ARTICLES

Vibrational analysis for the nuclear–electronic orbital method

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The methodology for a vibrational analysis within the nuclear–electronic orbital (NEO) framework is presented. In the NEO approach, specified nuclei are treated quantum mechanically on the same level as the electrons, and mixed nuclear–electronic wave functions are calculated variationally with molecular orbital methods. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions. The NEO potential energy surface depends on only the classical nuclei, and each point on this surface is optimized variationally with respect to all molecular orbitals as well as the centers of the nuclear basis functions. The NEO vibrational analysis involves the calculation, projection, and diagonalization of a numerical Hessian to obtain the harmonic vibrational frequencies corresponding to the classical nuclei. This analysis allows the characterization of stationary points on the NEO potential energy surface. It also enables the calculation of zero point energy corrections and thermodynamic properties such as enthalpy, entropy, and free energy for chemical reactions on the NEO potential energy surface. Illustrative applications of this vibrational analysis to a series of molecules and to a nucleophilic substitution reaction are presented. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569913]

I. INTRODUCTION

Recently the nuclear–electronic orbital (NEO) method has been developed for the calculation of mixed nuclear–electronic wave functions. In this method, specified nuclei are treated quantum mechanically on the same level as the electrons. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals, as well as the centers of the nuclear basis functions. Significant correlation effects may be included using a multiconfigurational self-consistent-field (MCSCF) method. One advantage of the NEO approach is that nuclear quantum effects are incorporated during the electronic structure calculation, rather than subsequently calculated as a correction factor. In addition, the Born–Oppenheimer separation of electrons and nuclei is avoided, and excited vibrational–electronic states may be calculated. This method is computationally practical for a wide range of chemical reactions, and its accuracy may be improved systematically.

The NEO approach is particularly useful for systems in which only a subset of the nuclei are treated quantum mechanically. For example, often only the hydrogen nuclei are chosen for the quantum subsystem, while all other nuclei are included in the classical subsystem. The specified quantum nuclei are treated analogously to the electrons, and properties of the system are averaged over the mixed nuclear–electronic wave function. The coordinates of the centers of the nuclear basis functions as well as the coefficients of the molecular orbitals are optimized variationally. As a result, the NEO potential energy surface depends explicitly on only the coordinates of the classical nuclei and has reduced dimensionality relative to the full nuclear potential energy surface. Moreover, the location and character of the stationary points may be substantially different for the NEO potential energy surface than for the full nuclear potential energy surface.

Previously a number of groups have investigated similar approaches. Tachikawa, Nakai and co-workers have developed the nuclear orbital molecular orbital (NOMO) method. They have implemented the NOMO–HF (Hartree–Fock) (Refs. 2 and 3). NOMO–CIS (configuration interaction method with singles) (Ref. 4), and NOMO–MBPT (many-body perturbation theory) (Ref. 5) approaches. Kreibich and Gross have developed a nuclear–electronic method based on density functional theory. Shigeta and co-workers have also explored related methods. To our knowledge, these previous groups have not calculated the Hessians or performed vibrational analyses within the nuclear–electronic framework. A vibrational analysis is required for the investigation of chemical reactions on the vibrational–electronic potential energy surface.

In this paper, we present the methodology to perform a NEO vibrational analysis and discuss the physical implications of such an analysis. The methodology involves the calculation of a numerical Hessian, the projection of this Hessian to remove the overall translational and rotational motions, and the diagonalization of the projected Hessian to determine the harmonic vibrational frequencies corresponding to the classical nuclei. The analysis of these frequencies allows the characterization of stationary points on the NEO potential energy surface. Specifically, minima have all real frequencies, transition states have one imaginary frequency, and higher-order saddle points have more than one imaginary frequency. This analysis also enables the calculation of zero point energy corrections and thermodynamic properties such as enthalpy, entropy, and free energy changes for reactions.
on the NEO potential energy surface. Furthermore, the numerical Hessian may be used in the generation of minimum energy paths, or intrinsic reaction coordinates, on the NEO potential energy surface. This paper presents illustrative applications of the vibrational analysis to a series of representative molecules, including HCN, the protonated water dimer, and triazene, as well as to the reaction profile for an identity nucleophilic substitution (SN2) reaction.

II. THEORY

The theoretical formulation for the NEO method is presented in Ref. 1. This previous paper includes the equations required for the implementation of the NEO–HF (Hartree–Fock), the NEO–CI (configuration interaction), and the NEO–MCSCF (multiconfigurational self-consistent-field) methods, as well as the equations for the NEO–HF and NEO–MCSCF gradients. The DZSPDN nuclear basis set is also described in Ref. 1. The NEO methodology has been implemented in the GAMESS electronic structure program.10

The present paper focuses on the NEO–HF method, although the analysis is directly applicable to other NEO methods such as NEO–CI and NEO–MCSCF. This section summarizes the NEO–HF method and presents the theoretical formulation for the NEO vibrational analysis.

