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Beyond Kohn–Sham Approximation: Hybrid Multistate Wave Function and Density Functional Theory

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Abstract

A multistate density functional theory (MSDFT) is presented in which the energies and densities for the ground and excited states are treated on the same footing using multiconfigurational approaches. The method can be applied to systems with strong correlation and to correctly describe the dimensionality of the conical intersections between strongly coupled dissociative potential energy surfaces. A dynamic-then-static framework for treating electron correlation is developed to first incorporate dynamic correlation into contracted state functions through block-localized Kohn–Sham density functional theory (KSDFT), followed by diagonalization of the effective Hamiltonian to include static correlation. MSDFT can be regarded as a hybrid of wave function and density functional theory. The method is built on and makes use of the current approximate density functional developed in KSDFT, yet it retains its computational efficiency to treat strongly correlated systems that are problematic for KSDFT but too large for accurate WFT. The results presented in this work show that MSDFT can be applied to photochemical processes involving conical intersections.

Graphical abstract

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ASSOCIATED CONTENT

Supporting Information

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Summary of the computational method and additional computational details of optimization of block-localized Kohn–Sham orbitals and the optimized structures and vectors. (PDF)

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Kohn-Sham density functional theory (KS-DFT) and linear-response time-dependent density functional theory (TDDFT) have become indispensable tools for studying ground state and excited states of atoms and molecules as well as condensed-phase materials thanks to their balance of accuracy and efficiency.¹ Despite the remarkable success, they are typically not adequate to treat strongly correlated systems with characteristic features of multiple unpaired electrons and degenerate or nearly degenerate electronic states.^{2–5} A particular example is illustrated by conical intersections at geometries where two or more electronic states are degenerate; here TDDFT fails completely, although it often performs very well in vertical excitation energies for many molecules with errors of less than ~ 0.3 eV.⁶ The role of conical intersections in photochemistry to allow efficient nonradiative transitions has been well-established, and they are also essential in many nonadiabatic processes.^{7,8} The standard approaches to probe conical intersections are based on multireference (MR) wave function methods at much greater computational costs, such as the complete active space self-consistent field (CASSCF) and the multireference configuration interaction (MRCI) models. The failure of TDDFT to describe conical intersections is also well known;² there is a lack of interaction between the ground (reference) state and the excited (response) states. Consequently, the branching space, defined by the gradient difference and derivative coupling vectors, has only one degree of freedom, and this greatly impedes their applications to photochemistry.

Several methods have already been developed to introduce coupling between the ground state and excited states in DFT. A natural modification of the original formalism is the spin-flip (SF) TDDFT,⁹ which starts from a variationally optimized high-spin state (e.g., the triplet state) to generate the lower spin ground and excited states (S_0 , S_1 , etc.) by single-electron transitions along with an $\alpha \rightarrow \beta$ spin inversion. Hence the singlet ground and excited states are treated in the same footing to correctly recover the dimensionality of the intersection space. The SF-TDDFT method has been applied to a variety of systems and used in geometry optimization to determine conical intersections.^{4,10} Working in the framework of TDDFT, Li et al. replaced the matrix elements of the Tamm-Dancoff

approximation by the wave function results to introduce coupling between the reference ground state and excited state.¹¹ Yang et al. started from a two-electron deficient (N-2) reference to target the neutral (N) ground state and excited states by adding two electrons; thereby, both the ground and excited states are modeled in the same way to break the unphysical degeneracy.³ An alternative approach is based on ensemble DFT,^{12,13} which has been extended to include state-interaction (SI) along with state-average (SA) optimizations.¹⁴ Along a similar line, configuration interaction using constrained or block-localized DFT has been used to describe ground and excited states and the conical intersections.^{15,16}

In this Letter, we present a multistate density functional theory (MSDFT) to determine conical intersections and to model systems intrinsically characterized by degenerate states. Furthermore, MSDFT provides a “dynamic-then-static” framework to treat electron correlation by including dynamic correlation in the active configurations first, followed by diagonalization of the Hamiltonian in the dynamically correlated states to incorporate static correlation. MSDFT builds up on and makes use of the vast resources and excellent performance of the approximate density functional developed in KSDFT, yet it is practical for treating systems that are difficult by KSDFT and too large by accurate wave function theory (WFT).

