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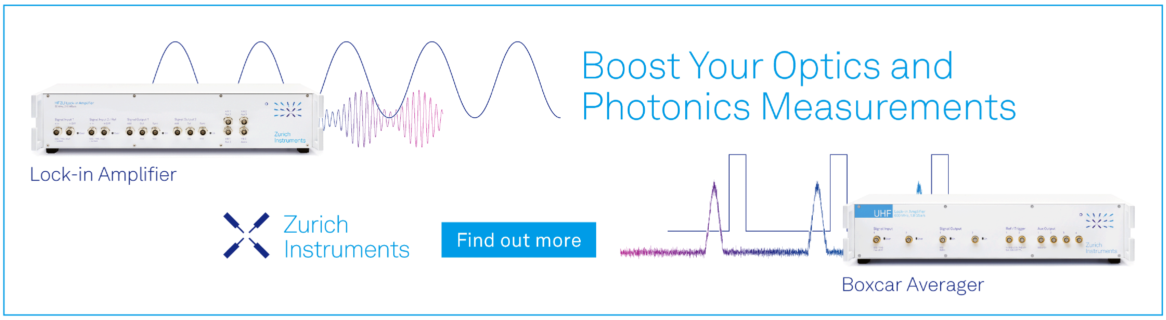

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ABSTRACT

The quantum chemistry community has developed analytic forces for approximate electronic excited states to enable walking on excited state potential energy surfaces (PES). One can thereby computationally characterize excited state minima and saddle points. Always implicit in using this machinery is the fact that an excited state PES only exists within the realm of the Born-Oppenheimer approximation, where the nuclear and electronic degrees of freedom separate. This work demonstrates through *ab initio* calculations and simple nonadiabatic dynamics that some excited state minimum structures are fantastical: they appear to exist as stable configurations only as a consequence of the PES construct, rather than being physically observable. Each fantastical structure exhibits an unphysically high predicted harmonic frequency and associated force constant. This fact can serve as a valuable diagnostic of when an optimized excited state structure is non-observable. The origin of this phenomenon can be attributed to the coupling between different electronic states. As PESs approach one another, the upper surface can form a minimum that is very close to a near-touching point. The force constant, evaluated at this minimum, relates to the strength of the electronic coupling rather than to any characteristic excited state vibration. Nonadiabatic dynamics results using a Landau-Zener model illustrate that fantastical excited state structures have extremely short lifetimes on the order of a few femtoseconds. Their appearance in a calculation signals the presence of a nearby conical intersection through which the system will rapidly cross to a lower surface.

Quantum chemistry methods for electronic excited states have undergone tremendous development, with a toolbox ranging from simple tractable methods such as single excitation configuration interaction (CIS) and time-dependent density functional theory (TDDFT) to increasingly accurate and sophisticated equation-of-motion coupled cluster (EOM-CC) methods, as well as designer excited state wavefunctions of the multiconfiguration or complete active space (CAS) type. All such methods define the S^{th} excited state potential energy surface (PES), $E_S(\mathbf{R})$, in terms of the Cartesian nuclear coordinates, $\mathbf{R}$, as a consequence of the clamped nucleus (i.e. Born-Oppenheimer) approximation. The resulting force, $\mathbf{F}_S = -\frac{\partial E_S}{\partial \mathbf{R}}$, allows one to walk on the PES and optimize excited state structures or transition structures.[1–9] Great effort has therefore gone into evaluating forces associated with excited state energies from CIS,[10] TDDFT,[11–15] EOM-CC,[16–18] and CAS[19] The same surface-walking optimization algorithms used for ground states can then be applied.[20–23] Such methods are available in standard electronic structure codes, such as the Q-Chem software,[24] which is used for all calculations reported here.

In comparison to the ground state, walking along an excited state PES to locate optimized structures comes with additional challenges.[25–27] The primary of which being that the excited state PES landscape is shaped by the coupling between nearby electronic states. As electronic states become close in energy, the coupling can distort the PES forming near-touching points with strong first-order derivative couplings. These near-touching points have been shown to signal the presence of a nearby conical intersection.[28,29] When a surface walking algorithm finds a local minimum that is close to a near-touching point, the increased curvature around the intersection can cause one of the resulting vibrational frequencies to be unphysically and enormously high. However, as illustrated below, these local minima are not dynamically stable and thus the anomalous frequencies are not physically observable. Rather, they result from a breakdown in the Born-Oppenheimer approximation and are fantastical artifacts of the PES being a poor mathematical construct.