A. Summary of the NEO–HF method

In the NEO approach, the system is divided into three parts: \(N_e\) electrons, \(N_p\) quantum nuclei, and \(N_c\) classical nuclei. The equations presented in Ref. 1 are derived for fermionic quantum nuclei, but the extension to bosons is straightforward. At the Hartree–Fock level the total nuclear–electron wave function can be approximated as a product of single-configurational electronic and nuclear wave functions:

\[
\Psi_{tot}(\mathbf{r}, \mathbf{p}) = \Phi^e_0(\mathbf{r}) \Phi^p_0(\mathbf{p}),
\]

where \(\Phi^e_0(\mathbf{r})\) and \(\Phi^p_0(\mathbf{p})\), respectively, are antisymmetrized wave functions (determinants of spin orbitals) representing the electrons and fermionic nuclei such as protons. (Here \(\mathbf{r}^e\) and \(\mathbf{p}^p\) denote the spatial coordinates of the electrons and quantum nuclei, respectively.)

The total energy expression for a restricted Hartree–Fock (RHF) treatment of the electrons and a high-spin open-shell treatment of the quantum nuclei is given by

\[
E = 2 \sum_{i}^{N_e/2} h_{i,i} + \sum_{i}^{N_p/2} \sum_{j}^{N_p/2} \left[ 2(\psi^e_i \psi^e_j | \psi^e_i \psi^e_j) - (\psi^e_i \psi^e_j | \psi^p_i \psi^p_j) \right]
\]

\[
+ \sum_{i}^{N_p} h_{i,i} + \frac{1}{2} \sum_{i}^{N_p} \sum_{j}^{N_p} \left( (\psi^p_i \psi^p_j | \psi^p_i \psi^p_j) \right) - \sum_{i}^{N_e/2} \sum_{j}^{N_e/2} \sum_{l}^{N_p} \left( \psi^e_i \psi^e_j | \psi^p_l \psi^p_l \right) - \sum_{i}^{N_e/2} \sum_{j}^{N_e/2} \sum_{l}^{N_p} \left( \psi^e_i \psi^e_j | \psi^p_l \psi^p_l \right),
\]

where the integrals are defined as

\[
h_{i,j}^p = \int d\mathbf{r}_j \psi^p_\theta^\ast(\mathbf{r}_j) h^p(\mathbf{r}_j) \psi^p_\theta(\mathbf{r}_j),
\]

\[
h^e(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A}^{N_p} \frac{Z_A}{r_{iA}},
\]

\[
h^p(i') = -\frac{1}{2M_{i'}} \nabla_{i'}^2 + \sum_{A}^{N_p} \frac{Z_A Z_{i'w}}{r_{i'w}},
\]

\[
(\psi_i^e \psi_j^e | \psi_l^p \psi_l^p) = \int d\mathbf{r}_j \int d\mathbf{r}_l \psi^e_i(\mathbf{r}_j) \psi^e_j(\mathbf{r}_j) \frac{1}{r_{l1}^{12}} \psi^p_l(\mathbf{r}_j) \psi^p_l(\mathbf{r}_j),
\]

and analogously for two-particle integrals involving the quantum nuclei. Here the spatial molecular orbitals for the electrons are denoted \(\psi^e_i\) and the spatial molecular orbitals for the quantum nuclei are denoted \(\psi^p_i\). The unprimed indices \(i, j\) refer to electrons, the primed indices \(i', j'\) refer to quantum nuclei, and the indices \(A, B\) refer to classical nuclei. The masses, charges, and distances, respectively, are denoted by \(M, Z, r\) with the appropriate subscripts.

The spatial orbitals for the electrons and the quantum nuclei are expanded in Gaussian basis sets (where there are \(N_{bf}^e\) electronic basis functions and \(N_{bf}^p\) nuclear basis functions):

\[
\psi^e_1(\mathbf{r}) = \sum_{\mu} c_{\mu}^e \varphi^e_{\mu}(\mathbf{r}),
\]

\[
\psi^p_1(\mathbf{r}) = \sum_{\mu} c_{\mu}^p \varphi^p_{\mu}(\mathbf{r}).
\]

