this case, inclusion of anharmonicity increases the deviation of the calculated hydrogen stretch frequency compared to the experimental value. This deviation is attributed to limitations of the underlying DFT method on the basis of the similar trend observed in the conventional DFT calculations including anharmonic corrections. Moreover, coupled-cluster singles and doubles with perturbative triples (CCSD(T)) calculations²⁷ produce a hydrogen stretch frequency of 1195 cm⁻¹ with a harmonic treatment and 1343 cm⁻¹ with an anharmonic treatment, in good agreement with the experimental value. The magnitude of the increase in frequency due to anharmonic effects in these CCSD(T) calculations is similar to that observed with NEO-DFT(V), confirming that the anharmonic effects are being described in a reasonable manner.

In this Letter, we present an efficient method for computing the NEO Hessian matrix and a novel strategy for calculating the vibrational frequencies of the entire molecule. The NEO Hessian matrix is required for characterizing stationary points on the NEO potential energy surface and for generating the IRC or minimum energy path. However, the NEO Hessian matrix alone is not sufficient to compute vibrational frequencies composed of both classical and quantum nuclei. For this purpose, we devised an extended NEO Hessian that depends on the expectation values of the quantum nuclei as well as the coordinates of the classical nuclei. Diagonalization of this extended NEO Hessian, which relies on input from NEO-TDDFT, produces vibrational modes that are directly

Table 1. Vibrational Frequencies (in cm^{-1}) Calculated with Conventional DFT in Conjunction with Harmonic and Anharmonic Treatments and with NEO-DFT(V)

	vibrational mode	experiment	NEO-DFT(V) ^a	conv. anharmonic ^b	conv. harmonic ^b
HCN ^c	CH stretch	3311	3317	3321	3439
	CN stretch	2097	2191	2177	2201
	CH bend	712	789	753	773
HNC ^d	NH stretch	3653	3645	3644	3814
	NC stretch	2024	2100	2073	2105
	NH bend	462	568	464	480
HCFO ^e	CH stretch	2976	2947	2942	3081
	CO stretch	1834	1885	1861	1891
	CH in-plane bend	1344	1329	1341	1370
	CF stretch	1070	1075	1049	1069
	CH out-of-plane bend	1000–1050	1061	1019	1039
HCF ₃ ^f	OCF scissor	661	665	659	665
	CH stretch	3035	2988	2999	3119
	CH bend	1376	1353	1360	1388
	CF asymmetric stretch	1152	1134	1117	1139
	CF symmetric stretch	1137	1128	1118	1133
	CF simultaneous bend	700	693	688	694
	FCF scissor	508	501	497	501
FHF ^{-g}	FH stretch	1331	1695	1615	1451
	FH bend	1286	1302	1287	1360
	FF stretch	583	617	557	625

^aNEO-DFT/B3LYP/epc17-2 with electronic and nuclear basis sets given in the text. ^bDFT/B3LYP; cc-pVTZ basis set for heavy nuclei and cc-pV6Z (cc-pV6Z*) basis set for the hydrogen for anharmonic (harmonic) treatment. ^cExperimental data from ref 22. ^dExperimental data from ref 23. ^eExperimental data from ref 24. ^fExperimental data from ref 25. ^gExperimental data from ref 26.

related to those measured spectroscopically. Application of this NEO-DFT(V) approach to a series of five molecules illustrates that this approach accurately includes anharmonic effects of the hydrogen nuclei. This general theoretical formulation opens up a broad spectrum of new directions for both DFT and wave function-based multicomponent quantum chemistry.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcllett.9b00299](https://doi.org/10.1021/acs.jpcllett.9b00299).

Proof that the derivative of the NEO energy with respect to the expectation value of the quantum nucleus vanishes; additional tables of computed vibrational frequencies with different methods for comparison (PDF)

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Notes

The authors declare no competing financial interest.

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