Diabatic models with transferrable parameters for generalized chemical reactions

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Abstract. Diabatic models applied to adiabatic electron-transfer theory yield many equations involving just a few parameters that connect ground-state geometries and vibration frequencies to excited-state transition energies and vibration frequencies to the rate constants for electron-transfer reactions, utilizing properties of the conical-intersection seam linking the ground and excited states through the Pseudo Jahn-Teller effect. We review how such simplicity in basic understanding can also be obtained for general chemical reactions. The key feature that must be recognized is that electron-transfer (or hole transfer) processes typically involve one electron (hole) moving between two orbitals, whereas general reactions typically involve two electrons or even four electrons for processes in aromatic molecules. Each additional moving electron leads to new high-energy but interrelated conical-intersection seams that distort the shape of the critical lowest-energy seam. Recognizing this feature shows how conical-intersection descriptors can be transferred between systems, and how general chemical reactions can be compared using the same set of simple parameters. Mathematical relationships are presented depicting how different conical-intersection seams relate to each other, showing that complex problems can be reduced into an effective interaction between the ground-state and a critical excited state to provide the first semi-quantitative implementation of Shaik’s “twin state” concept. Applications are made (i) demonstrating why the chemistry of the first-row elements is qualitatively so different to that of the second and later rows, (ii) deducing the bond-length alternation in hypothetical cyclohexatriene from the observed UV spectroscopy of benzene, (iii) demonstrating that commonly used procedures for modelling surface hopping based on inclusion of only the first-derivative correction to the Born-Oppenheimer approximation are valid in no region of the chemical parameter space, and (iv), demonstrating the types of chemical reactions that may be suitable for exploitation as a chemical qubit in some quantum information processor.
1. Introduction

Though chemical reactions involve complicated restructuring of the electronic and nuclear configuration and dynamics, it can be useful to use the simplification of envisaging reactions as occurring along a single reaction coordinate. This basic concept forms the conceptual framework of Transition-State Theory and much of modern chemistry. Modern electronic-structure calculation methods can predict wide ranges of properties to within the accuracy of experimental measurements, capturing all chemical and spectroscopic features of the system, but such approaches rarely provide insight into why processes occur and have to be repeated for each small system variation. Diabatic models can be used to interpret these calculations, however, revealing the chemical features controlling the process. Basically, simple forms, called diabatic surfaces, are used to describe the reactants and products, and then these surfaces are coupled together in some way to mimic the Born-Oppenheimer surfaces coming from the electronic-structure calculations. Our purpose here is to do this in such a way that the parameters involved can be transferred between systems, and that their values can be used to express why processes happen in terms of simple and intuitive chemical descriptions.

Parallel but equivalent ways of doing this have been developed since the 1950’s assuming that the diabatic states are harmonic and that the coupling between them is linear. One of these, whose symbolism and approach we follow herein, is Hush’s theory of adiabatic electron transfer [1-7], with many critical results also being established by others working in the electron-transfer field [8-12]. Closely related are the polaron models from solid-state physics [13-14] and the Rashba spin Hamiltonian [15], but a different approach from the field of spectroscopy has been the Pseudo-Jahn-Teller effect (PJTE) developed by Bersuker and others [16-20] that focuses on spectroscopic states as “reactants” and “products” coupled through Herzberg-Teller [21] vibronic coupling [22-25]. At the basic level, these approaches are all equivalent [26], and can remain so even after extension to include multiple nuclear motions [27] (as is required to describe processes involving conical intersections) or multiple electronic states [28], but the convenience with which they may be applied to different problems varies.

The basic model is sketched in figure 1, as it is usually presented in adiabatic electron-transfer theory relevant to general chemical reactivity. In simple cases involving symmetric isomerization reactions, only 3 parameters are often sufficient to describe complex Born-Oppenheimer ground and excited electronic states, increasing to 4 parameters to include any reaction asymmetry. In figure 1, these parameters are represented as the resonance energy $J$, the reorganization energy $\lambda$, the reaction exothermicity $-E_o$, and the geometry difference between the diabatic reactants and products $2Q_m$. Another parameter that is involved but rarely manifested is the reduced mass $m$ for the nuclear motion. These parameters can be represented in many other ways, however, with e.g., in the literature of PJTE it being common to replace $\lambda$ and $Q_m$ with the force constant $k$ and vibronic coupling constants $\alpha$. As shown later, transformation between these representations involve no approximation and hence all observable properties are equally described independent of the mathematical representation used. The advantage of the parameter representation shown in the figure is that all parameters are transferrable and can be independently measured directly by simple experiments, and all parameters are easy to deduce from high-level calculations, leading to the widespread adoption of this representation. Also, we will show that these parameters result is a great simplification of the problem compared to the PJTE representation, allowing physical insight to be deduced. However they are represented, the model parameters control a very wide range of observable quantities, from geometries to infrared spectra to electronic spectra to redox potentials to spin distributions to reaction rate constants. The minimum number of parameters required increases when bystander chemical processes and their associated diabatic surfaces interfere with the processes of interest, but here our focus is on how such scenarios can still be reduced to a minimalist description.
Our aim here is to allow general chemical reactivity and spectroscopy to enjoy the well-established benefits coming from adiabatic electron-transfer theory. Hush focused on electron-density changes smoothly throughout the transition from reactants to products, manifesting through manifold properties accessible to high-level calculations and experimental observations [1-7,29-41]. These properties include not just the rate constants for electron-transfer reactions but also ground-state energies and vibration frequencies as well as electronic spectral properties. An important phenomenon identified using this approach is \textit{intervalence spectroscopy} [5] involving intermolecular motion of charge induced by light absorption. This led to the design and synthesis of the Creutz-Taube ion [42], an unprecedented chemical species in which two Ru atoms appear to share a π bond across an intervening pyrazine bridging ligand. It also forms the basis for understanding of primary charge separation in natural and artificial solar-energy harvesting systems used in plants, bacteria, organic photovoltaics and artificial photosynthesis, as well as the reverse process, light emission in organic light-emitting diodes. A critical feature of the approach is that it leads to very many analytical or numerically exactly-solvable relationships linking system properties, as recently summarized in a number of contexts [28,43-46]. Exemplary in Hush’s description of intervalence compounds is that he showed how from measurement of the visible absorption spectrum of the dye Prussian blue, it was possible to deduce kinetics parameters critical to the understanding of the charge conductivity of the material [5]. A related modern application was the demonstration of how protein mutagenesis controls the output voltage produced following primary charge separation during bacterial photosynthesis [47] and the development of a formalism for understanding modern Stark Spectroscopy [48] and its application to photosynthetic systems [49]. The critical feature is the universality of the model parameters for the qualitative description of system properties. Simple models can also be extended to universal quantitative ones provided that full quantum solutions [26,50], sufficient interfering processes [43,51-52], and motions orthogonal to the reaction coordinate are also included [27,53-54]. The assignment [55] of the Q-band spectrum of chlorophyll-a, arguably the world’s most important chromophore whose properties display a strong pseudo-Jahn-Teller effect, following 50 years of intense debate, provides another example of the power of this approach.

Looking at the wider perspective, since the inception of the quantum theory of matter, the application of diabatic models in this capacity was envisaged. This is clear in the founding works, of London [56-57] as well as von Neumann and Wigner [58] for general adiabatic and non-adiabatic reactions, Eyring and Polanyi in the LEP potential-energy surface for reactions [59-60], Horiiuti and Polanyi [61] for proton transfer reactions, Wall and Glockler [62] for isomerization reactions like ammonia inversion, and Hush for hydrogen transfer reactions [29]. Central qualitative ideas became imbedded in chemical culture such as symmetry breaking [6,16-20,63-67], understanding of aromaticity through the concept of resonance energy [68] and Shaik’s “twin state” concept [69-73], as well as the \textit{reaction force} description of classic chemical reactions [74-76] that leads naturally to the
Hammond-Leffler postulate [77-78], etc. Shaik’s twin-state description is particularly provocative as it tells that the properties of the ground-state of a molecule are intricately coupled to the properties of an excited “twin” state.

