Electron-Proton Correlation for Hydrogen Tunneling Systems

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Hydrogen tunneling is important for numerous chemical and biological processes. We study this phenomenon with a multiconfigurational nuclear-electronic orbital approach. Our results demonstrate that a single configuration nuclear-electronic wave function is inadequate to describe hydrogen tunneling systems because such wave functions do not include the essential electron-proton correlation. A state-averaged multiconfigurational approach is proposed as a practical method for potentially including sufficient electron-proton correlation to obtain delocalized nuclear-electronic wave functions for these systems.

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Hydrogen tunneling is essential to a wide range of chemical and biological processes, including photosynthesis, respiration, and enzyme reactions [1]. The elucidation of the underlying principles of these important processes requires a detailed microscopic understanding of this fundamentally quantum mechanical phenomenon. In conventional electronic structure calculations, the electronic wave function is calculated in a field of nuclei represented as classical point charges. This conventional approach breaks down for hydrogen tunneling systems, which require a quantum mechanical treatment of the hydrogen nucleus. Invoking the Born-Oppenheimer separation of the hydrogen nucleus and the electrons, the hydrogen vibrational wave functions can be calculated for the nucleus moving in a symmetric double well potential representing the electronic ground state, as shown in Fig. 1 [2–4]. An alternative perspective is provided by the recently developed multiconfigurational nuclear-electronic orbital (NEO) approach [5,6], in which specified nuclei are treated quantum mechanically on the same level as the electrons without invoking the Born-Oppenheimer separation [7–11].

In this Letter, we use the NEO approach to provide new insights into fundamental aspects of electron-proton correlation in hydrogen tunneling systems. We show that a single configuration Hartree-Fock nuclear-electronic wave function is inadequate for the description of hydrogen tunneling systems. In conventional electronic structure theory, electron correlation is defined as the difference between the exact energy and the single configuration Hartree-Fock energy and is divided into two different effects: nondynamical correlation arises from the influence of other configurations that are close in energy to and mix strongly with the Hartree-Fock configuration, and dynamical correlation arises from difficulties in describing the r^{-1} potential energy interactions that become singular as the electron separation distance $r \rightarrow 0$ [12]. Typically nondynamical correlation is required to obtain qualitatively correct electronic wave functions for certain types of systems (e.g., diradicals and bond-breaking reactions), while dynamical correlation is included to enhance the quantitative accuracy of electronic energies for general systems. Within the framework of the NEO approach, electron-proton correlation can also be divided into nondynamical and dynamical effects. We find that dynamical correlation plays a more central role in the calculation of nuclear-electronic wave functions because an electron and proton have opposite charges that lead to attractive Coulomb interactions, in contrast to the repulsive Coulomb interactions between electrons. Our analytical and numerical calculations for model systems elucidate the underlying physical nature of both nondynamical and dynamical electron-proton correlation. Moreover, we propose the state-averaged multiconfigurational NEO approach as a practical method for potentially including sufficient electron-proton correlation in applications to chemically and biologically relevant hydrogen tunneling systems.

We illustrate the basic concepts of electron-proton correlation with several model systems. The simplest model system is comprised of one electron and one proton that are each represented by one basis function centered at $\mathbf{R}_1$ and another identical basis function centered at $\mathbf{R}_2$, where $\mathbf{R}_1$ and $\mathbf{R}_2$ denote spatial coordinates. The two electronic basis functions are denoted φ_1^e, φ_2^e and the two nuclear

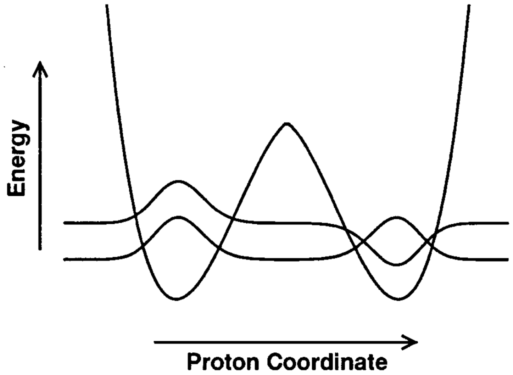

FIG. 1. Schematic picture of a hydrogen nucleus moving in a symmetric double well potential. The lowest two nuclear vibrational wave functions are depicted.

basis functions are denoted φ_1^p, φ_2^p, where the subscripts 1 and 2 indicate the basis function center. (Here the dependence of the electronic basis functions on the electron coordinate and the dependence of the nuclear basis functions on the proton coordinate are omitted for clarity.) The overlaps of the electronic and nuclear basis functions are S_{12}^e and S_{12}^p. Based on the symmetry of this simple model system, the electronic and nuclear wave functions are expected to be delocalized equally over the two basis function centers (i.e., the wave function is a two-point representation of a free particle plane wave solution).