In the adiabatic representation, conical intersections are relatively common on excited state potential energy surfaces; and the dynamics around these regions are of interest in areas such as reaction and photochemistry,[30–34] material science and design,[35–38] and in the development of new technologies.[39–42] Experimental techniques, such as time-resolved spectroscopies, are beginning to attain the sensitivity required to discern signatures of passage through intersections.[43–47] Of equal importance, theoretical modeling serves a key role in our understanding of their impact in the aforementioned processes and areas of study. Despite progress, identifying these regions of the PES remains a challenge for quantum chemistry algorithms.[48–51] The brute force approach relies on the calculation of first-order derivative coupling vectors which, while effective, can amount to the dominant computational expense and render the procedure intractable for larger system sizes.[52–56] Alternative methods, such as carrying out quasi-classical and quantum molecular dynamics simulations[57–59] and measuring the density of avoided crossings,[60] have been presented. Methods to find the minimum energy crossing point (MECP) between two different states have also been developed,[61,62] as the MECP plays an important role in non-radiative relaxation.

The purpose of this communication is to illustrate and explain how a standard analytical gradient-based geometry optimization procedure may identify molecular configurations as excited state minima which are not dynamically stable. A hallmark of such an instability is an anomalously large vibrational frequency and force constant. As some representative examples, we will present the excited state PESs of gas-phase phosphine (PH_3) where a geometry optimization using EOM-CCSD theory converges to a fantastical molecular configuration. A harmonic vibrational analysis at this local minimum identifies a single normal mode with an unexpectedly strong force constant. Confirming that this local minimum results from a breakdown of the Born-Oppenheimer approximation, the vibrational dependence of the first-order derivative coupling identifies the existence of a close-by, strongly-coupled, near-touching point. Next, a TDDFT analysis of tris(bipyridine)ruthenium(II) (RuBPY) is presented where we see the same type of behavior occurring with multiple minima on multiply-coupled excited state PESs. This second example clearly illustrates the relationship between the strength of the first-order derivative coupling and the second derivative of the excited state energy. Finally, a simple dynamical analysis based on the ubiquitous Landau-Zener model of an electronically non-diabatic curve-crossing illustrates that these fantastical minima are, in fact, unstable and have exceptionally short lifetimes.

Our first example of a fantastical excited state minimum energy structure is PH_3 and because it is easily tractable with EOM-CCSD we are assured our analysis has not been skewed by a more modest level of electronic structure theory. A schematic of the energy ordering and minimum energy configurations is shown in Fig. 1. In its ground electronic state, PH_3 has A_1 symmetry in the C_{3V} point group. PH_3's first excited state has A_1 symmetry and its second excited state is a degenerate pair of states with E symmetry. An excitation into the A_1 state optimizes to a symmetric T-shaped configuration, also of A_1 symmetry, but in the C_{2V} point group (see middle panel of Fig. 1). Upon excitation into one of the degenerate E states, PH_3 will lower symmetry to the C_S point group by lengthening one of its P–H bonds and optimizing to a higher energy A'' minimum and a lower energy A' minimum energy configuration. A near-touching point between the S_1 and S_2 PESs emerges close to the A' minimum along a combined vibrational degree of freedom that both bends and breaks the planar symmetry.

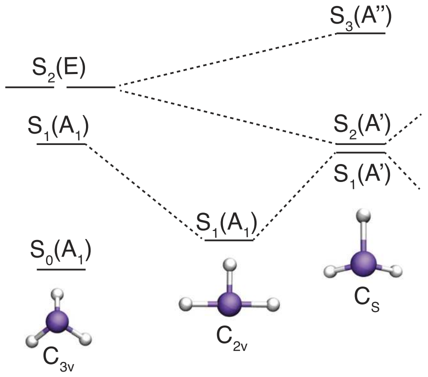

FIG. 1. A schematic of the possible stationary points on the excited state PESs of PH_3. At the C_{3V} geometry, the S_1 excited state is A_1 symmetry and the S_2 excited state is a degenerate pair of E symmetry states. A geometry optimization splits the E electronic states into a lower energy $S_2(A')$ state and a higher energy $S_3(A'')$ state in the C_S point group. The near-touching point between the $S_1(A')$ and $S_2(A')$ surfaces occurs near the $S_2(A')$ minimum.