This throws into dismay claims often made about density-functional theory (DFT) since its inception that it is only a ground-state theory as only the ground-state density is directly considered. However, the changes to the ground state caused by any perturbation can always be expressed in terms of response functions that mix in excited states, so DFT ground-state potential-energy surfaces always depict how the calculation method represents both ground and excited states. A simple example of this is that it was once believed that generalized-gradient functionals correctly described polyacetylene and general extended π systems as they predict realistic values for bond-length alternations and other singlet ground-state geometry features. However, because of its asymptotic potential error it grossly misrepresents excited states, leading to very poor values of molecular polarizabilities and eventually to the discovery that it predicts a triplet ground-state for polyacetylene rather than the observed singlet one [79]. So from a qualitative perspective, simple diabatic models and what they imply about chemical reactivity and spectroscopy have indeed had a profound effect on general chemical thinking.

However, the same cannot be said for semi-quantitative analyses. For example, Shaik’s qualitative description of twin states effects controlling the properties of aromatic compounds [69-73] was never converted into quantitative modelling, like what flows easily from adiabatic electron-transfer theory. Parameters are never transferred between systems and molecules, e.g., a completely different diabatic model would be developed for chemical and spectroscopic processes of the ammonium cation than that which would be developed for processes of ammonia itself. At one level, different simple parameters describing these two molecules are demanded as electron correlation effects reshape and reorder orbitals as a result of the change in electron occupation. This effect, e.g., provides the mechanism by which molecular ionization energies and electron affinities calculated by Hartree-Fock theory as energy differences between species with different electron numbers differ from those obtained using Koopmans’ theorem. However, such changes are generally small and one expects that the chemical and structural properties of the ammonium cation should, to a realistic level of approximation, be specifiable simply in terms of the analogous properties of ammonia itself. At an even more basic level, for different properties of the same molecule like its ground state structure and spectroscopy, its excited state structure and spectroscopy, and its reactivity in each state are usually generated individually for each process of concern rather than developing a single model for all properties. The dreams of the founders of quantum chemical theory have thus been realized in full only for electron transfer reactions.

In this review, we present a fundamental feature only just recognized [28] as a defining element of molecular potential-energy surfaces. Utilizing it, diabatic models can be produced for many types of chemical processes that involve transferrable parameters- parameters whose values depict wide-ranging properties, parameters who values can be transferred between systems. This provides a unification of manifold descriptions of chemical processes taught to students into a single conceptual formalism. Applications of this formalism to understanding why the chemistry of first-row elements is so different to that of later row ones, to understanding aromaticity, to designing chemical quantum computers, and to understanding the basics of Born-Oppenheimer breakdown and non-adiabatic chemical processes. In terms of understanding general Born-Oppenheimer breakdown, the one-dimensional model described herein obviously cannot deal with processes involving direct conical intersections, but analogues are drawn to known fully general mathematical results coming from the field of Catastrophe Theory [80-83] which indicate that the primary conclusions reached provide examples of generally expected results.
2. Semi-quantitative application of transferrable diabatic models to systems other than electron transfer: multiple coupled conical-intersection seams

The reason that parameters previously derived for general chemical reactions cannot be transferred between properties or between systems is that the effect of the number of electrons involved in the chemical processes was not taken into account analytically within the models [28]. This means that the effect of varying electron number gets treated implicitly rather than explicitly, modifying the values of deduced parameters.

Comparison is made between different scenarios in which one, two, or four electrons are critically involved are sketched in figure 2. The one-electron scenario (or one-hole scenario) is typical of electron-transfer reactions: just two molecular orbitals are involved, and two possible diabatic electronic states are produced named $G$ (often corresponding closely to the Born-Oppenheimer adiabatic ground-state $g$) and it’s singly excited state $S$ (often corresponding closely to the Born-Oppenheimer adiabatic excited state $s$). This scenario generates a single conical intersection seam depicting locations at which the two adiabatic states become degenerate, and through the PJTE [17-20], this seam implicitly controls all system properties. Standard relations of adiabatic electron-transfer theory arise from this scenario [26,28,44,84].

For a chemical reaction involving a molecule with a typical closed-shell electron configuration, two electrons are involved in the occupied orbital of interest whilst the other orbital of interest must be unoccupied. An example of this is say the ammonia inversion reaction for which the critical orbitals are the nitrogen lone-pair orbital $n$ and the symmetric $\sigma^{*}_{NH}$ orbital. However, as figure 2 shows, the two electrons may be distributed in three ways, the ground diabatic state $G$ and the single-excited diabatic state $S$ as before, but now also a doubly excited diabatic state $D$. If strong vibronic coupling between the $n$ and $\sigma^{*}_{NH}$ orbitals dominates variations in the structural, chemical, and spectroscopic properties of the system, then this coupling manifests equally strongly between $G$ and $S$ as between $S$ and $D$. Three critical conical intersection seems thus connect the diabatic surfaces, a low energy one between $g$ and $s$ that is typically critical to understanding ground-state properties, plus higher-energy ones that are more difficult to access between $g$ and $d$ and between $s$ and $d$. Because $D$ strongly perturbs $S$, the shape of the $g\rightarrow s$ seam is also strongly perturbed and no longer reflects the pure interaction between $S$ and $G$.

For the inversion reaction of the ammonia cation, only one electron is present in the lone-pair orbital and hence only two adiabatic states can be generated using these orbitals; this situation is directly analogous to electron-transfer problems. The shape of the conical intersection seam is distorted significantly for ammonia inversion, however, accommodating the addition of the $D$ state. Simple diabatic models focusing only on the apparent critical states, the $G$ and $S$ diabatic states, fail to include this distortion and so the values of the diabatic-model parameters are perceived to be quite different for the neutral and cationic molecules.

Shown also in figure 2 is the scenario for an aromatic molecule like benzene. For it, the HOMO and LUMO orbitals are doubly degenerate, so critical chemical processes such as the isomerization between its Kekulé structures that are dominated by excitations involving these orbitals intrinsically
involve 7 coupled diabatic states, the $G$ and $S$ states as before, now three different ways of making a $D$ states, plus in addition a triply excited state $T$ and quadrupally excited state $Q$. All diabatic states interact with each other to generate a multitude of conical-intersection seams with greatly varying shapes. The properties of the critical lowest-energy seam, that between $g$ and $s$, are modified to accommodate all other higher-energy seams. So whilst a single calculation based on the PJTE [17-20] manifested by the $g$-$s$ seam is likely to be very apt for the quantitative modelling of critical observed properties, the deduced parameters will not be global properties of the coupled orbital system but instead effective parameters depicting the modification of the intrinsic properties associated with the presence of the higher-energy seams.

To produce simple semi-quantitative models involving universally apt diabatic parameters, one must allow multiple seams with their varying shapes to be explicitly representable within the mathematical description used [28]. To do this, the number of diabatic electronic states involved must be expanded from two, as used in previous typical calculations exploiting the PJTE, to encompass all strongly coupled states and their generated conical-intersection seams. This is clearly 3 states for typical closed-shell chemical reactions but a useful approximation for aromatic reactions is to represent the 3 $D$ states by single state, making a 5-state model. We start with the traditional PJTE Hamiltonian [16-20] for a two-state linearly coupled system

$$H^{2D} = \begin{bmatrix} T + \frac{k}{2}Q^2 & \alpha Q \\ \alpha Q & T + \frac{k}{2}Q^2 + 2J \end{bmatrix}$$

(1)

which describes the $G$ and $S$ states produced when one electron (or hole) is distributed in two orbitals, where $Q$ is the reaction coordinate, $k$ is the force constant depicting harmonic vibration in this mode, $J$ is the electronic coupling (or resonance energy), $\alpha$ is the vibronic coupling constant, and $T = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Q^2}$ is the nuclear kinetic energy operator where $m$ is the effective mass of the oscillator.