The Dynamic-Then-Static Ansatz

Liu and Hoffmann recently categorized methods for treating electron correlation into three main families based on the order that static and dynamic correlation effects are evaluated:¹⁷ (1) static-then-dynamic, (2) dynamic-then-static, and (3) static-dynamic-static. They presented an iterative configuration interaction approach,^{17,18} which falls into the static-dynamic-static category. The first category includes a large majority of MR perturbation methods in WFT, and further discussion of these approaches is provided in ref 17.

In the dynamic-then-static category¹⁹ used in the present multistate density functional theory, the key idea is to first construct an effective Hamiltonian for a primary or active space, consisting of N_p determinants or spin-adapted configuration state functions (CSF), $\{|\Psi_A\rangle; A = 1, \dots, N_p\}$, such that dynamic correlation is included. In the second step, the adiabatic ground and excited states are determined by configuration interaction among the states in the active space. The active space typically consists of low-lying energy configurations. A special case is when $N_p = 1$, in which the ground state is well-separated from all other states and single reference methods (such as KSDFT) can be adequately used. It is of particular interest to consider systems with strong correlations, including a description of the conical intersections of different potential energy surfaces. In this case, more than one state is needed, but a small number will be sufficient in the active space, and this is the focus of the present study.

The effective Hamiltonian for the active space is formally constructed by contracting the effects (i.e., dynamic correlation) of the remaining N_x states in the full CI (FCI) spectrum of the Schrödinger equation for an n -electron system, where $N_x = N_f - N_p$, with N_f being the total number of FCI states. The I th low-lying energy state $|\Phi_I\rangle$ ($I < N_p$) of the FCI solution is written in terms of the active states¹⁷

$$|\Phi_I\rangle = \sum_{a=1}^{N_f} c_{aI} |\psi_a\rangle = \sum_{A=1}^{N_p} a_{AI} |\Psi_A\rangle \quad (1)$$

where $|\psi_a\rangle$ spans all possible determinants (FCI) for the n -electron system and the second equation is a singular value decomposition of the FCI vector, $\mathbf{c} = (\mathbf{U}' \boldsymbol{\sigma}) \mathbf{V}^\dagger = \mathbf{U} \mathbf{a}$, of rank N_p . The contracted functions that form the active space are formally defined by

$$|\Psi_A\rangle = \sum_{a=1}^{N_f} U_{aA} |\psi_a\rangle \quad (2)$$

which includes all dynamic correlation from states external to the active space. Throughout this paper, the symbols $A, B, \dots$ specify basis configurations, and $I, J, \dots$ denote adiabatic states.

A critical issue to make this approach practical is to incorporate dynamic correlation in eq 2 without a knowledge of the coefficients $\{U_{aA}\}$ in the first place. This is accomplished in MSDFT by projecting the total correlation energy in DFT onto $\{|\Psi_A\rangle\}$,¹⁶ which separates static correlation among the active state, with dynamic correlation included for each individual configuration.

Multistate Density Functional Theory

In the “dynamic-thenstatic” ansatz, there are two computational steps: (1) the definition and optimization of the active states and (2) the diagonalization of the effective Hamiltonian to yield the adiabatic ground and excited states. Although delocalized molecular orbitals can be used to define $\{|\Psi_A\rangle\}$, an equivalent, localized valence-bond (VB) representation is more illustrative for discussion and intuitive for interpreting results, and this is used in the following discussion.

For a given Lewis structure, the n -electron molecular system is partitioned into M_A fragments also called blocks, each consisting of n_m electrons ($\sum n_m = n$) and μ_m atomic orbital basis functions. A block-localized (BL) determinant is written as

$$|\Psi_A\rangle = N_A \hat{A} \{\varphi_1^A \dots \varphi_{M_A}^A\} \quad (3)$$

where $\hat{A}$ is the antisymmetrizer, N_A is a normalization factor, and φ_m^A is a product of block-localized Kohn–Sham (BLKS) orbitals of fragment m . These orbitals are linear combinations of the atomic basis assigned to the corresponding block; they are orthogonal within a given block but nonorthogonal in different blocks. Spin-adapted CSFs are constructed by combining several determinants to represent the corresponding covalent and ionic states. The determinant functions $\{|\Psi_A\rangle\}$ are *variationally* optimized *separately* as in

standard KSDFT, except that the electron density is obtained from nonorthogonal BLKS orbitals for the particular state.¹⁶