Consider the application of the NEO-HF (Hartree-Fock) method, in which the wave function is the product of an electronic and nuclear determinant, to this model system. The NEO-HF energy can be calculated variationally, and the lowest energy solution corresponds to a nonphysical wave function in which the electronic and nuclear densities are localized on one center:

$$\Psi_{\text{loc}}^{\text{HF}} = \varphi_1^e \varphi_1^p, \tag{1}$$

with energy

$$E_{\text{loc}}^{\text{HF}} = (\varphi_1^e|h^e|\varphi_1^e) + (\varphi_1^p|h^p|\varphi_1^p) - (\varphi_1^e\varphi_1^e|\varphi_1^p\varphi_1^p). \tag{2}$$

(The standard notation for the matrix elements is defined in Ref. [5].) Note that an analogous wave function $\Psi_{\text{loc},2}^{\text{HF}}$ with identical energy is localized on center 2. If we impose $D_{\infty h}$ symmetry, we obtain the symmetric delocalized wave function

$$\Psi_{\text{deloc}}^{\text{HF}} = \frac{1}{2\sqrt{(1+S_{12}^e)(1+S_{12}^p)}}(\varphi_1^e + \varphi_2^e)(\varphi_1^p + \varphi_2^p) \tag{3}$$

and, invoking the zero differential overlap approximation [13], the corresponding energy is

$$E_{\text{deloc}}^{\text{HF}} = E_{\text{loc}}^{\text{HF}} + \frac{1}{2}[(\varphi_1^e\varphi_1^e|\varphi_1^p\varphi_1^p) - (\varphi_1^e\varphi_1^e|\varphi_2^p\varphi_2^p)]. \tag{4}$$

In general, $(\varphi_1^e\varphi_1^e|\varphi_1^p\varphi_1^p) > (\varphi_1^e\varphi_1^e|\varphi_2^p\varphi_2^p)$, so $E_{\text{deloc}}^{\text{HF}} > E_{\text{loc}}^{\text{HF}}$. Although the zero differential overlap approximation is not rigorous, the relation between the localized and delocalized NEO-HF energies is valid for reasonable separations between the two basis function centers. The localized and delocalized nuclear wave functions are shown in Fig. 2. As discussed above, the localized nuclear wave function is nonphysical, whereas the delocalized nuclear wave function is qualitatively correct.

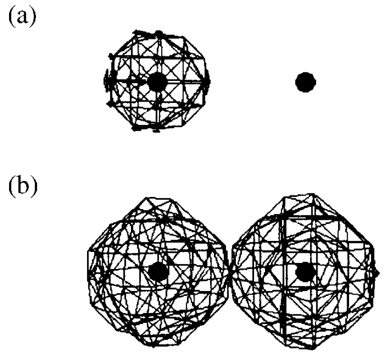

FIG. 2. Schematic picture of (a) localized and (b) delocalized nuclear molecular orbitals for a symmetric hydrogen tunneling system. The localized wave function is nonphysical, whereas the delocalized wave function is qualitatively correct.

The physical origin of the localized nuclear wave function in the NEO-HF approach is the attractive Coulomb interaction between the electron and the proton. For an analogous model system with two electrons, rather than one electron and one proton, the lowest energy Hartree-Fock solution is delocalized because of the repulsive Coulomb interaction between the two electrons. In this case, the electron-electron interaction terms corresponding to the electron-nuclear interaction terms in Eqs. (2) and (4) have opposite signs. As a result, the delocalized wave function is lower in energy than the localized wave function for an analogous model system with two electrons. This example illustrates that the opposite sign of the Coulomb interaction between the two particles leads to fundamentally different behavior for nuclear-electronic and pure electronic wave functions.

The accuracy of the NEO-HF solution can be systematically improved using multiconfigurational methods. For the NEO-CI (configuration interaction) and NEO-MCSCF (multiconfigurational self-consistent-field) methods, the wave function is a linear combination of products of electronic and nuclear determinants. In NEO-CI only the CI coefficients are optimized, while in NEO-MCSCF the electronic and nuclear molecular orbitals as well as the CI coefficients are optimized. Consider a NEO-CI calculation for the simple model system described above with a complete active space comprised of the following symmetric, delocalized orbitals:

$$\begin{aligned} \psi_{\text{deloc}}^{e,+} &= \frac{1}{\sqrt{2(1+S_{12}^e)}}(\varphi_1^e + \varphi_2^e), & \psi_{\text{deloc}}^{e,-} &= \frac{1}{\sqrt{2(1-S_{12}^e)}}(\varphi_1^e - \varphi_2^e), \\ \psi_{\text{deloc}}^{p,+} &= \frac{1}{\sqrt{2(1+S_{12}^p)}}(\varphi_1^p + \varphi_2^p), & \psi_{\text{deloc}}^{p,-} &= \frac{1}{\sqrt{2(1-S_{12}^p)}}(\varphi_1^p - \varphi_2^p). \end{aligned} \tag{5}$$