Figure 2 presents an EOM-EE-CCSD/aug-cc-pVDZ analysis of the PESs of four states of PH_3 as a function of the normal mode coordinate (Q). Also shown, as a function of Q, is the second derivative of the excited $S_2(A')$ state energy [panel (c)] (giving the fantastical force constant) along with the first-order derivative coupling between this state and the lower-in-energy $S_1(A')$ state [panel (d)]. The anomalous normal mode [panel (a)] consists of a bending motion of the equatorial hydrogen atoms that have both in- and out-of-plane character with a stretching of the axial P–H bond. The low-lying excited state PESs [panel (b)] consist of two singlet A' states followed by two higher-energy A'' states. A harmonic vibrational analysis at the fantastical $S_2(A')$ minimum (see Fig. S5) predicts that the vibrational frequency is 6876 cm^{-1} which is ≈5 times greater than the average vibrational frequency of 1277 cm^{-1}. Remarkably, at the point where the first-order derivative coupling reaches a maximum, which occurs just off the minimum at $Q \approx 0.006$ Å, the second derivative of the $S_2(A')$ state energy reaches a maximum. The vibrational frequency at this point on the PES is even greater (8552 cm^{-1}) when compared to the frequency at the minimum. Walking along the PES of this normal mode illustrates that the second derivative of the $S_2(A')$ PES increases synchronously with the first-order derivative coupling. The curvature of the PES is significantly changing as a result of the electronic couplings.

Our second example, shown in Fig. 3, treats the B3LYP/def2-SVP excited state PESs of RuBPY. The analysis of this fantastical excited state landscape consists of four PESs [panel (b)] connected by normal mode Q with five points of near touching occurring between them. A schematic of the anomalous normal mode degree