In MSDFT, the diagonal matrix elements of the effective Hamiltonian are simply the KSDFT energies of the BLKS determinants

$$H_{AA} = E^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})] \quad (4)$$

where $\rho_A^{\text{ms}}(\mathbf{r})$ is the electron density for state A and any “standard” (LDA, GGA, or hybrid) exchange-correlation functional $E_{\text{xc}}^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})]$ can be used to determine $E^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})]$, although the computational details are slightly different,¹⁶ involving nonorthogonal orbitals. In the CSF basis, their matrix elements are obtained by transformation from the determinant values.

The off-diagonal matrix elements can easily be determined in WFT,^{20–22} and they are functions of the individual states as well as the transition density $\rho_{AB}(\mathbf{r}) = \langle \Psi_A | \hat{\rho}(\mathbf{r}) | \Psi_B \rangle$, and this has been used previously in the mixed molecular orbital and valence bond (MOVB) theory.²² However, a density functional dependent on the transition density does not exist within the KSDFT framework. In MSDFT, the concept of *transition density functional* (TDF), $E^{\text{TDF}}[\rho_{AB}(\mathbf{r})]$, between states $|\Psi_A\rangle$ and $|\Psi_B\rangle$ is introduced to determine the off-diagonal matrix elements. It includes two components: (1) the electronic coupling between the nonorthogonal wave functions (dominantly for static correlation) and (2) a transition density contribution to account for dynamic correlation interactions between coupled states. Although there is currently no density functional approximation to $E^{\text{TDF}}[\rho_{AB}(\mathbf{r})]$, it can be approximated in a similar way as in KSDFT¹

$$H_{AB} \equiv E^{\text{TDF}}[\rho_{AB}(\mathbf{r})] = \langle \Psi_A | H | \Psi_B \rangle + V_c^{\text{TDF}}[\rho_{AB}(\mathbf{r})] \quad (5)$$

Here H is the electronic Hamiltonian, and the exact (wave function type) exchange between states $|\Psi_A\rangle$ and $|\Psi_B\rangle$ with an overlap $S_{AB} = \langle \Psi_A | \Psi_B \rangle$ is automatically included in the first part, whereas the remaining correlation contribution is grouped into the density functional in the second term. Although a density functional directly dependent on $\rho_{AB}(\mathbf{r})$ may be developed, to forge ahead, it is approximated by an overlap-weighted average of the KS correlation energies for the two interacting states^{16,23}

$$V_c^{\text{TDF}}[\rho_{AB}(\mathbf{r})] \approx \frac{\lambda}{2} S_{AB} (E_c^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})] + E_c^{\text{KS}}[\rho_B^{\text{ms}}(\mathbf{r})]) \quad (6)$$

where λ is unity, but it could be optimized in the future either as a parameter or as a functional. Note that the approximation in eq 6 for the correlation contribution to the TDF correctly reduces to the pure state limits ($A = B$).

The coefficients $\mathbf{a} = \{a_{AI}\}$ in eq 1 are determined by diagonalizing the generalized secular equation $\mathbf{H}\mathbf{a} = E\mathbf{S}\mathbf{a}$. Consequently, the electron density and energy functional for the ground state ($I=0$) and the excited ($I < N_p$) states, $|\Phi_I\rangle$, in MSDFT are given as follows

$$\rho_I(\mathbf{r}) = \sum_{A=1}^{N_p} \{a_{AI}^2 \rho_A^{\text{ms}}(\mathbf{r}) + \sum_{B \neq A} a_{AI} a_{BI} \rho_{AB}(\mathbf{r})\} \quad (7)$$

$$E_I^{\text{MS}}[\rho_I(\mathbf{r})] = \sum_{A=1}^{N_p} \{a_A^2 E^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})] + \sum_{B \neq A} a_{AI} a_{BI} E^{\text{TDF}}[\rho_{AB}(\mathbf{r})]\} \quad (8)$$

Note that Coulson structure weights $\{w_A\}$ can be obtained from the coefficients $\{a_{AI}\}$, providing a quantitative measure of the relative contributions of configurations in the active space.²⁴ Equations 7 and 8 are the key results of this work.