For this simple model system, assuming that $S_{12}^e = S_{12}^p = 0$, the CI solution is of the form

$$\Psi_{\mathrm{deloc}}^{\mathrm{CI}} = \frac{1}{\sqrt{2}}(\psi_{\mathrm{deloc}}^{e,+}\psi_{\mathrm{deloc}}^{p,+} + \psi_{\mathrm{deloc}}^{e,-}\psi_{\mathrm{deloc}}^{p,-}) = \frac{1}{\sqrt{2}}(\varphi_1^e\varphi_1^p + \varphi_2^e\varphi_2^p), \tag{6}$$

$$E_{\mathrm{deloc}}^{\mathrm{CI}} = E_{\mathrm{loc}}^{\mathrm{HF}} - (\varphi_1^e\varphi_2^e|\varphi_1^p\varphi_2^p). \tag{7}$$

This wave function is delocalized over the two centers and has lower energy than that of the nonphysical localized NEO-HF solution. (Note that if the overlaps are not assumed to be zero, the two configurations in Eq. (6) will be weighted differently, but the densities will still be symmetric.) To summarize the results for this simple model system, $E_{\mathrm{deloc}}^{\mathrm{HF}} > E_{\mathrm{loc}}^{\mathrm{HF}} > E_{\mathrm{deloc}}^{\mathrm{CI}}$.

In practice, typically the electron and proton are represented by more than a single basis function at each center. Consider an extension of the above model system in which the electron and proton are each represented by two basis functions centered at $\mathbf{R}_1$ and two identical basis functions centered at $\mathbf{R}_2$. The two basis functions at each center are Gaussians with different exponents. Table I provides numerical results for a model system of this type. In this case, the localized molecular orbitals are different for the two Hartree-Fock solutions given in Eqs. (1) and (3). As a result, the proof that $E_{\mathrm{deloc}}^{\mathrm{HF}} > E_{\mathrm{loc}}^{\mathrm{HF}} > E_{\mathrm{deloc}}^{\mathrm{CI}}$ given above for the simplest model system is not valid for general molecular systems. For the molecular systems studied so far, however, we have found that the lowest energy NEO-HF solution is localized mainly on one center. (Note that this phenomenon is analogous to symmetry breaking that has been observed in conventional electronic structure theory [16,17].) As Table I shows, an active space comprised of the two electronic and two nuclear molecular orbitals of the type given in Eq. (5) results in a NEO-MCSCF wave function that is localized on one center. Thus, the inclusion of only nondynamical correlation is not sufficient for obtaining a delocalized, symmetric wave function. Furthermore, Table I illustrates that an active space comprised of all four electronic and nuclear molecular orbitals (i.e., a full CI calculation) is required to obtain a delocalized, symmetric wave function. These calculations indicate that electron-proton dynamical correlation is critical for hydrogen tunneling systems.

TABLE I. NEO-CI and NEO-MCSCF energies for a simple model system consisting of one electron and one proton, each represented by two Gaussian basis functions centered at $x = -0.325$ Å and two identical basis functions centered at $x = 0.325$ Å. A Slater-type orbital electronic basis set[14] and the DZSPDN nuclear basis set [5] (including only *s*-type orbitals) are used. The active space for the NEO-CI calculations is comprised of molecular orbitals obtained from a NEO-HF calculation with $D_{\infty h}$ symmetry. An active space of (4, 4) corresponds to a full CI calculation. The (1, 1) NEO-MCSCF energy is the variational NEO-HF energy, and the (1, 1) NEO-CI energy is the $D_{\infty h}$ NEO-HF energy. The numbers in italics correspond to localized nuclear wave functions, and the other numbers correspond to delocalized nuclear wave functions. The energies are given in atomic units relative to the variational NEO-HF energy. These calculations were performed with a modified version of the GAMESS program [15].