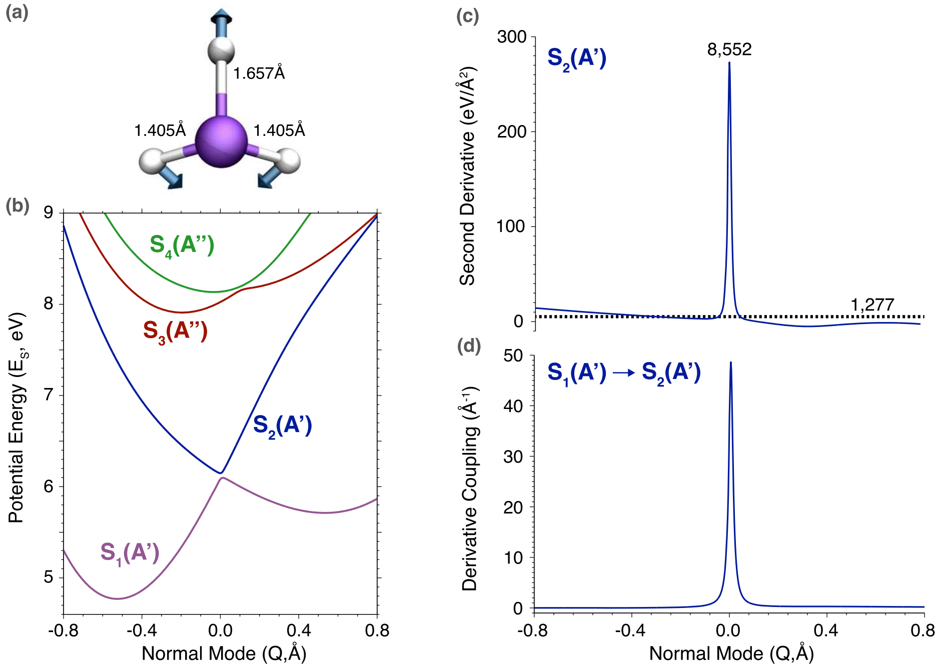

FIG. 2. (a) The fantastical normal mode degree of freedom (Q) of PH_3 on the $S_2(A')$ excited state. (b) The PESs as a function of this normal mode coordinate. (c) The second derivative of the $S_2(A')$ PES as a function of normal mode coordinate. The corresponding maximum vibrational frequency (cm^{-1}) is shown above the peak with the average frequency shown as a dashed line. (d) The first-order derivative coupling between the $S_1(A')$-$S_2(A')$ states as a function of normal mode coordinate. The $S_2(A')$ excited state is at a minimum in all Cartesian directions at Q = 0.

of freedom [panel (a)] involves a symmetric pyridine-pyridine stretch on two of the bipyridine ligands. Walking along a relatively small displacement (±0.1 Å) reveals that when the first-order derivative coupling [panel (d)] reaches a maximum, the second derivative of the S_3 energy [panel (c)] reaches an inflection point. A harmonic vibrational analysis at the fantastical S_3 minimum predicts that the vibrational frequency is 11 801 cm^{-1} which is ≈9 times higher than the average vibrational frequency of 1313 cm^{-1}. At the closest near-touching point ($Q \approx 0.0004$ Å), the predicted vibrational frequency is an enormous 12 271 cm^{-1}. Similar to the excited states of PH_3, what is found by geometry optimizing the S_3 excited state of RuBPY are potential minima with anomalously large vibrational frequencies and force constants coincident with strong first-order derivative couplings. The enormous vibrational frequency at the minimum is characteristic of the presence of multiple close-by, near-touching points between the S_2, S_3, and S_4 surfaces.

These examples are more fully understood through a simple dynamical analysis based on the venerable Landau-Zener model,[63–65] which illustrates that an excited state PES minimum having such an anomalously large force constant will have an extremely short lifetime and thus cannot truly be considered a stable point on an excited state PES. Figures 2 and 3 shows for PH_3 and RuBPY that, in the adiabatic representation, the high vibrational frequencies at these minimum energy geometries are accompanied by strong first-order derivative couplings. In the alternative view of a strictly diabatic representation however, these regions of large first-derivative couplings correspond to weak coupling between the diabatic states.

The Landau-Zener model presents the simplified case of two linear diabatic potential energy surfaces as a function of a single vibrational degree of freedom, which cross at $Q = 0$, and have a constant coupling matrix element between them. After transforming from the diabatic basis of the Landau-Zener model into the adiabatic basis, the force constant at the minimum $(Q = 0)$ of the upper adiabatic state E_+ is:

$$\left.\frac{\partial^2 E_+}{\partial Q^2}\right|_{Q=0} = \frac{(G_I - G_J)^2}{4\Delta}, \tag{1}$$

where G_I and G_J denote the slopes of the diabatic potential energy surfaces and Δ is the constant diabatic coupling matrix element. As shown in Eq. (1), when the diabatic coupling is weak (e.g. near zero), the force constant of the upper adiabatic state is near infinite. If one adopts the Landau-Zener model’s assumption of a constant nuclear velocity $\dot{Q}$ through this avoided crossing then the standard Landau-Zener population of the upper adiabatic state is:

$$P = 1 - \exp\left(\frac{-2\pi\Delta^2}{\hbar\dot{Q}|G_I - G_J|}\right), \tag{2}$$

where P denotes the population loss of E_+ after a *single* pass through the avoided crossing region.