Several remarks can be made.

- a. In MSDFT, the ground-state density ρ_0 is a configuration-weighted sum of electron densities from multiple determinants as well as contributions from their transition densities (eq 7), and the ground-state energy is written as an *implicit functional* of ρ_0 with the same structural weights on the basis configurations in the active space (eq 8). If the ground state for a system is well-separated from all other states, that is, $N_p = 1$, then MSDFT naturally reduces to KSDFT (see below). For situations involving degenerate or nearly degenerate states, the system-dependent static correlation is treated with two or more configurations.
- b. The electron densities and energy functionals for the excited states are treated exactly on the same footing as the ground state in MSDFT (eqs 7 and 8). Therefore, the method provides excitation energies and has the correct dimensionality to describe conical interactions. The physical basis for a multideterminant representation of the ground-state density has long been established in ensemble density functional theory (EDFT).^{12,13,25} Although there are similarities, MSDFT differs from EDFT because transition density functional is introduced to account for electronic coupling between different states (eq 5).⁵ Equation 7 is consistent with the ensemble v_s -representability in EDFT because the determinants²⁶ in MSDFT can easily be orthogonalized.²⁷ Importantly, the density and functional in eqs 7 and 8 are not the “ensemble” density and energy but rather they represent the electron densities and energies of the corresponding adiabatic ground and excited states of the system. Note also that a thermally-assisted-occupation DFT method^{28,29} that employs fractional occupations as in the grand canonical approach has been developed to represent the multideterminant character for systems with strong correlation with good results for the ground state.

- c. The ground-state energy in many multiconfiguration DFT methods is typically obtained by adding the pure dynamic correlation from KSDFT to the MR energy that takes into account static correlation, $E^{\text{MR}} + E_{\text{xc}}^{\text{KS}}[\rho_0]$. However, because static and dynamic correlations are not separable, this combination results in double counting of correlation effects. In MSDFT, ρ_0 is not used directly to determine dynamic correlation. The latter is obtained as a configuration-weighted (not to be confused with the “ensemble weight” in EDFT) sum of the pure dynamic correlation within each (localized) determinant:

$E_c^{\text{MS}}[\rho_0(\mathbf{r})] = \sum_A w_{A0} E_{\text{xc}}^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})]$, where w_{A0} is a Coulson configuration weight. Thus nondynamic correlation is excluded from E_c^{MS} by construction.

However, $E_{\text{xc}}^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})]$ contains a component that may be regarded as dynamic correlation within the active space. This part of the correlation can be approximated and removed using second-order Møller–Plesset perturbation theory (MP2) with the restriction that only active orbitals are included

$$E_{\text{xc}}^{\text{KS2}}[\rho_A^{\text{ms}}(\mathbf{r})] = E_{\text{xc}}^{\text{KS}}[\rho_A^{\text{ms}}(\mathbf{r})] - \sum_{i < j} \sum_{a < b}^{\in A' \in A'} \frac{|(ia|jb) - (ib|ja)|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (9)$$

where the summations run over occupied (i and j) and unoccupied (a and b) orbitals defining the active space in configuration A , and the superscript KS2 indicates that dynamic correlation estimated by MP2 in the active space has been removed from the KS functional. The primes indicate that the summations are limited within a given block and only the BLKS orbitals corresponding to those used to form the active space (i.e., spin-coupled configurations) with an energy gap greater than 0.04 a.u. are included. Because the number of orbitals in the active space is very small compared with the virtual space, the correction to remove double counting of dynamic correlation introduces little extra computational cost.