Equation (1) is sometimes called Holstein Hamiltonian [13-14] and is equivalent in form to the Rabi Hamiltonian for spin dynamics [85-86] (as the full Jahn-Teller Hamiltonian is equivalent to the Rashba spin Hamiltonian [15]). Assuming that electron-correlation effects do not significantly modify the properties of the involved orbitals as orbital occupancy is changed, it can be immediately generalized [27-28,54] to include $D$ and then $T$ and $Q$ as [28]

$$H^{3D} = \begin{bmatrix} T + \frac{k}{2}Q^2 & \alpha Q & 0 \\ \alpha Q & T + \frac{k}{2}Q^2 + 2J & \alpha Q \\ 0 & \alpha Q & T + \frac{k}{2}Q^2 + 4J \end{bmatrix}$$

(2)

for two electrons in two orbitals, and
for four electrons in four orbitals. The form shown for the two-state system is typical of vibronic coupling Hamiltonians used in spectroscopy but can be transformed by a 45° rotation of the electronic basis set. This makes the Hamiltonian typically used in electron-transfer theory using a basis set representing diabatic reactant and product states having different equilibrium geometries, as depicted in figure 1:

\[
H^{2L} = \begin{bmatrix}
T + \frac{k}{2} Q^2 & \alpha Q & 0 & 0 & 0 \\
\alpha Q & T + \frac{k}{2} Q^2 + 2J & \alpha Q & 0 & 0 \\
0 & \alpha Q & T + \frac{k}{2} Q^2 + 4J & \alpha Q & 0 \\
0 & 0 & \alpha Q & T + \frac{k}{2} Q^2 + 6J & \alpha Q \\
0 & 0 & 0 & \alpha Q & T + \frac{k}{2} Q^2 + 8J
\end{bmatrix}
\]

(3)

where \( Q_m = \alpha / k \) and \( \lambda = 2kQ_m^2 = \frac{2\alpha^2}{k} = 2\alpha Q_m \). In this representation, the coordinates \( \pm Q_m \) specify the geometries of the uncoupled reactant and product species, whilst the role of \( J \) as the resonance energy linking the reactants to products is clearly displayed. The representations \( H^{2L} \) used in adiabatic electron-transfer theory and \( H^{2D} \) used in PJTE theory are formally equivalent and lead to identical Born-Oppenheimer potential energy surfaces and indeed all observable properties. While similar transformations yield new equations for description of the other scenarios in terms of localized chemical structures:

\[
H^{3L} = \begin{bmatrix}
T + \frac{k}{2} (Q + \sqrt{2}Q_m)^2 + 2J + \frac{\lambda}{2} & -\sqrt{2}J & 0 \\
-\sqrt{2}J & T + \frac{k}{2} Q^2 + 2J + \lambda & \sqrt{2}J \\
0 & \sqrt{2}J & T + \frac{k}{2} (Q - \sqrt{2}Q_m)^2 + 2J + \frac{\lambda}{2}
\end{bmatrix}
\]

(5)

and

\[
H^{3L} = \begin{bmatrix}
T + \frac{k}{2} (Q + \sqrt{2}Q_m)^2 & \frac{3\lambda}{4} & J + \frac{2J}{\sqrt{3}} & 0 & J + \frac{2J}{\sqrt{3}} & 0 \\
\frac{2J}{\sqrt{3}} & T + \frac{k}{2} (Q + Q_m)^2 - \frac{\lambda}{4} & -\frac{4J}{\sqrt{3}} & 0 & -J + \frac{2J}{\sqrt{3}} & 0 \\
0 & -\frac{4J}{\sqrt{3}} & T + \frac{k}{2} Q^2 & \frac{4J}{\sqrt{3}} & 0 & -J + \frac{2J}{\sqrt{3}} \\
J + \frac{2J}{\sqrt{3}} & 0 & \frac{4J}{\sqrt{3}} & T + \frac{k}{2} (Q + Q_m)^2 - \frac{\lambda}{4} & -J - \frac{2J}{\sqrt{3}} & 0 \\
0 & -J + \frac{2J}{\sqrt{3}} & 0 & -J - \frac{2J}{\sqrt{3}} & T + \frac{k}{2} (Q - \sqrt{2}Q_m)^2 - \frac{3\lambda}{4}
\end{bmatrix}
\]

(6)
The localized and delocalized representations are formally equivalent but expose critical properties in different ways. The delocalized (spectroscopic extended PJTE) description shows how vibronic coupling acts as a ladder operator to successively couple each diabatic state to the previous one, whilst the localized (kinetics) description readily depicts chemical reactions and shows what happens as conical intersections are approached (i.e., as \( J \rightarrow 0 \)). In this limit, the off-diagonal matrix elements disappear in the localized representation, revealing Born-Oppenheimer surfaces depicting molecular isomers with distinctly different equilibrium geometries. However, these equilibrium geometries occur at \( Q = \pm Q_m \) for \( H_{2L} \), \( Q = 0, \pm \sqrt{2} Q_m \) for \( H_{3L} \), and \( Q = 0, \pm Q_m, \pm \sqrt{3} Q_m \) for \( H_{3L} \). Hence the fundamental properties of the lowest-energy conical-intersection seam involved with the ground state change significantly as more and more coupled diabatic excited states are added. The parameters describing individual conical intersections and the perceived two-state PJTE are therefore not transferrable ones; transferrable parameters are only generated when all interacting diabatic states are included in the mathematical description.

Both sets of extended Hamiltonians can be transformed into other equivalent forms that reduce the complex problems to either uncoupled Born-Oppenheimer representations (shown in cyan) or else just coupled pairs of diabatic states. The coupled pairs of states then appear to be simple two-dimensional problems equivalent to problems from adiabatic electron-transfer theory and traditional PJTE theory. For reactions involving a single doubly occupied orbital and single unoccupied orbital, this yields

\[
H^{3D'} = \begin{bmatrix}
T + \frac{k}{2} Q^2 & 0 & \sqrt{2} \alpha Q \\
0 & T + \frac{k}{2} Q^2 + 2J & 0 \\
\sqrt{2} \alpha Q & 0 & T + \frac{k}{2} Q^2 + 4J
\end{bmatrix}
\]

(7)

\[
H^{3L'} = \begin{bmatrix}
T + \frac{k}{2} (Q + \sqrt{2} Q_m)^2 + 2J + \frac{\lambda}{2} & 0 & 2J \\
0 & T + \frac{k}{2} Q^2 + 2J + \lambda & 0 \\
2J & 0 & T + \frac{k}{2} (Q - \sqrt{2} Q_m)^2 + 2J + \frac{\lambda}{2}
\end{bmatrix}
\]

(8)

and indicates that the single-excitation can be decoupled whilst the ground state and doubly excited state appear to be connected analogously to the states involved in an electron-transfer application except for a renormalization of the parameters: the apparent vibronic coupling constant and nuclear displacement are \( \sqrt{2} \) times larger than expected, whilst the apparent resonance energy is doubled. For the case of aromatic processes, the situation is not so simple with equation (6) indicating a rescaling of the displacement by a factor of \( \sqrt{3} \) in the weak-coupling limit of \( 2 |J| / |\lambda| \ll 1 \), but in the alternate strong-coupling limit appropriate to benzene, the Hamiltonians can be transformed instead into
indicating a doubling of the displacement and quadrupling of the resonance energy. Equations (7)-(10) capture the critical features associated with Shaik’s concept that the ground-state has a “twin” excited state with intimately linked properties [69-73]. Previously, however, the twin state was presumed to be the singly excited state, but these equations show that the twin state is always the most excited state possible for the system in hand—the singly excited state for electron transfer, the doubly excited state for most chemical reactions, and the quadrupally excited state for aromatic systems. In this process, general chemical reactions involving many electrons and many interrelated conical-intersection seams are mapped onto a simple two-state model. In aromatic molecules the singly excited state is actually twinned to the triply excited state [28].