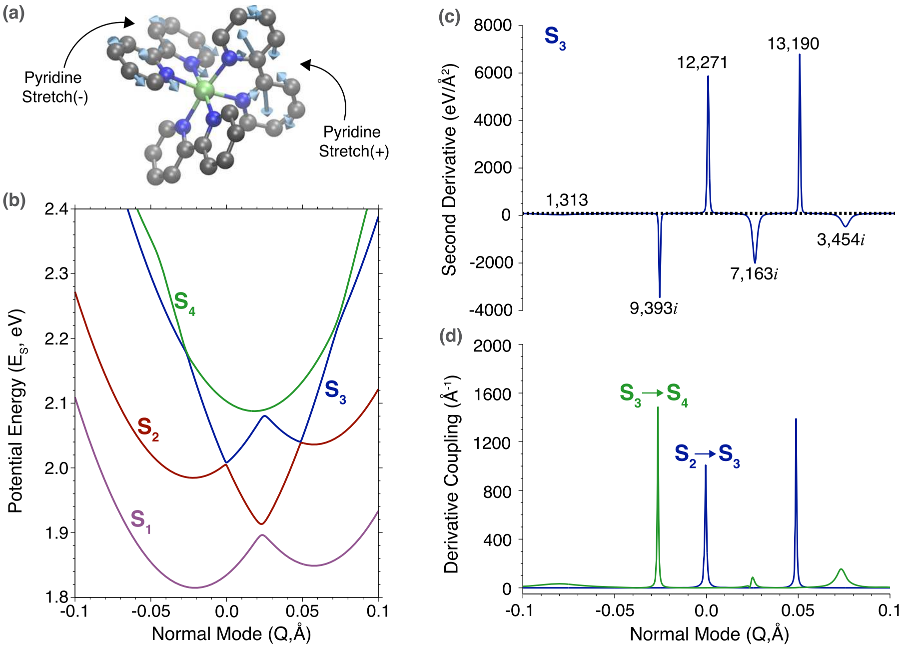

FIG. 3. (a) The fantastical normal mode degree of freedom (Q) of RuBPY on the S_3 excited state. The normal mode consists of a symmetric pyridine-pyridine streching motion on two of the bipyridine ligands oscillating in- and out-of-phase. (b) The PESs of the lowest four excited states as a function of Q. (c) The second derivative of the S_3 excited state energy as a function of Q with the local maximum and minimum vibrational frequencies (cm^{-1}) displayed above the peaks. The average vibrational frequency is shown as a dashed line. (d) The first-order derivative coupling between the S_3–S_4 (green) and S_2–S_3 (blue) states as a function of Q. The S_3 excited state is at a minimum in all Cartesian directions at $Q = 0$.

The Landau-Zener model was used to predict the lifetimes of the fantastical minimum energy configurations of PH_3 and RuBPY. For this analysis, the upper and lower state PESs around each fantastical minimum were fit to linear functions and represented as diabatic surfaces. Since only two states for each system were included in the model, the coupling between the diabatic states (Δ) was obtained directly from the energy splittings of the adiabatic states. Since the hopping probability depends on the strength of this coupling, Δ is an approximate non-adiabatic coupling. In order to include the effects of re-crossing, classical molecular dynamics trajectories on the linear PESs were employed with the crossing times, and the resulting velocities at the crossing point, solved for analytically. ~10 000 trajectories were initialized with positions and momenta sampled from the vibrational ground state probability density of the corresponding linearized PESs. The velocity $\dot{Q}$ was then inserted into Eq. (2) and the results were averaged. Further details of the linear fit and the molecular dynamics approach can be found in the supplementary material.

The population decay as a function of time is shown in Fig. 4. Fitting these curves to a first-order exponential function reveals that these fantastical minimum energy structures are incredibly short-lived. The average lifetime of the $S_2(A')$ minimum energy configuration of PH_3 is only 3.76 fs. Likewise, the S_3 minimum energy configuration of RuBPY is only 5.60 fs. It's important to note that these are conservative estimates of the lifetimes since the dynamics were initialized from the vibrational ground state. Realistically, as the near-touching points are approached from further away (e.g. the Franck-Condon region), the nuclear velocities would likely be much greater and the population would decay even faster.