(Here the unprimed indices \(\mu, \nu, \sigma, \lambda\) refer to electronic basis functions, and the primed indices refer to nuclear basis functions.) The Hartree–Fock equations have been derived using the standard variation method to minimize the energy in Eq. (2) with respect to both the electronic and nuclear molecular orbitals. The resulting Hartree–Fock–Roothaan equations are

\[
\sum_{\nu} F_{\mu \nu}^e c_{\nu}^e = e_{\nu} c_{\nu}^e \sum_{\nu} S_{\mu \nu}^e c_{\nu}^e, \quad i = 1, \ldots, N_e/2,
\]

\[
\sum_{\nu'} F_{\mu' \nu'}^p c_{\nu'}^p = \rho_{\mu' \nu'}^p \sum_{\nu'} S_{\mu' \nu'}^p c_{\nu'}^p, \quad i' = 1, \ldots, N_p.
\]
and the standard one-particle and two-particle parts are defined as

\[ \hat{h}_{\mu \nu}^e = \int d\mathbf{r}_1 \psi_{\mu}^e(1) \psi_{\nu}^e(1), \]

\[ \hat{h}_{\mu \nu}^p = \int d\mathbf{r}_1 \psi_{\mu}^p(1) \psi_{\nu}^p(1), \]

\[ G_{\mu \nu}^e = \sum_{\kappa \sigma} P_{\kappa \sigma}^e \left[ (\psi_{\kappa}^e \psi_{\sigma}^e \psi_{\nu}^e \psi_{\mu}^e) - \frac{1}{2} (\psi_{\kappa}^e \psi_{\sigma}^e \psi_{\nu}^e \psi_{\mu}^e) \right]. \]

The energy gradient with respect to the nuclear coordinates for the NEO–HF method in the atomic orbital basis is

\[ \frac{\partial E}{\partial R_n} = \sum_{\mu \nu} W_{\mu \nu}^e \frac{\partial h_{\mu \nu}^e}{\partial R_n} + \sum_{\mu \nu \lambda \kappa} \left\{ \frac{1}{2} P_{\mu \nu}^e P_{\lambda \kappa}^e - \frac{1}{2} P_{\mu \lambda}^e P_{\nu \kappa}^e \right\} \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \sum_{\mu \nu} W_{\mu \nu}^p \frac{\partial h_{\mu \nu}^p}{\partial R_n} + \sum_{\mu \nu} \sum_{\lambda \kappa} P_{\mu \lambda}^p P_{\nu \kappa}^p \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \frac{1}{2} \sum_{\mu \nu} \sum_{\lambda \kappa} \left\{ P_{\mu \nu}^p P_{\lambda \kappa}^p - P_{\mu \lambda}^p P_{\nu \kappa}^p \right\} \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \sum_{\mu \nu} W_{\mu \nu}^e \frac{\partial S_{\mu \nu}}{\partial R_n} + \sum_{\mu \nu} \sum_{\lambda \kappa} P_{\mu \lambda}^p P_{\nu \kappa}^p \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n}.

For fixed classical nuclei and quantum nuclear basis function centers, the electronic and nuclear Hartree–Fock–Roothaan equations can be solved iteratively to self consistency utilizing convergence accelerators previously developed for electronic structure theory.\(^\text{11}\) In our calculations, the nuclear Fock equations are fully converged after each step in the iterative procedure for the solution of the electronic Fock equations. Other iterative schemes are possible and may be more efficient for different types of systems.

The energy gradient with respect to the nuclear coordinates for the NEO–HF method in the atomic orbital basis is

\[ E_{\text{NEO}}(\mathbf{R}_{\text{class}}) = \sum_{\mu \nu} W_{\mu \nu}^e \frac{\partial h_{\mu \nu}^e}{\partial R_n} + \sum_{\mu \nu \lambda \kappa} \left\{ \frac{1}{2} P_{\mu \nu}^e P_{\lambda \kappa}^e - \frac{1}{2} P_{\mu \lambda}^e P_{\nu \kappa}^e \right\} \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \sum_{\mu \nu} W_{\mu \nu}^p \frac{\partial h_{\mu \nu}^p}{\partial R_n} + \sum_{\mu \nu} \sum_{\lambda \kappa} P_{\mu \lambda}^p P_{\nu \kappa}^p \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \frac{1}{2} \sum_{\mu \nu} \sum_{\lambda \kappa} \left\{ P_{\mu \nu}^p P_{\lambda \kappa}^p - P_{\mu \lambda}^p P_{\nu \kappa}^p \right\} \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n} - \sum_{\mu \nu} W_{\mu \nu}^e \frac{\partial S_{\mu \nu}}{\partial R_n} + \sum_{\mu \nu} \sum_{\lambda \kappa} P_{\mu \lambda}^p P_{\nu \kappa}^p \frac{\partial (\mu \nu | \lambda \kappa)}{\partial R_n}.