Ten chemical processes for which transferrable diabatic-model parameters have been determined are shown in figure 3, with their parameters given in table 1. These span a wide range of chemical phenomena from isomerization to aromaticity to small-molecule spectroscopy to organic conductors to natural and artificial molecules for solar-energy conversion. A critical property considers whether the ground-state has a single well or a double minimum: a double well is found whenever [44]

$$\left( \frac{E_0}{\Delta E} \right)^2 < \left[ 1 - \left( \frac{2|J|}{\lambda} \right)^{2/3} \right] \left[ 1 + \left( \frac{2|J|}{\lambda} \right)^{2/3} \right]$$

or

$$\left( \frac{E_0}{\Delta E} \right)^2 < \left[ 1 - \left( \frac{2|J|}{\lambda} \right)^{2/3} \right] \left[ 1 + \left( \frac{2|J|}{\lambda} \right)^{2/3} \right]$$

where $\Delta E = (\lambda^2 + 4J^2)^{1/2}$ is the electronic energy gap. For weak coupling with $2J/\lambda \rightarrow 0$, a double well occurs whenever $|E_0|/\lambda < 1$ but for symmetric systems with $E_0 = 0$, symmetry breaking occurs whenever $|E_0|/\lambda < 1$.

Hence from table 1, benzene has high symmetry (2|J|/\lambda = 3.3) whilst ammonia has low symmetry (2|J|/\lambda = 0.8).
Figure 3. Some sample molecular systems (0 [87-89], 1 [90-91], 2 [92-93], 3 [46,94], 4 [95], 5 [96], 6 [97], 7 [43,46], 8 [47,50], and 9 [46]) with electronic states that can be described using two coupled diabatic potential-energy surfaces. OMe is methoxy, PHY is phytyl; tBu is tertiary butyl; A is ammonia; FcPC$_{60}$ is Zinc, [(5,10,16,21-tetakis[3,5-bis(1,1-dimethylethyl)phenyl]-13-[4-(1',5'-dihydro-1'-methyl-2'H-[5,6]fullereno-C$_{20}$$^+_{66}$)$_{14}$[1,9-c]pyrrol-2'-yl]phenyl]-1,12-dihydro-23H,25H-diimidazol[4,5-d:4',5'-j]porphin-2-yl-kN$_{23}$,kN$_{24}$,kN$_{25}$,kN$_{26}$]ferrocenato(2-)], (SP-4-1); Alq3 is mer-tris(8-hydroxyquinolinato)aluminum(III); DPP is ruthenium(5+), decammin[μ-[4,4'-((1ε,3ε)-1,3-butadiene-1,4-diyl)bis[pyridine-kN]]di- (9CI). Reproduced from Reimers J R, McKemmish L, McKenzie R H, and Hush N S 2015 Phys. Chem. Chem. Phys. 17 24640 with permission of the PCCP Owner Societies.

| System | $\frac{2|J|}{\hbar\omega}$ | $\frac{\Delta E}{\hbar\omega}$ | $\frac{E_0}{\hbar\omega}$ | $\frac{\Delta\epsilon}{\hbar\omega}$ | $\frac{Q_s}{\hbar\omega}$ |
|--------|--------------------------|----------------------------|------------------------|---------------------------|---------------------|
| 0 FcPC$_{60}$ | 0.029 | 0.15 | -13 | 0.06 | 45 |
| 1 DPP | 0.043 | 0.08 | 0 | 0.11 | 11 |
| 2 Alq3 | 0.08 | 0.16 | 0 | 0.14 | 6.3 |
| 3 PYR | 0.3 | 0.095 | 1.3 | 0.67 | 0.28 |
| 4 BNB | 0.74 | 0.18 | 0 | 1.11 | 0.10 |
| 5 CT | 0.80 | 0.089 | 0 | 1.68 | 0.045 |
| 6 CT-OMe | 0.80 | 0.089 | 1.5 | 1.68 | 0.045 |
| 7 NH$_3$ | 0.80 | 0.006 | 0 | 6.45 | 0.003 |
| 8 PRC | 1.8 | 0.41 | 0.6 | 1.39 | 0.065 |
| 9 Benzene | 3.3 | 0.010 | 0 | 12.6 | 0.001 |

3. Usefulness of having transferrable parameters

Once the simple two-state one-mode model is established, many analytical results are available relating ground-state and excited-state structural, spin density, electrochemical potential, and kinetic properties (see, e.g., [2,5-6,8-10,13-14,16-20,27-29,34,44,48,98-100]), with other equations also available for multi-mode situations (see e.g., [27,54,99]). Standard relationships from parallel PTJE studies [16-20] can also be applied. Such relationships provide insight into fundamental chemical processes. Here we consider how benzene chemistry can be related to carbon chemistry involving
standard single and double bonds, as well as to understanding why first-row chemistry is so different to the rest.

3.1. Deducing the CC bond lengths in ethane and ethylene from properties of benzene

Standard relationships from adiabatic electron-transfer theory or PJTE theory apply directly to the ground state and its twin state, and it is possible to generate many parallel ones relating to properties of other states involved in multi-electron systems [28]. Here we provide a simple example of the power of this approach, determining the bond-length alternation in hypothetical cyclohexatriene (a Kekulé structure of benzene) from only the observed ground-state and singly-excited state spectral properties and the atomic masses [28]. The motion involved is sketched in figure 4 in terms of an internal bending angle \( \phi \) that produces C-C bonds of alternating length. Formally, the resulting “bond-length alternation” is defined as the difference between the bond lengths of the resulting single bonds and the double bonds, and the deduced value of 0.109 Å is in excellent agreement with the value of 0.113 Å estimated based on analysis of observed bond lengths for related conjugated molecules [101].

From equation 3, the vertical excitation energy of the twin Born-Oppenheimer state \( g \) from the benzene ground state \( s \) is \( 8|J| \), whilst that for the singly excited state \( s \) is \( 2|J| \). The observed excitation energy for \( s \) is 4.77 eV and hence \( |J| = 2.4 \) eV. The relationships between the Born-Oppenheimer vibration frequencies in the various states are [28]

\[
\frac{2|J|}{\lambda} = \frac{\omega_s^2}{\omega_q^2 - \omega_s^2} = \frac{\omega_q^2 + \omega_s^2}{\omega_s^2 - \omega_g^2}.
\]

Using the observed values of \( \omega_s = 1309 \text{ cm}^{-1} \) and \( \omega_s = 1564 \text{ cm}^{-1} \) (n.b., the excited state frequency exceeds the ground state frequency owing to the underlying double-well structure) yields \( 2|J|/\lambda = 3.34 \). Misinterpretation of \( s \) as the twin state \( q \) of \( g \) would have yielded \( 2|J|/\lambda = 5.68 \) instead; using the correct value then leads to \( \lambda = 1.43 \) eV, otherwise \( \lambda = 0.84 \) eV. The force constant \( k \) for the vibration can be determined from the known [102] moment of inertia associated with the rotation by \( \phi \) combined with the diabatic vibration frequency \( \omega \). This is given simply by \( \omega = \omega_s \) when all states are included and by \( \omega = \omega_s (1 + \lambda/2|J|)^{1/2} \) if the twin state is incorrectly identified as \( s \) instead of \( q \). Using the correct relationship leads to \( k = 0.43 \text{ eV/Å}^2 \), otherwise 0.37 eV/Å². The force constant is related to the geometry \( \phi_m \) corresponding to hypothetical cyclohexatriene without any resonance stabilization by

\[
\lambda = 2k \left( \frac{\phi_m}{2} \right)^2
\]

if all states are included (equation 10), leading to \( \phi_m = 2.58^\circ \) and hence a bond length alternation of 0.109 Å, close to the value deduced [101] from experimental data of 0.113 Å. Assuming that \( s \) is the twin state would have lead instead to (equation 4)

\[
\lambda = 2k \phi_m^2
\]
which, when combined with the analogous previous results, leads to a bond-length alternation of just 0.045 Å.