Furthermore, one could construct a first-order factor, similar to that introduced by Savin and coworkers³⁰

$$\gamma_A = 1 - E_A^{(2)} / E_A^{\text{MP2}} \quad (10)$$

where $E_A^{(2)}$ is the second term in eq 9 and E_A^{MP2} is the total MP2 energy for state $|\Psi_A\rangle$. Thus

$$E_{\text{xc}}^{\text{KS2}}[\rho_A^{\text{ms}}] = \gamma_A E_{\text{xc}}^{\text{KS}}[\rho_A^{\text{ms}}] \quad (11)$$

which reduces exactly to $E_{xc}^{KS}[\rho_A^{ms}]$ for a single determinant (because there is no unoccupied orbital in the active space), and $E_{xc}^{KS2}[\rho_A^{ms}] = 0$ in the limit of full CI, when all virtual orbitals are in the active space (thus, $E_A^{(2)} = E^{MP2}$). Higher order perturbations could be used, which would greatly increase computational costs; however, this provides a simple and systematic connection from KSDFT to FCI. Therefore, the MSDFT approach may be regarded as a WFT and DFT hybrid.

- d. This brings us to another possible approximation for the dynamic correlation contribution to the transition density functional in eq 5 using perturbation theory

$$V_c^{TDF}[\rho_{AB}] \approx \langle \Psi_A | H | \Psi_B^{(1)} \rangle + \langle \Psi_A^{(1)} | H | \Psi_B \rangle + \langle \Psi_A^{(1)} | H | \Psi_B^{(1)} \rangle \quad (12)$$

where $|\Psi_A^{(1)}\rangle$ and $|\Psi_B^{(1)}\rangle$ are first-order corrections to $|\Psi_A\rangle$ and $|\Psi_B\rangle$. The first two terms and the last term in eq 12 account for, respectively, dynamic contributions from the active-external block and external-external block, respectively. Equation 12 and its high-order generalization may be used to guide the development an explicit transition density functional. Note that the zeroth-order term is already included in eq 5.

- e. In MSDFT, the BLKS orbitals are variationally optimized by KSDFT, independently for each determinant configuration; the BLKS orbitals are fully relaxed, nonorthogonal, and different for different configurations. This is different from typical CI and SA MCSCF approaches in WFT, in which a common set of orbitals is used for all configurations. The procedure provides an optimal and clear definition of the reference state for dynamic correlation via KSDFT (as compared to MRPT). Because the orbitals for each state have been individually optimized, just a diagonalization of the Hamiltonian is needed, rather than simultaneous optimization of both the orbital and configurational coefficients as in MCSCF.
- f. The reference function defined by eq 3^{16,22} may be compared with the spin-coupled valence bond (SCVB) method.^{31,32} In SCVB, delocalized single-electron orbitals are used, among which all spin-coupled configurations are included; in the limit of including ionic VB configurations, SCVB is equivalent to CASSCF with n electrons in n orbitals. On the contrary, in MSDFT, orbitals are block-localized and spin coupling is taken into account only between blocks critical for bonding interactions of interest (e.g., the electron pair involved in the dissociation of a single bond). A single blocklocalized determinant (BLKS determinant) is employed to approximate the SCVB function for the entire block, greatly reducing the number of configurations in the active space. Because orbitals are block localized, the inclusion of ionic VB-like configurations is more important in MSDFT to represent charge delocalization than that in SCVB. Of course, dynamic correlation is incorporated in the reference (basis) functions in MSDFT, whereas it is treated as a post-SCF correction in SCVB.^{31,32}

- g. The MSDFT method provides a strategy to directly obtain diabatic states at construction (DAC),³³ which will be presented elsewhere.

Illustrative Cases

The MSDFT calculations are performed using a modified version of GAMESS. Two representative systems involve symmetry-induced intersections in Jahn–Teller molecules and the potential energy surfaces in the photo-dissociation of NH₃. The PBE0 density functional is used in all computations with the cc-pVDZ basis for the Jahn–Teller systems and aug-cc-pVTZ for ammonia. For open-shell systems, spin-polarized (unrestricted) KSDFT³⁴ is used, and the procedure for optimizing block-localized orbitals has been described in refs 16 and 22. Since the active space is very small here, γ_A is set to one. These systems are chosen because they have previously been studied and their excitation energies and conical intersections have been well-characterized for comparison.