The NEO potential energy surface is optimized iteratively with respect to the nuclear basis function centers. The surface depends explicitly on the nuclear basis function centers and parametrically on the classical nuclear positions. Each point corresponding to a fixed \(\mathbf{R}_{\text{cent}}\) and \(\mathbf{R}_{\text{class}}\) on this nuclear basis function surface is optimized variationally with respect to the molecular orbital coefficients by solving the Hartree–Fock–Roothaan equations in Eqs. (10) and (11) using iterative techniques. Each point on the NEO potential energy surface \(E_{\text{NEO}}(\mathbf{R}_{\text{class}})\) is obtained using geometry optimization techniques to minimize \(E_{\text{NEO}}(\mathbf{R}_{\text{cent}}; \mathbf{R}_{\text{class}})\) with respect to the nuclear basis function centers \(\mathbf{R}_{\text{cent}}\). The gradient with respect to the nuclear basis function centers for the surface \(E_{\text{NEO}}(\mathbf{R}_{\text{cent}}; \mathbf{R}_{\text{class}})\) is given by Eq. (22).

The NEO potential energy surface may be described in terms of the location and characterization of the stationary points. The stationary points on the NEO potential energy surface are defined to be geometries at which the gradients of the energy with respect to the classical nuclear coordinates \(\mathbf{R}_{\text{class}}\) are zero. (Note that by definition the gradients with respect to the nuclear basis function centers are zero at all points on the NEO potential energy surface.) The gradient with respect to the classical nuclear coordinates for each point on the NEO potential energy surface is given by Eq. (22). The gradient expression is the same for the nuclear basis function centers and the classical nuclear coordinates because the nuclear basis function surface \(E_{\text{NEO}}(\mathbf{R}_{\text{cent}}; \mathbf{R}_{\text{class}})\) is optimized with respect to the molecu-
lar orbital coefficients, and the NEO surface $E_{\text{NEO}}(R_{\text{class}})$ is optimized with respect to the molecular orbital coefficients and the nuclear basis function centers. The stationary points on the NEO potential energy surface are located using geometry optimization techniques. These stationary points may be characterized by calculating a Hessian matrix (i.e., second derivative matrix) for the NEO potential energy surface.

The elements of the Hessian matrix $K$ can be calculated numerically with the following expression:

$$K_{ij} = \left( \frac{\partial^2 E_{\text{NEO}}}{\partial R_i \partial R_j} \right)_{R_{\text{class}}} = \left. \left( \frac{\partial g_i}{\partial R_j} \right)_{R_{\text{class}}} \right|_{R_{\text{class}}} \cdot$$

where the subscript $R_{\text{class}}$ denotes the coordinates of the classical nuclei corresponding to the point on the NEO potential energy surface at which the second derivative is being evaluated. The gradients are defined as

$$g_i = \left( \frac{\partial E_{\text{NEO}}}{\partial R_{\text{class},i}} \right)_{R_{\text{class}}} = \frac{\partial E_{\text{NEO}}}{\partial R_{\text{class},i}} \cdot$$

Although the calculations presented in this paper were obtained with Eq. (25), which requires a single displacement of coordinate $R_{\text{class},i}$ by an amount $\delta$, the second derivative can also be calculated symmetrically with a double displacement. The mass-weighted Hessian $K'$ is defined as

$$K'_{ij} = \frac{1}{\sqrt{m_i m_j}} K_{ij} \cdot$$

Diagonalization of the mass-weighted Hessian leads to the set of eigenvalues $\{\lambda_i\}$, which are used to calculate the harmonic vibrational frequencies

$$\nu_i = \sqrt{\lambda_i} \cdot$$

We have implemented the numerical calculation of the Hessian and the determination of the harmonic vibrational frequencies within the NEO framework. Note that for each coordinate displacement required to calculate the numerical Hessian [i.e., Eq. (25)], the energy must be optimized with respect to the nuclear basis function centers to remain on the NEO potential energy surface.

For the exact Hessian, the eigenvalues corresponding to overall translation and rotation of the entire molecule are zero because the energy and gradient are invariant to these motions. As a result, for nonlinear (linear) molecules, six (five) of the frequencies are zero. For the numerical Hessian, the eigenvalues corresponding to overall translational and rotational motions are not exactly zero due to numerical error. The Hessian matrix can be projected to make these eigenvalues identically zero:

$$K'^P = (I - P) K' (I - P) \cdot$$

where $I$ is the identity matrix and $P$ is the projection matrix defined in Ref. 13. We have implemented this projection procedure and the Sayvetz conditions$^{14}$ for the NEO method. Note that only the classical nuclei are included in the calculation of the projection matrix (i.e., the masses of the quantum nuclei are neglected).