We see that recognition of the presence of higher-energy conical intersection seams has significant repercussions for the actual properties of the lowest-energy seam and hence the ground-state structure. Recognition of the intrinsic relationships involved leads to equations depicting many properties in terms of simple expressions. Shaik’s “twin state” concept led to qualitative understanding of various key properties [61,62,63,64,65] but never led to quantitative analysis owing to its misidentification of the actual state that is twin to the ground state.

3.2. Why ammonia is so different to phosphine, stilbene, and the other group XV hydrides

The inversion reaction in the XH₃ series of molecules involves the mixing of the X lone-pair orbital n with the symmetric antibonding orbital σ*ₓₓₓₓ as a function of the out-of-plane torsional angle τ that distorts the geometry from planar to pyramidal [43]. The HXH bond angle θ also changes with this motion simple according to

\[ 2 \cos \theta = 3 \sin^2 \tau - 1. \]  

(16)

Table 3 indicates that the observed [28] bond angles contract from the hypothetical value of 120° for a planar structure to 108° for NH₃ to 93° for PH₃ for 90° in BiH₃. A critical question is as to why there is such a large difference between ammonia and phosphine, with then only little change as one goes further down the periodic table. Another question is as to what limiting angle would be expected if the periodic table could be extended down to many more rows, whilst a third question concerns what happens when one of these molecules is ionized to make XH₃⁻. Traditional chemical explanations such as Valence-Shell Electron-Pair Repulsion Theory (VSEPR) [103-105] either just decree N to be tetrahedral and P to be octahedral or else assign atom sizes to fit the results, but they do not explain why N is so different to P. VSEPR provides no insight into what the chemistry might be like on later rows of the periodic table, and whilst it explains the basic result that the bond angles in the radical cations are larger than those in the neutral molecules, it makes no quantitative prediction of the magnitude of the effect. Traditional analyses made using PJTE approaches [106] analyzed in terms of change to the resonance energy, force constant, and vibronic coupling constants accurately describe calculated and experimental data but do not perceive the relationships between the key variables and provide no explanation as to why these quantities change in the way they do between NH₃ and PH₃ and therefore have not led to basic understanding.

Table 3. Estimates of the critical parameters for XH₃ inversion reactions coming from (i) observed or calculated data for the ground-state equilibrium torsional angle τₑ (or equivalently bond angle θₑ) and barrier height Δ𝐸†, Jₑ, and λₑ, and (ii) from calculated vertical transition energies at the planar and ground-state equilibrium geometries to the twin state q [43], J₂ and λ₂.

| XH₃ | τₑ | θₑ | Δ𝐸† | Jₑ | λₑ | EOM-CCSD/VTZ | τₑ | θₑ | Δ𝐸† | Jₑ | λₑ | J₂ | λ₂ |
|-----|----|----|-----|----|----|-------------|----|----|-----|----|----|----|----|
| NH₃ | 21.4 | 107.5 | 0.22 | 0.82 | 23⁰ | 28⁰ | 22.8 | 0.27 | 0.79 | 20.4⁰ | 26⁰ | 0.85 | 38 | 45 |
| PH₃ | 32.9 | 93.3 | 1.38 | 0.48 | 10⁰ | 21⁰ | 32.5 | 1.5 | 0.50 | 12.1 | 24 | 0.53 | 14 | 27 |
| AsH₃ | 33.8 | 92.0 | 1.38 | 0.44 | 8⁰ | 17⁰ | 33.5 | 1.82 | 0.45 | 11.0 | 24 | 0.48 | 13 | 26 |
| SbH₃ | 34.2 | 91.5 | 1.63 | 0.41 | 8⁰ | 19⁰ | 33.8 | 1.99 | 0.44 | 10.9 | 25 | 0.43 | 10 | 24 |
| BiH₃ | 35.1 | 90.3 | 1.67 | 0.36 | 6⁰ | 16⁰ | 34.7 | 2.65 | 0.38 | 10.7 | 28 | 0.34 | 9 | 25 |

ᵃ: large errors arise from valence/Rydberg orbital inversion modifying τₑ, combined with the instability of equation (16) as of 2Jₑ/λₑ → 1.
ᵇ: Δ𝐸† extrapolated from observed transitions and/or calculated data only up to 0.5 eV.
While just two orbitals are sufficient to describe the chemistry of the inversion reaction, attempting to apply the appropriate diabatic models leads immediately to difficulties as most observed spectra are dominated by Rydberg transitions rather than the valence states of interest. This creates not only the experimental challenge of isolating key high-energy spectroscopic transitions but also the conceptual one of understanding how the Rydberg states interact with and so distort the valence-state surfaces. As a result, the basic 3-state \((G, S, D)\) diabatic description must be augmented by adding the lowest Rydberg state \(R\), its double excitation \(DR\), and the combined Rydberg-Valence double excitation \(RV\) \([43]\). High-level calculations provide a large amount of data and allow all transitions to be followed as a function of the torsional (or bond) angle changes. However, the interesting regions of the potential-energy surfaces range out to torsional angles of 50° (bond angles down to 68°) and so anharmonic effects also become important. The simplest quantitative diabatic model that could describe the shapes of all key adiabatic potential-energy surfaces out to such angles was found to have 11 parameters: the basic 3 diabatic-model parameters expanded to 5 to allow for (small) changes in orbital properties with occupation, expanded to 8 to include anharmonicity, and finally expanded to 11 to include the Rydberg states. While this complexity seems to destroy the desired simplicity and generality of the diabatic chemical description, at least 24 parameters are required to describe the same data using a (non-physical) Taylor expansion of each of the calculated adiabatic surfaces, whilst all of the 11 diabatic-model parameters have clear physical meaning. The power of the diabatic approach remains apparent as it led to the reassignment of many observed high-energy bands in the absorption spectrum of ammonia, bands previously described as Rydberg transitions that were actually intense valence absorptions instead \([43]\). What results is a comprehensive analysis of a wide range of experimental and high-level computational data, isolating key excited-state resonances located well above the ionization continua of the XH\(_3\) series.

Such a quantitative analysis provides the basis for qualitative understanding. Assuming that the notion of twin states still holds, the properties of the ground state \(g\) and its twin-state \(d\) may be considered in isolation, allowing effective 2-state model parameters to be deduced from the properties of the ground-state surface and the vertical excitation energy of the twin state at the planar geometry. As the diabatic-model parameters depict many different observable properties, this process may be conducted in many different ways and the process only makes clear sense if the deduced parameters are insensitive to the method used. Here we report in table 3 on two possible ways of doing this.