Symmetry-Induced Conical Intersection

Jahn–Teller active molecules, such as cyclopropenyl radical (C₃H₃[•]) and benzene cation radical (C₆H₆^{•+}), represent a special type of conical intersection, where the degeneracy of the electronic state is lifted by nontotally symmetric vibrations. An insightful analysis was provided by Paterson et al.³⁵ Here we focus on the qualitative description of the intersections with MSDFT by using just the covalent VB configurations in the active space, while quantitative energies can be obtained by including ionic (zwitterion bond) configurations in the treatment. The Jahn–Teller geometries at the conical intersections are optimized for C₃H₃[•] at the *D*_{3h} symmetry and for C₆H₆ at the *D*_{6h} symmetry.

For C₃H₃[•], there are three possible spin combinations in the covalent VB space, each consisting of four orbital blocks to represent the σ -framework (18 electrons) and three singly occupied p orbitals on carbon atoms. At the symmetry-induced conical intersection, the gradient difference (*GD*) and derivative coupling (*DC*) vectors are described by Paterson et al.,³⁵ which are the e' normal vibrational modes lying in the molecular plane (Supporting Information).³⁵ The potential energy surfaces along these two coordinates are depicted in Figure 1a for the ground and excited states. Restricting the planar geometry, distortion along the *GD* vector leads to a saddle point at *C*_{2v} symmetry on the ground-state PES with one short and two long CC bonds, which separates two energy minima, also of *C*_{2v} symmetry but having one long and two short CC distances. Moving away from the *C*_{2v} symmetry along the *DC*(*h*) direction results in a cone from MSDFT; however, TDDFT produces a spurious seam with KSDFT reference energy higher than the TDDFT excited state (not shown).

The Jahn–Teller geometry and ultrafast electron dynamics at the conical intersection of C₆H₆^{•+} can be probed by photoelectron spectroscopy and have been studied by Robb and coworkers.^{36,37} As pointed out by these authors,^{36,37} the moat around the conical intersection is characterized by three pairs of quinoid and antiquinoid VB configurations, with the former as the minima and the latter as the transition states on the ground-state PES. We used 12 configurations (Scheme 1), including different cation and radical combinations

to represent the VB states in MSDFT, to yield the PES shown in the branching space (Figure 1b). Following Vacher et al.,³⁸ the vibrational mode that leads to the quinoid structure represents to the *GD* vector and that has sheered motions of atoms on the opposite side corresponds to the *DC* vector (Scheme 1). The energies at the critical points in this minimum active space are about 0.2 to 0.3 eV higher than the CASSCF values,³⁷ but the key features of the adiabatic potential energy surfaces are fully characterized in comparison with the CASSCF surface (Figure 1b), in accord with the VB-based interpretation by Robb and coworkers.^{36,37}

Photodissociation of Ammonia

Photodissociation of NH_3 to $\text{NH}_2 + \text{H}$ has been extensively studied, and it is chosen because this process has been considered to embody the key challenges encountered in strongly correlated dissociative potential energy surfaces.^{39,40} We employed 12 CSFs for the ground and excited states (Figure 2). Specifically, each σ_{NH} bond is described by a spin-adapted covalent configuration $|\sigma_{\text{cov}}^{\text{NH}_a}\rangle = N_{\text{cov}}^a (\hat{A}\{\varphi_c^6 n^2 \bar{\varphi}_{s_H}\} + \hat{A}\{\varphi_c^6 n^2 \bar{\varphi}_{s_H}\})$ along with two ionic states, and the $n\sigma^*$ state is represented by $|\sigma_{\text{ex}}^{\text{NH}_a}\rangle = N_{\text{ex}}^a (\hat{A}\{\varphi_c^8 \bar{n} s_H\} + \hat{A}\{\varphi_c^8 n \bar{s}_H\})$. In all calculations two of the N–H bonds are fixed at the experimental value (1.055 Å), which is slightly longer than MRPT result (1.039 Å), and the three H–N–H angles are kept at 120°.³⁹