We emphasize that the Hessian matrix for the NEO potential energy surface is fundamentally different from the Hessian matrix for the full nuclear potential energy surface because each point on the NEO potential energy surface is optimized with respect to the nuclear basis function centers. The optimization with respect to the nuclear basis function centers maintains the translational and rotational invariance of the classical nuclei. The physical significance of this optimization may be illustrated with the diatomic molecule HCl. If the H nucleus is treated quantum mechanically in the NEO approach, the NEO potential energy surface depends on only the three coordinates of the Cl atom. These three coordinates correspond to the translational degrees of freedom for the molecule. Thus, the HCl molecule within the NEO framework is analogous to a single atom in a conventional electronic structure calculation for which all nuclei are treated classically. As expected, the diagonalization of the NEO Hessian matrix for HCl results in three zero eigenvalues, indicating that the NEO energy is translationally invariant for HCl. If the nuclear basis function centers were not optimized for each step of the numerical Hessian calculation, however, the eigenvalues of the HCl Hessian matrix would no longer be zero and the NEO energy would not be translationally invariant. An analogous argument may be applied to larger molecules in terms of both translational and rotational invariance. An alternative approach that would also maintain translational and rotational invariance would be to define the positions of the nuclear basis function centers with respect to the positions of specified classical nuclei (i.e., to constrain the distance between the nuclear basis function center and the Cl atom for the HCl molecule). This alternative approach is problematic for a hydrogen transfer reaction, where the position of the hydrogen nuclear basis function center relative to the classical donor and acceptor nuclei changes during the reaction. Moreover, the optimization of the nuclear basis function centers avoids the bias introduced by this alternative approach.

The analysis of the Hessian can be used to characterize stationary points on the NEO potential energy surface and to calculate zero point energy corrections. A NEO point with all positive frequencies is a minimum, a NEO point with only one imaginary frequency is a transition state, and a NEO point with more than one imaginary frequency is a higher-order saddle point. The zero point energy (ZPE) (i.e., zero temperature vibrational energy) correction is

$$ZPE = \frac{1}{2} \sum_i h \nu_i \cdot$$

where the summation is over all positive frequencies.

The Hessian may also be used to calculate thermodynamic quantities such as vibrational enthalpy, entropy, and free energy changes. The vibrational contributions to the enthalpy, entropy, and free energy are$^{12,15}$

$$H_{\text{vib}} = k_B \sum_i \left( \frac{h \nu_i}{2k_B} + \frac{h \nu_i}{k_B} \exp(h \nu_i/k_B T) - 1 \right) \cdot$$

where $k_B$ is Boltzmann's constant and $T$ is the temperature.
\[
S_{\text{vib}} = R \sum_i \left( \frac{1}{k_B T} \exp \left( \frac{h \nu_i}{k_B T} \right) - 1 \right) - \ln \left( 1 - \exp \left( \frac{h \nu_i}{k_B T} \right) \right),
\]

where \( h \) is Planck’s constant, \( k_B \) is Boltzmann’s constant, \( R \) is the ideal gas constant, and the summations are over all positive frequencies. The translational and rotational contributions to the thermodynamic quantities can be calculated in the usual way for the NEO structures. In general, the quantum nuclei should be included in the calculation of the translational and rotational thermodynamic quantities (i.e., for the calculation of the center of mass and the moments of inertia). Thus, for the calculation of translational and rotational thermodynamic quantities, the molecule should be viewed as having \( N_c + N_p \) atoms and therefore \( 3(N_c + N_p) \) degrees of freedom. (In practice, the positions of the quantum nuclei can be approximated to be either the basis function centers or the expectation values of the quantum nuclear coordinates for localized molecular orbitals.) There are three translational and three (two) rotational degrees of freedom for a nonlinear (linear) molecule. The remaining degrees of freedom are vibrational, where some are the nonzero classical vibrational modes calculated from the NEO Hessian and the remainder are quantum vibrational modes included in the NEO vibrational–electronic energy. The quantum vibrational and electronic contributions to the thermodynamic quantities can be calculated from the excited NEO vibrational–electronic states. Often the contributions from these excited states are negligible because the splittings between the states are much larger than the thermal energy. These excited states are not included at the NEO–HF level but will be included for NEO–MCSCF and NEO–CI calculations of thermodynamic quantities.

Although we have presented this vibrational analysis in the framework of the NEO–HF method, the analogous procedure is applicable to NEO extensions such as multiconfigurational methods (i.e., NEO–CI and NEO–MCSCF), assuming the availability of analytical gradients. Reference 1 presents the analytical gradients for the NEO–MCSCF method. This vibrational analysis is also valid with different basis sets and with multiple basis function centers. All of this methodology has been included in the NEO implementation within the GAMESS electronic structure program.\(^{10}\)