First, we consider the vertical excitation energies to the twin state \(d\), labelling the deduced parameters as \(J_2\) and \(\lambda_2\), using the EOM-CCSD \([107-108]\) method and valence triple-zeta \([109-111]\) (VTZ) basis sets to calculate the transition energies using MOLPRO \([112]\). The important relationships here are simply \([28,43]\)

\[
\begin{align*}
4|J_2| &= \text{vertical excitation energy at the planar geometry } \tau=0 \\
2\lambda_2 &= \text{vertical excitation energy at the ground-state adiabatic minimum } \tau=\tau_c.
\end{align*}
\]

Next, we determine parameters named \(J_u\) and \(\lambda_u\), from just the values of the adiabatic ground-state well depth \(\Delta E^\dagger\) and equilibrium angle \(\tau_c\) using

\[
\left(\frac{2J_u}{\lambda_u}\right)^2 = 1 - \left(\frac{\tau_c}{\tau_m}\right)^2
\]

(18)

\[
\lambda_u = 4\Delta E^\dagger \left(1 - \frac{2|J_u|}{\lambda_u}\right)^2.
\]

This approach requires knowledge of the third parameter \(\tau_m\) (equivalent to \(Q_m\) in equations (4)-(10)) specifying the torsional angle in the absence of resonance. Many alternative ways of independently estimating all three parameters are known, and it was found that these result in \(\tau_m\) (and hence the XHX angle \(\theta_m\)) being identified as universal parameters for the whole XH\(_3\) series \([43]\). This can be
understood by noting that the diabatic orbitals can be identified as \( sp \) hybrids based on the natures of the interacting \( n \) and \( \sigma^*_{\text{NH}} \) orbitals. Simple geometry assuming that the diabatic angles are produced by maximizing overlap between the hydrogen \( 1s \) orbitals and the three \( X \) orbitals orthogonal to a \( sp \) hybrid, as shown in Figure 5, then leads to

\[
\tau_m = \text{atan} \left( \frac{1}{2} \right) = 26.6^\circ, \quad \theta_m = \text{acos} \left( \frac{1}{5} \right) = 101.5^\circ \tag{19}
\]

and is appropriate for the electron-transfer-type case in which one electron is involved in the reaction. This scenario therefore describes the bond angle in the limit of no resonance energy for the \( \text{XH}_3^+ \) series. When two electrons are involved, the effect of the \( S-D \) interaction is to distort the ground state, scaling \( \tau_m \) out to

\[
\tau_m = \sqrt{2} \text{atan} \left( \frac{1}{2} \right) = 37.6^\circ, \quad \theta_m = \text{acos} \left[ \frac{3}{2} \sin^2 \left( \sqrt{2} \text{atan} \left( \frac{1}{2} \right) - \frac{1}{2} \right) \right] = 86.7^\circ \tag{20}
\]

for \( \text{XH}_3 \). These equations provide the answer to the fundamental question as to what would the limiting geometry be for \( X \) being on the infinite row of the periodic table. Assuming that the diabatic angles universally take this value, \( J_u \) and \( \lambda_u \) can be immediately determined from the adiabatic well depth and equilibrium geometry using equation 16.

![Figure 5](image_url)  

Values of \( J_u \) and \( \lambda_u \), deduced from experimental data and from CCSD/VTZ data are given in table 3. These show the same trends but absolute values differ by up to a factor of two. Such sensitivity arises as the values of \( 2J_u/\lambda_u \), which are also given in the table, are not far from one, the limit at which Equation (16) becomes unstable. Improved calculations at the CCSD(T)/aug-cc-pCVQZ level give results much closer to the experimental ones, with the differences between the calculated results serving to highlight how difficult it can be to extract simple characteristic data for real systems displaying manifold bystander processes. Comparing values deduced by two very different approaches utilizing computed data, \( J_u \) and \( \lambda_u \) compare well to \( J_2 \) and \( \lambda_2 \) except for the case of \( \text{NH}_3 \). The poor agreement for \( \text{NH}_3 \) stems from the strong interaction between the valence and Rydberg states manifested in the calculations and so is itself a useful result, pointing to a key physical feature.

Most importantly, all three methods used to determine the critical ratio \( 2J_u/\lambda_u \) reported in table 3 yield very similar results, indicating that this feature can be robustly determined from experimental and (medium quality) calculated data. The subtle effects that dominate excitation energies and
transition-state energies especially when $2J/\lambda \approx 1$ do not influence this ratio to the same extent as they influence the perceived resonance and reorganization energies themselves. Equation (16) shows that just their ratio controls the equilibrium geometry and hence it is this robustly determined property that is responsible for the large change in bond angle observed between ammonia and phosphine. Indeed, for ammonia, these ratios are much larger (ca. 0.8) than they are for PH$_3$ – BiH$_3$ (ca. 0.5 – 0.4), explaining the parallel abrupt change in geometry observed. The critical question concerning why nitrogen prefers tetrahedral coordination whilst phosphorous and the heavier elements prefer octahedral coordination then can be answered by finding why the value of $2J/\lambda$ changes so abruptly between NH$_3$ and PH$_3$. Table 3 shows that there is an abrupt change in $\lambda$ between NH$_3$ and PH$_3$ but that the change in $J$ appears as the square of that in $\lambda$. So there is a common process involved in modifying both quantities, with the resonance energy being a clearer indicator. Hence we focus on why this quantity changes so much.

Equation (2) indicates that $4|\lambda|$ is essentially the increase in energy when both electrons are taken from the lone-pair orbital $n$ to the $\sigma^*_{XH}$ orbital at the planar geometry. We find that while the lone-pair orbital change smoothly down the periodic table, discontinuous changes occur to $\sigma^*_{XH}$. Figure 6 indicates the source of this discontinuity [43], showing the $\sigma^*_{NH}$ and $\sigma^*_{AsH}$ orbitals evaluated using minimal (STO-3G) basis sets as well as those augmented by a single Rydberg $s$ function. For NH$_3$, the antibonding orbital contracts significantly when the Rydberg orbital is present. This happens because the valence orbital is higher in energy than the Rydberg orbital, and these two significantly interact leading to “bonding” and “antibonding” pairs. The combination that is most relevant to the twin state of the ground state is the antibonding combination, one which has a nodal surface separating its inner (valence dominated) and outer (Rydberg dominated) regions. The presence of this nodal surface compresses the valence orbital. However, the orbital ordering reverses between NH$_3$ and PH$_3$, so that for heavier elements the most relevant combination is the bonding one. This allows the antibonding orbital to delocalize and spread out. The twin state is made through double-occupation of the antibonding orbital. When this orbital is compressed, the intra-orbital electron-electron repulsion energy is dramatically increased, increasing the orbital energy and hence the resonance energy. As the properties of the ground state are intimately linked to the properties of its twin state, the properties of ammonia are distinctly different to those of the rest of the Group-XV hydrides. This effect is likely to be generally descriptive of the properties of first-row elements compared to those of later rows. Virtual-orbital mixing is a long-recognized process affecting excited-states known as “Rydbergization” [113-114]. What we see here is that the ground-state is the “twin-state” to an affected excited state, so that whatever happens to the excited state also becomes important for understanding ground-state properties.

Figure 6. Isodensity surfaces of the unoccupied $\sigma^*_A$ valence orbital of NH$_3$ and AsH$_3$ that controls hybridization, at its planar D$_{3h}$ structure, evaluated using the Hartree-Fock method. Reproduced with permission from Reimers, McKemmish, McKenzie and Hush 2015 Phys. Chem. Chem. Phys. 17 24618 with permission of the PCCP Owner Societies.
4. Usefulness of having a general model for chemical processes

Being able to describe wide-ranging chemical processes using a consistent model enables global questions to be addressed concerning the types of chemistry appropriate for certain needs, and the accuracy of computational approaches used to model chemical processes. We consider general issues associated with failure of the Born-Oppenheimer approximation, and the question as to what type of chemical reaction would be best suited for application in a chemical quantum qubit.