The ground-state ($1A_1$) minimum of NH_3 has a C_{3v} symmetry, and it is changed to D_{3h} at the excited state ($2A_1$) equilibrium. The total energy of NH_3 at the ground-state minimum is –56.51832 a.u. from MSDFT, which is slightly lower than the PBE0 value (–56.51661 a.u.), suggesting that there is little double counting of correlation. The adiabatic excitation energy is estimated to be 6.10 eV (Figure 2), slightly greater than experiment (5.92 to 5.96 eV). Along the minimum-energy path of a stretched N–H bond (reduced to B_1 state), a saddle point is encountered before reaching the conical intersection between the two surfaces at a C_{2v} symmetry. The conical intersection is located at 2.163 Å with an energy of 5.36 eV above ammonia, which is somewhat longer than the minimum-energy (5.16 eV) conical intersection point (1.990 Å) determined by Truhlar and coworkers;³⁹ the agreement is reasonable considering that the excited-state geometries are not fully optimized in the present study. The transition state is found at 1.284 Å with a barrier height of 0.24 eV, in concert with the best available values (1.298 Å and 0.22 eV).³⁹ The good agreement between MSDFT with experimental and computational results shows that the present multistate approach can provide quantitative description of the PES for ammonia photodissociation. For comparison, without including dynamic correlation in the CSFs using the mixed molecular orbital and valence bond (MOVB) method with the optimized BLKS orbitals, the computed bonding energy and excitation energy are, respectively, about 1 and 0.6 eV smaller than those from MSDFT and experiments.

The insert in Figure 2 shows that the degeneracy at the conical intersection is lifted by moving away from the planar geometry, producing a correct double-cone topology using MSDFT. However, as previously shown (not duplicated here),^{3,11} KSDFT and TDDFT calculations result in a spurious curved seam of intersections due to incorrect dimensionality. Furthermore, these calculations also suffer from convergence and instability issues with

imaginary eigenvalues. For comparison, CASSCF calculations require an (8,7) active space (490 determinants), but most are high-lying energy states that are unimportant to A_1-B_1 state coupling, while quantitative results can only be obtained with MRPT correction to account for dynamic correlation. In MSDFT, dynamic correlation is built into the CSFs, and a multistate approach using a standard density functional developed for KSDFT, with 12 CSFs (18 determinants) in the present study, is able to quantitatively capture the key features involving strongly coupled dissociative surfaces.

In summary, we propose a multistate density functional theory for treating systems with strong correlation and describing the conical intersections between strongly coupled dissociative potential energy surfaces. MSDFT is different from ensemble DFT because the electron densities and energies for ground and excited states are obtained on the same footing; a transition density functional is introduced to account for state interactions. If the ground state for a system is well-separated from all other states, then only one configuration is needed and MSDFT naturally reduces to KSDFT. In the limit that all virtual orbitals are included in the active space, MSDFT becomes FCI as in wave function theory. Thus MSDFT can be regarded as a hybrid DFT and WFT. The method is built on and makes use of the vast resources of the approximate density functional developed in KSDFT, yet it retains its computational efficiency to treat strongly correlated systems that are problematic using KSDFT but too large for accurate WFT. Excellent qualitative and quantitative results have been obtained in the test cases, including Jahn–Teller active molecules and the photodissociation of ammonia. The results presented here show that MSDFT can be applied to photochemical processes involving conical intersections.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Computed potential energy surfaces for the ground and the first excited state for cyclopropenyl radical (a) and benzene cation radical (b) along the gradient difference (g) and derivative coupling (h) vector directions (see the text).

Figure 2. Potential energy curves of the ground and $n\sigma^*$ excited states of planar NH_3 along a stretched N-H bond at the C_{2v} symmetry using MSDFT and mixed molecular orbital and valence bond (MOVB) calculations. The two horizontal bars are the MSDFT and MOVB (WFT without dynamic correlation) energies at the optimized geometry of ammonia at the C_{3v} symmetry. The insert depicts the double-cone topology of the potential energy surfaces in the branching space as the dissociating hydrogen moving away from the planar geometry. The PBE0 density functional and aug-cc-pVTZ basis set are used in MSDFT calculations.

Scheme 1. Schematic Representation of the Valence Bond Configurations Used in MSDFT for Benzene Cation Radical^a

^aDeformation from the D_{6h} Jahn-Teller geometry in the center along the gradient difference vector (red) leads to the quinoid configuration on the right and the antiquinoid structure on the left. There are three equivalent pairs forming the moat around the conical intersection.