III. RESULTS

We have performed geometry optimizations and calculated Hessian matrices for a series of molecules. For each system, we performed both a conventional electronic structure calculation in which all nuclei are treated classically and a NEO calculation in which one or all hydrogen nuclei are treated quantum mechanically. The electronic basis set used for HCN, the protonated water dimer, and triazene was 6-31G(d,p)\(^{16–19}\) and the electronic basis set used for the \( \text{S}_2 \text{O}_2 \) reaction was 6-31+G(d,p) (Ref. 20) to include diffuse functions for anions. The nuclear basis set used for all NEO calculations is DZSPDN with a single nuclear basis function center for each hydrogen nucleus. The DZSPDN basis set includes two each of \( s, p, \) and \( d \)-type Gaussians, resulting in a total of 20 nuclear basis functions per hydrogen.\(^1\) The electronic basis functions corresponding to each quantum hydrogen are centered at the same position as the corresponding nuclear basis function center. We computed the geometries and frequencies for HCN, \( \text{H}_2\text{O}^+ \), and \( \text{N}_3\text{H}_3 \). Furthermore, we calculated the reaction profile for an identity nucleophilic substitution (\( \text{S}_2\text{O}_2 \)) reaction. We do not expect these results to be quantitatively accurate because they are calculated at the Hartree–Fock level. The aim of these calculations is to illustrate the underlying principles involved in the NEO vibrational analysis rather than to provide quantitatively accurate results.

Figure 1 depicts the NEO optimized structure for the HCN molecule. In the NEO calculations, the hydrogen nucleus is treated quantum mechanically. Therefore, the NEO potential energy surface is analogous to the six-dimensional conventional surface for a diatomic molecule. Removing the five overall translational and rotational motions, the NEO–HF potential energy surface has only one vibrational frequency, 2543 cm\(^{-1}\), which corresponds to the C–N vibrational motion. The C–N distance is similar for the conventional RHF (1.1328 Å) and NEO–HF (1.1331 Å) calculations.

The protonated water dimer (\( \text{H}_2\text{O}^+ \)) has been the focus of many theoretical studies.\(^{21–23}\) These previous studies indicate that this system is highly sensitive to the level of theory and the basis set. At the RHF level, the \( C_1 \) symmetry structure is a minimum and the \( C_2 \) symmetry structure is a transition state. For higher levels of theory including electron correlation, however, the \( C_2 \) symmetry structure is a minimum and the \( C_1 \) symmetry structure is a transition state.\(^{21}\) For all levels of theory, the potential energy surface is extremely flat for this system. Thus, quantitatively accurate results for the protonated water dimer require large basis sets and the inclusion of electronic correlation. We emphasize that the aim of the present calculations is only to illustrate the utility of the NEO methodology and not to provide quantitatively accurate results for this specific system.

In our initial studies of the protonated water dimer, we performed a NEO–HF calculation in which only the central hydrogen nucleus is treated quantum mechanically. We found that the \( C_2 \) symmetry structure is a minimum and the \( C_1 \) symmetry structure is a transition state 0.02 kcal/mol higher in energy. For comparison, at the conventional RHF/
6-31G(d,p) level, the \( C_s \) symmetry structure is a minimum and the \( C_2 \) symmetry structure is a transition state 0.15 kcal/mol higher in energy. Interestingly, the NEO approach alters the nature of the Hartree–Fock stationary points in a similar manner as the inclusion of electronic correlation. The imaginary frequency for the conventional RHF \( C_2 \) transition state is 452 cm\(^{-1}\), and the mode is dominated by the motion of the central hydrogen nucleus. In the NEO calculation, however, this central hydrogen is treated quantum mechanically. The imaginary frequency for the NEO–HF \( C_s \) transition state is 149 cm\(^{-1}\), and the mode is dominated by the twisting motion of the four exterior hydrogen nuclei. Note that the physical meaning of the imaginary mode is fundamentally different for the conventional RHF and NEO–HF calculations for this system. Figure 2 provides a comparison between the conventional RHF and NEO–HF geometries with \( C_2 \) and \( C_s \) symmetries. The most significant difference is the O–O distance for the \( C_2 \) symmetry stationary point, where the conventional RHF distance is 2.3619 Å and the NEO–HF distance is 2.3950 Å.

We also performed a NEO calculation in which all five hydrogen nuclei are treated quantum mechanically. As for the HCN molecule, the resulting NEO potential energy surface is six dimensional. Removing the five overall translational and rotational motions, the single vibrational mode of frequency 673 cm\(^{-1}\) corresponds to the O–O vibrational motion. The NEO–HF O–O distance is 2.3930 Å, which is virtually identical to the conventional RHF distance of 2.3941 Å.

In addition, we performed NEO calculations for triazene (\( N_2H_3 \)). In these NEO calculations, all three hydrogen nuclei were treated quantum mechanically, so the NEO potential energy surface is nine dimensional. Removing the overall translational and rotational motions, there are three molecular vibrations with frequencies 787, 1133, and 1832 cm\(^{-1}\) corresponding to the vibrational motions of the nitrogen atoms. As shown in Fig. 3, the NEO–HF geometry is similar to the conventional RHF geometry for triazene.