4.1. Fundamental nature of Born-Oppenheimer breakdown

The Born-Oppenheimer approximation may be applied to any of the previous Hamiltonians by parametrically diagonalizing them as a function of the nuclear coordinate. For the two-state systems $H^{2L}$ and $H^{2D}$, we add an energy asymmetry $E_0$ to allow for exothermic or endothermic reactions as sketched in figure 1, revising them to

$$H^{2L} = \begin{bmatrix} T + \frac{\hbar \omega}{2}(Q + Q_m)^2 + J - \frac{\lambda}{4} & J \\ J & T + \frac{\hbar \omega}{2}(Q - Q_m)^2 + J - \frac{\lambda}{4} + E_0 \end{bmatrix}$$

and

$$H^{2D} = \begin{bmatrix} T + \frac{\hbar \omega}{2}Q^2 + \frac{E_0}{2} & \alpha Q - \frac{E_0}{2} \\ \alpha Q - \frac{E_0}{2} & T + \frac{\hbar \omega}{2}Q^2 + 2J + \frac{E_0}{2} \end{bmatrix},$$

where now dimensionless normal coordinates are used for simplicity ($Q \rightarrow Q / (\hbar \omega)^{1/2}, \ k \rightarrow \hbar \omega, \ T \rightarrow -\hbar \omega / 2 \times \partial^2 / \partial Q^2$) [102]. Diagonalization of either of these equations leads to Born-Oppenheimer [115-117] adiabatic ground-state and excited-state potential-energy surfaces $\epsilon_\pm(Q)$, as shown in figure 1, where [7]

$$\epsilon_\pm(Q) = \frac{E_0}{2} + \frac{\lambda}{4} + \frac{\hbar \omega}{2}Q^2 \pm \left( \frac{E_0}{2} - \hbar \omega Q_mQ \right)^2 + J^{1/2}.$$  

(23)

Using them, the original Hamiltonians may be equivalently represented in the Born-Oppenheimer electronic-state basis as

$$H^{BO} = \begin{bmatrix} T + \epsilon_-(Q) + \Delta H^{DC}(Q) & \Delta P^{FD}(Q) \frac{\partial}{\partial Q} + \Delta H^{SD}(Q) \\ \Delta P^{FD}(Q) \frac{\partial}{\partial Q} + \Delta H^{SD}(Q) & T + \epsilon_+(Q) + \Delta H^{DC}(Q) \end{bmatrix}.$$  

(24)

Almost all modern calculations are performed neglecting all terms except $T + \epsilon_\pm(Q)$, known as the Born-Oppenheimer approximation:

$$H^{BO} \approx \begin{bmatrix} T + \epsilon_-(Q) & 0 \\ 0 & T + \epsilon_+(Q) \end{bmatrix}.$$  

(25)

This is a type of adiabatic approximation as there are no terms linking the different electronic states and hence the problem separates into independent ones for the electronic and nuclear motions. Including the diagonal correction $\Delta H^{DC}(Q)$ only also constitutes an adiabatic approximation known as the Born-Huang approximation [116-117]:

4. Usefulness of having a general model for chemical processes
\[
H^{BO} \approx \begin{bmatrix}
    T + \varepsilon_-(Q) + \Delta H^{DC}(Q) & 0 \\
    0 & T + \varepsilon_+(Q) + \Delta H^{DC}(Q)
\end{bmatrix},
\]
which is often described as embodying a mass-dependent correction to the two Born-Oppenheimer molecular potential-energy surfaces
\[
\varepsilon^{BH}_\pm (Q) = \varepsilon_\pm (Q) + \Delta H^{DC}(Q).
\]
The terms $\Delta \rho^{FD}(Q)$ and $\Delta H^{SD}(Q)$ provide first-derivative (momentum) and second-derivative (kinetic energy) nonadiabatic corrections that couple the two adiabatic basis states.

For the two-state one-harmonic-model, the three correction terms to the Born-Oppenheimer approximation evaluate as [44]
\[
\begin{align*}
\Delta \rho^{FD}(Q) &= \frac{h \omega}{2} \frac{Q_c}{Q_x^2 + (Q - Q_x)^2} \\
\Delta H^{DC}(Q) &= \frac{1}{2 \hbar \omega} \left( \Delta \rho^{FD}(Q) \right)^2 \\
\Delta H^{SD}(Q) &= \frac{2}{\hbar \omega} \frac{Q - Q_x}{Q_c} \left( \Delta \rho^{FD}(Q) \right)^2
\end{align*}
\]
where $Q_x$ is the location of the intersection of the localized diabatic surfaces,
\[
Q_x = \frac{E_0}{\lambda} Q_m
\]
and $Q_c$ is the diameter of the cusp formed at the crossing point,
\[
Q_c = \frac{2 |f|}{\lambda} Q_m.
\]
The critical role of the cusp diameter in determining the properties of chemical reactions was first recognized by London [57,118], forming the basis of the adiabatic theory of electron transfer developed by Hush [2,5]. As a conical intersection seam is approached, $Q_c \to 0$ and so all three Born-Oppenheimer corrections diverge to infinity.

Equation (26) presents a hierarchy of terms with the diagonal correction and second-derivative correction scaling as the square of the first-derivative one. Such scaling is in general independent of the number of nuclear degrees of freedom considered [119-122]. Based upon this hierarchy, for nonadiabatic electron-transfer reactions and other processes occurring near conical intersections, it is typical to only include the first-derivative term in calculations. Away from conical intersections say in the reactant or product valleys, the influence of the derivative corrections is greatly reduced owing to the large energy gap that develops between the two adiabatic surfaces, but such a scaling does not apply to the diagonal correction. It is therefore common practice when considering ground-state vibration frequencies and redox potentials to include only it when accurate calculations are desired.

The one-mode two-state model is useful in that it allows numerically exact results to be deduced for all observable properties simply and easily through solution of (any one of) the diabatic Hamiltonians [44]. It can also be extended to multi-mode multi-state problems including modes of different symmetry [27] (e.g., the electrochemical, spin resonance, electronic spectroscopy, vibrational spectroscopy, Stark spectroscopy, etc., of the special-pair radical cation in bacterial photosynthesis can be quantitatively modelled [47,49] in quick time using a 70-mode 4-state model [50], the Q-band spectra of the chlorophyllides can be fitted using a real-time algorithm involving 52 modes and 2 states [55], etc.). However, solution of the problem using Born-Oppenheimer basis functions is intrinsically unstable, requiring vibrational basis sets with dimensions found to scale empirically as conical intersections are approached as $1/6Q_c^2$ [44]!.

A simple way to understand this result is to note
that the diagonal correction is sharply spiked at the crossing point $Q = Q_x$ of the diabatic surfaces and
adds an extra height of
\[ \Delta A E^\downarrow = \left( \Delta H^{\text{DC}} (Q) \right)_{\text{max}} = \frac{\hbar \omega}{8Q_x^2} \]  
(31)
to the Born-Oppenheimer transition-state energy (or saddle point energy for the inverted region) $\Delta E^\downarrow$. This correction also grows alarmingly as conical intersections are approached, as shown in table 1 for some illustrative examples. Essentially we see that surface-hopping or other non-adiabatic calculations cannot be performed accurately unless all vibrational levels of energy less than $\Delta A E^\downarrow$ are included in the basis set.