In summary, this work serves to highlight striking features of excited state potential energy surfaces which are associated with walking downhill to a minimum on an upper state, j, that is near a seam of intersection with a lower state, $(j-1)$. We know abstractly that the very concept of a potential energy surface, $E_j(\mathbf{R})$ is an idealization of the strict Born-Oppenheimer separation of electron motion $(\mathbf{r})$ from nuclear motion $(\mathbf{R})$, which yields the electronic Schrödinger equation, $\hat{H}_e \Psi_j(\mathbf{r};\mathbf{R}) = E_j(\mathbf{R})\Psi_j(\mathbf{r};\mathbf{R})$. For most purposes, the PES is an incredibly valuable as well as quantitatively valid construct, because it gives rise to fundamental chemical concepts such as molecular structure, and thus reaction mechanism as the passage between a sequence of such structures. However, when we walk on $E_j(\mathbf{R})$ and obtain optimized structures and their properties, such as vibrational frequencies, we tend to assume those results are valid while forgetting that the PES itself is an idealization. Our discovery of non-observable ("fantastical") optimized excited state structures that are associated with the upper surface of a conical intersection highlights the need to not unconditionally accept well-characterized excited state PES minima as physically meaningful.

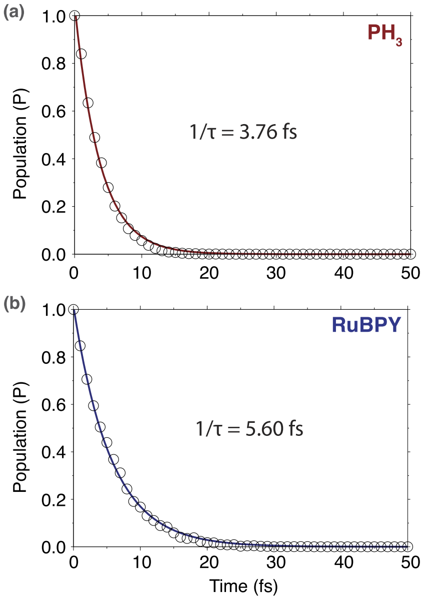

FIG. 4. The average Landau-Zener populations (after considering re-crossings) of the upper adiabatic state as a function of time. ~10 000 trajectories were sampled from the linearized PESs ground vibrational state distributions. (a) The population decay of the $S_2(A')$ excited state of PH_3 as a function of time. (b) The population decay of the S_3 excited state of RuBPY as a function of time. The lifetime $1/\tau$ is shown in the inset.

In the case of the fantastical excited state minimum structures we reported, there is a clear signature of Born-Oppenheimer breakdown in the form of unphysical artifacts in the harmonic vibrational frequency analysis. Specifically there is an enormously high frequency (and force constant) that far exceeds normal values. This "mega-mode" arises from the very sharp form of the PES on the upper state, as is visually evident, for example in the extreme curvature associated with the lowest S_2 and S_3 structures in Fig. 3(b). Furthermore, although it depends on the strength of the electronic coupling matrix elements, these fantastical minimum energy configurations are typically unstable with incredibly short lifetimes. To demonstrate the exceptionally short-lived occurrences of these metastable configurations a Landau-Zener analysis was presented. For the representative examples of PH_3 and RuBPY, a conservative analysis predicted lifetimes of less than 10 fs out of the excited states of interest. Clearly, these minimum energy configurations are unphysical artifacts of the Born-Oppenheimer approximation.

We therefore recommend examining the results of excited state PES optimizations to make sure the resulting structures are not fantastical. If a fantastical structure is discovered, with its associated mega-mode, it serves as an indicator of a very near-by seam of crossing, rather than a conventional minimum structure.

SUPPLEMENTARY MATERIAL

A more detailed discussion of the Landau-Zener model for describing the near intersection of two states, including the behavior of the resulting force constant and plots showing the linear fits of the LZ parameters at the fantastical optimized structures of the two systems (PH_3 and RuBPY) discussed in the text and details of the calculated lifetimes. Additional computational details are also provided, including details of geometry optimizations, the evaluation of the force constants, and the dependence on finite displacement of the second derivative along the mega-mode for PH_3.

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AUTHOR DECLARATIONS

Conflict of Interest

MHG is a part-owner of Q-Chem Inc, whose software was used for the developments and calculations reported here.

Author Contributions

Justin J. Talbot: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Juan E. Arias-Martinez**: Conceptualization (equal); Formal analysis (supporting); Methodology (supporting); Writing – review & editing (supporting). **Stephen J. Cotton**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Methodology (equal); Writing – review & editing (equal). **Martin Head-Gordon**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Methodology (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study is available from the corresponding author upon request.

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