To illustrate the calculation of stationary points for a chemical reaction on the NEO potential energy surface, we examined the following \( S_N2 \) reaction:

\[
\text{Cl}^- + \text{CH}_3\text{Cl} \rightleftharpoons \text{ClCH}_3 + \text{Cl}^-.
\]

In the NEO calculations, the three hydrogen nuclei are treated quantum mechanically. As for triazene, the NEO potential energy surface is nine dimensional with three vibrational modes after removal of the six overall translational and rotational motions. The NEO transition state structure is shown in Fig. 4. The C–Cl distance at the transition state is similar for the NEO–HF (2.4066 Å) and conventional RHF (2.3954 Å) methods. The imaginary frequency is also similar for the NEO–HF (421 cm\(^{-1}\)) and conventional RHF (426 cm\(^{-1}\)) methods, and the mode is dominated by the motion of the carbon and chlorine atoms. Note that these imaginary frequencies are similar because the nuclei treated quantum mechanically in the NEO calculations do not contribute significantly to this imaginary mode.

The energy profile for this reaction is illustrated schematically in Fig. 5.\(^{24}\) The reaction involves the initial formation of a reactant ion–molecule complex, which has a complexation energy \( \Delta E_{\text{comp}} \) relative to separated reactants. The reactant complex surmounts the central activation barrier.
The overall activation barrier relative to separated reactants is denoted \( \Delta E_{\text{cent}} \), which breaks down into the ion–molecule complex and finally into separated products. The activation barrier relative to separated reactants is denoted \( \Delta E_{\text{ovr}} \). The calculations were done with \( C_{3v} \) symmetry for the reactant and reactant complex and \( D_{1h} \) symmetry for the transition state. Table I presents the NEO–HF and conventional RHF energies with and without zero point energy corrections, as well as the enthalpies and free energies at 298 K corresponding to the three types of barriers defined in Fig. 5. Note that the aim of these calculations is to illustrate the application of the NEO approach to chemical reactions rather than to obtain quantitatively accurate results. Previous studies have shown that electronic correlation is required to obtain quantitatively accurate results for this \( \text{S}_2\text{N}_2 \) reaction.

The NEO–HF and conventional RHF results are very similar for the \( \text{S}_2\text{N}_2 \) reaction. This similarity arises because the hydrogen atoms are not actively participating in the chemical reaction (i.e., bonds involving hydrogen atoms are not broken or formed). The NEO approach is expected to differ significantly from conventional electron structure approaches for reactions involving the transfer of a hydrogen nucleus. As mentioned in Ref. 1, however, hydrogen transfer reactions require the use of multiple basis functions and multiconfigurational wave functions.

**IV. CONCLUSIONS**

This paper presents the methodology and illustrative applications for a vibrational analysis within the NEO framework. In the NEO approach, specified nuclei are treated quantum mechanically on the same level as the electrons. Each point on the NEO potential energy surface is optimized variationally with respect to the electronic and nuclear molecular orbital coefficients and the nuclear basis function centers. The stationary points on the NEO potential energy surface are defined to be geometries at which the gradients with respect to the classical nuclear coordinates are zero. These stationary points may be located using geometry optimization techniques. The NEO vibrational analysis methodology involves the calculation, projection, and diagonalization of a numerical Hessian to obtain the harmonic vibrational frequencies corresponding to the classical nuclei. This analysis allows the characterization of stationary points on the NEO potential energy surface, the calculation of zero point energy corrections, and the calculation of thermodynamic properties such as enthalpy, entropy, and free energy for chemical reactions on the NEO potential energy surface.

The NEO vibrational analysis will be particularly useful for applications to hydrogen transfer reactions, which exhibit substantial nuclear quantum effects. For these types of reactions, the transferring hydrogen nucleus is treated quantum mechanically and the minimum energy path includes the significant nuclear quantum effects such as zero point energy and hydrogen tunneling. This approach maintains the conceptual picture of a reaction path, while eliminating the difficulties associated with large curvature of the reaction path for the transfer of light nuclei. For many hydrogen transfer reactions, the nuclear wave function corresponding to the transferring hydrogen is bilobal at the transition state. The application of NEO to these types of hydrogen transfer reactions requires the use of multiple nuclear basis function centers and multiconfigurational wave functions. The NEO vibrational analysis methodology is directly applicable to these types of reactions and will allow the location and characterization of stationary points, as well as the calculation of energetics and thermodynamic properties, for hydrogen transfer reactions.

The application of the NEO approach to hydrogen transfer reactions is analogous to conventional calculations for electron transfer reactions. In the NEO approach, the reaction coordinate of the minimum energy path for a hydrogen transfer reaction depends explicitly on only the classical nuclei.