Active space (Nuclear, electronic)	NEO-CI	NEO-MCSCF
(1,1)	+0.076 706 42	*0.000 000 00*
(2,2)	+0.043 717 00	*−0.000 606 73*
(4,2)	+0.043 708 44	*−0.000 607 56*
(2,4)	+0.001 793 78	*−0.000 619 77*
(4,4)	−0.000 619 78	−0.000 619 78

Unfortunately, a full CI calculation is not feasible for realistic chemical systems. To avoid the nonphysical localization of the NEO-MCSCF solution, we have implemented state-averaged NEO-MCSCF, where the molecular orbitals are optimized to minimize the energy of an equally weighted linear combination of the lowest two states (i.e., the two nuclear states of the type shown in Fig. 1). We have found that state-averaged NEO-MCSCF solutions retain the delocalized nature of the NEO-CI wave functions. Thus, state-averaged NEO-MCSCF is a practical method for obtaining qualitatively reasonable, delocalized nuclear wave functions for symmetric hydrogen tunneling systems. A general issue arising in state-averaged MCSCF is the choice of the relative weights of the states. For hydrogen tunneling systems, we expect that equal weighting of the relevant two states will provide the most accurate tunnel splittings. The NEO analog to multireference configuration interaction or multireference perturbation theory will provide more quantitatively accurate nuclear-electronic wave functions [18].

Table II provides the results for two simple chemical systems, [Cl-H-Cl] and $[\text{Cl-H-Cl}]^-$. In both cases, the NEO-MCSCF wave functions are localized for the active spaces used, but the state-averaged NEO-MCSCF wave functions retain the delocalized character for the nuclear wave functions. Moreover, the state-averaged NEO-MCSCF energy is below the localized NEO-HF energy. We have observed a fundamental difference between the wave functions for the neutral and anionic chlorine systems. In the neutral case, the ground and excited state NEO-CI wave functions are of the forms $\chi_1^e\chi_1^p + \chi_2^e\chi_2^p$ [as found for the model system in Eq. (6)] and $\chi_1^e\chi_1^p - \chi_2^e\chi_2^p$, respectively. (Here χ_1^e, χ_2^e, χ_1^p, χ_2^p denote localized molecular orbitals.) In the anionic case, however, the ground and excited state NEO-CI wave functions are nearly single configurational with the forms $(\chi_1^e + \chi_2^e)(\chi_1^p + \chi_2^p)$ and $(\chi_1^e + \chi_2^e)(\chi_1^p - \chi_2^p)$, respectively. The difference in the character of the NEO-CI solutions for the neutral and anionic solutions arises from the differences in the electronic structures. The neutral system may be viewed as a hydrogen atom (i.e., a proton and electron) moving between two chlorine atoms with

TABLE II. Energies calculated for the neutral [Cl-H-Cl] and anionic $[\text{Cl-H-Cl}]^-$ systems with the two chlorine atoms separated by 3.34 Å. The 4-31G electronic basis set [19] is used for the chlorine atoms. The H is represented by the four electronic and four nuclear basis functions described in Table I, but the H basis function centers are at $x = \pm 0.337$ Å for the neutral system and $x = \pm 0.32$ Å for the anionic system. For both systems, the nuclear active space contains 4 nuclear molecular orbitals, and there are 32 core electrons in 16 molecular orbitals. The electronic active space for the neutral system includes 3 electrons in 6 molecular orbitals, and the active space for the anionic system includes 4 electrons in 4 molecular orbitals. The numbers in italics correspond to localized nuclear wave functions, and the other numbers correspond to delocalized nuclear wave functions. The energies are given in atomic units relative to the variational NEO-HF energy. These calculations were performed with a modified version of the GAMESS program [15].

Calculation	Neutral	Anionic
NEO-HF (variational)	*0.000 000*	*0.000 000*
NEO-HF ($D_{\infty h}$)	+0.131 715	+0.053 467
NEO-CI	+0.049 983	+0.041 647
NEO-MCSCF	*−0.011 128*	*−0.015 147*
SA NEO-MCSCF	−0.004 463	−0.005 051

unpaired electrons, while the anionic system may be viewed as a proton moving between two chloride ions with paired electrons. In the neutral system, the multiconfigurational nature of the nuclear-electronic wave function is essential to describe the bonding of the H atom to the chlorine atoms, whereas in the anionic system the electronic molecular orbitals are not as greatly influenced by the proton. Thus, nondynamical correlation plays a more important role in the neutral chlorine system [20].

To summarize, a single configuration Hartree-Fock nuclear-electronic wave function is inadequate for the description of hydrogen tunneling systems. The reference nuclear-electronic wave function for hydrogen tunneling systems may be single or double configurational, depending on the chemical nature of the system, and the additional inclusion of dynamical electron-proton correlation is essential to obtain a delocalized variational wave function. The importance of dynamical electron-proton correlation is due mainly to the attractive Coulomb interaction. State-averaged NEO-MCSCF is a practical method for calculating qualitatively correct bilobal nuclear-electronic wave functions. The elucidation of the fundamental nature of electron-proton correlation provides insight into the underlying physical principles of hydrogen tunneling.

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