**TABLE I. NEO–HF barriers for the \( \text{S}_2\text{N}_2 \) reaction depicted in Fig. 5.** The conventional RHF barriers are given in parentheses. The quantities provided are the NEO vibrational–electronic energy \( \Delta E \), the NEO vibrational–electronic energy with zero point energy corrections \( \Delta E(ZPE) \), the enthalpy \( \Delta H \), and the free energy \( \Delta G \) at 298 K.

<table>
<thead>
<tr>
<th>Barrier type</th>
<th>( \Delta E ) (( \Delta E(ZPE) ))</th>
<th>( \Delta H ) (( \Delta H ))</th>
<th>( \Delta G ) (( \Delta G ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complexation</td>
<td>9.17 (8.96) 9.00 (8.75)</td>
<td>8.99 (8.71) 3.65 (3.51)</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>6.35 (6.43) 6.10 (6.09)</td>
<td>5.60 (5.64) 13.24 (13.18)</td>
<td></td>
</tr>
<tr>
<td>Central</td>
<td>15.52 (15.39) 15.10 (14.83)</td>
<td>14.59 (14.35) 16.89 (16.69)</td>
<td></td>
</tr>
</tbody>
</table>

This paper presents the methodology and illustrative applications for a vibrational analysis within the NEO framework. In the NEO approach, specified nuclei are treated quantum mechanically on the same level as the electrons. Each point on the NEO potential energy surface is optimized variationally with respect to the electronic and nuclear molecular orbital coefficients and the nuclear basis function centers. The stationary points on the NEO potential energy surface are defined to be geometries at which the gradients with respect to the classical nuclear coordinates are zero. These stationary points may be located using geometry optimization techniques. The NEO vibrational analysis methodology involves the calculation, projection, and diagonalization of a numerical Hessian to obtain the harmonic vibrational frequencies corresponding to the classical nuclei. This analysis allows the characterization of stationary points on the NEO potential energy surface, the calculation of zero point energy corrections, and the calculation of thermodynamic properties such as enthalpy, entropy, and free energy for chemical reactions on the NEO potential energy surface.

The NEO vibrational analysis will be particularly useful for applications to hydrogen transfer reactions, which exhibit substantial nuclear quantum effects. For these types of reactions, the transferring hydrogen nucleus is treated quantum mechanically and the minimum energy path includes the significant nuclear quantum effects such as zero point energy and hydrogen tunneling. This approach maintains the conceptual picture of a reaction path, while eliminating the difficulties associated with large curvature of the reaction path for the transfer of light nuclei. For many hydrogen transfer reactions, the nuclear wave function corresponding to the transferring hydrogen is bilobal at the transition state. The application of NEO to these types of hydrogen transfer reactions requires the use of multiple nuclear basis function centers and multiconfigurational wave functions. The NEO vibrational analysis methodology is directly applicable to these types of reactions and will allow the location and characterization of stationary points, as well as the calculation of energetics and thermodynamic properties, for hydrogen transfer reactions.

The application of the NEO approach to hydrogen transfer reactions is analogous to conventional calculations for electron transfer reactions. In the NEO approach, the reaction coordinate of the minimum energy path for a hydrogen transfer reaction depends explicitly on only the classical nuclei.
analogous to the collective reaction coordinate in Marcus theory for electron transfer. The NEO reaction coordinate for hydrogen transfer does not depend on the transferring hydrogen coordinate for the same reason that the conventional reaction coordinate for electron transfer does not depend on the electron coordinates. The NEO transition state corresponds to the classical nuclear configuration for which the transferring hydrogen nuclear wave function is delocalized between the donor and acceptor classical nuclei. Analogously, the conventional transition state for electron transfer is the nuclear configuration for which the adiabatic electronic wave function is delocalized between the donor and acceptor, also described as the configuration for which the reactant and product diabatic electronic states are degenerate. In both the NEO approach for hydrogen transfer and the conventional approach for electron transfer, the imaginary mode at the transition state corresponds to the heavy-atom motion that drives the charge transfer reaction via the reorganization of the environment. In contrast, the imaginary mode at the transition state for a conventional hydrogen transfer minimum-energy path is dominated by the transferring hydrogen coordinate itself.

The description of hydrogen transfer reactions in terms of a collective, heavy-atom reaction coordinate together with a quantum mechanical representation of the transferring hydrogen has been shown to provide a physically meaningful framework for studying these reactions. The application of the NEO approach to hydrogen transfer reactions will provide mechanistic insight by enabling the identification of the dominant heavy-atom motions contributing to the collective reaction coordinate. These motions are significant because they correspond to the reorganization of the environment necessary for the charge transfer process. In addition, the NEO approach will allow accurate calculations of rates and kinetic isotope effects for hydrogen transfer reactions.

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