This general requirement for the convergence of any numerical calculation of full quantum dynamics performed using the Born-Oppenheimer representation immediately tells that the diagonal correction is globally important. Across the full parameter space of the model, we found no region in which including only the first-derivative correction in calculations led to results similar to the exact ones [44]. The widely applied practice of using just this term in non-adiabatic calculations is therefore invalid. On the contrary, we found that not only for processes occurring at potential-energy minima but also for processes near conical intersections, the diagonal correction alone may give useful results. Many processes labelled “non-adiabatic” and treated by surface-hopping mechanisms may indeed be much more accurately modelled as an adiabatic process on the Born-Huang ground-state surface, with crossing from reactants to products blocked simply by the high transition-state energy induced by $\Delta A E^\downarrow$ [44]. For example, in the inverted region in which the coupling is small (see [44] for the general case) and $\lambda > -E_0$ so that reactions become slower as they become more exothermic [8,10,123], no adiabatic transition-state is present in the Born-Oppenheimer surface and hence chemical reactions are interpreted usually in terms of surface hopping, but the associated Born-Huang surface almost always does contain an adiabatic transition state whose properties are a primary controlling element. However, in general, inclusion of all three Born-Oppenheimer corrections is required in order to obtain accurate results for processes near conical intersections.

Herein, all results are presented for a one-dimensional model descriptive of many processes that occur on slices formed near a multi-dimensional conical intersection. As these slices approach the conical intersection seam (i.e., as $J \rightarrow 0$), the cusp diameter approaches zero, dramatically enhancing the height of the barrier $\Delta A E^\downarrow$ as it narrows its width. That all three terms must be considered in full quantum dynamics is not an accident but a fundamental property of conical intersections.

Conical intersections form an example of a pitchfork bifurcation cusp catastrophe [80-83]. They thus form a subset of a well-studied area of mathematics. One of the general properties of such systems is that it is not possible to expand dynamics near the cusp using approximate hierarchical methods: dynamics becomes intrinsically chaotic, and only extensive complete solutions yield accurate results. This property is dimension independent, with the results found by comparing approximate and numerically exact quantum dynamics in the one-dimensional case providing a typical example. The one-dimensional model thus provides a critical test case for more general methods.

4.2. Choice of chemical reaction for use as a chemical quantum qubit

Chemical qubits have been suggested as possibly providing the basis for some quantum information processing technology [124], and have even been postulated as having a role in the phenomenon of consciousness [125-126]. Chemical qubits are based on the entanglement of nuclear and electronic motions involved in isomerization reactions. Armed with a model that allows all such processes to be consistently treated, it is possible to consider the whole chemical parameter space available and hence to recommend what types of reactions may prove suitable. Concerning a possible role in consciousness, we showed that the originally proposed model [125-126] involving tubulin-dimer isomerization was fundamentally flawed in that the proposed vibration was in fact an irreversible chemical reaction [127] and also that the proposed mechanism for coherence was in general untenable.
As no specific replacement qubit has been suggested, we have concluded that at the moment their proposal is without any current basis for scientific discussion [129].

More generally, the issue of coherence is critical when it comes to considering chemical quantum computers: qubit operation requires very long coherence times and hence great isolation of the qubit from its environment, yet function in some quantum information device requires the limiting classical states of the qubit to be easily read and written, requiring strong interaction [130]. Entanglement is the critical element of a quantum qubit and while any amount of entanglement is in principle useful [130], realistic devices require a large amount of entanglement of order $S = 1$, where $S$ is the von Neumann entropy of the system. This entropy ranges from zero for a classical system to unity for a completely entangled qubit. Evaluated across the parameter space of the single-mode two-state chemical model [46], the developed entanglement is shown in figure 7. Different plots show the entanglement as a function of $2J/\lambda$ and $\hbar \omega / \Delta E$ for different values of the energy asymmetry $E_0 / \hbar \omega$, with the Born-Oppenheimer surfaces sketched at a characteristic point on each plot. For symmetric isomerization reactions like ammonia inversion, the entanglement is near unity whenever $2J/\lambda < 1$ (localized double-well potential) and $\hbar \omega / \Delta E < 1$ (away from the region where the dynamic Jahn-Teller effect becomes important with clear vibrational energy levels forming in each well). This result documents the initial intuition leading to the postulate that chemical qubits could be useful for quantum information processing [124].

**Figure 7.** The entanglement (von Neumann entropy) $S_0$ of the ground vibronic level is shown as a function of $2J/\lambda$ and $\hbar \omega / \Delta E$ for various values of the energy asymmetry $E_0 / \hbar \omega$ taken as the effect of local environment on an otherwise symmetric isomerization reaction [46]. The Born-Oppenheimer potential-energy surfaces and associated entanglement are indicated for the key situation for each $E_0 / \hbar \omega$ value depicted by the red arrows. Values appropriate to the 10 sample molecular systems from figure 1 and table 1 are indicated, with molecules having large $|E_0 / \hbar \omega|$ grouped together on the right-most plot.

The simplest way to model the effects of environment on coherence and hence entanglement is to treat the environment as simply generating random fluctuations in the energy asymmetry $E_0$. Figure 7 shows what happens to the highly desired scenario for symmetric reactions when a small amount of
asymmetry modelled as $E_0 / \hbar \omega = 0.01$ is added. Entanglement is lost over much of the parameter space, remaining robust only when the coupling is strong and only a few vibrational levels fill the double-well region. Any practical qubit would need to be constructed using isomerization reactions having this very restrictive property. Increasing the asymmetry to the large but not unprecedented value of $E_0 / \hbar \omega = 0.1$, the maximum achievable entanglement becomes $S_0 = 0.67$ in a very small region of the parameter space, with higher levels of asymmetry seemingly preventing any practical device. Of the molecular systems considered, the dipyridyl polycene 1 and the Alq3 2 sit in the region of greatest entanglement and greatest environmental immunity, whilst BNB 4 and the Creutz-Taube ion 5 sit in a region where the entanglement never gets much more than one half but it is quite stable to environmental perturbation. Whether or not the ground-state vibrational density is bimodal (i.e., zero-point vibration is supported in each well) is a critical indicator of qubit performance [46].

5. Conclusions
The success in modern times in accurate modelling of complex data involving the PJTE and related effects has not been matched by parallel increases in conceptual understanding. Individual molecular properties are always complex, and understanding this complexity is always essential for accurate modelling. However, key aspects of the chemical process can usually be described in terms of some basic phenomenon, providing fundamental understanding. We show how such simplicity of understanding can be revealed amidst the complexity of results coming from high-level calculations and detailed experimental data, highlighting the roles played by high-energy states in controlling the properties of the low-energy states of direct interest. Simplicity has rarely been found in standard applications of PJTE theory as these are usually cast in terms of the resonance energy, the force constant, and the vibronic coupling constant as fundamental variables, yet by convolving the force constant and the vibronic-coupling constant to produce the reorganization energy means that many critical properties including the presence/absence of symmetry breaking is controlled simply by the dimensionless ratio of the resonance and reorganization energies. Application of this transformation is always possible and will always aid PJTE studies. More significantly, however, PJTE is usually applied only between the states of direct interest, producing numerically accurate methods involving effective two-state parameters rather than global transferrable parameters involved when all states sharing the same vibronic coupling are included in the analysis. Without understanding the overall structure of many interacting conical-intersection seams, basic simplicity cannot be obtained.

Simplicity delivers models with transferrable parameters usable in a wide range of related scenarios. Shaik’s concept that the ground-state is twinned to an excited state whose properties are directly linked is converted into a semi-quantitative analysis method. Conceptually, this means that the properties of the ground state can be understood through understanding the properties of its twin state and the relationships between them. This reveals that Rydbergization of the excited states of the first-row elements is the property that makes them so different to the elements in the later rows of the periodic table. It also shows how isomerization and symmetry breaking can be understood in general terms for all chemical processes, allowing a consistent platform for teaching chemistry to be established that is fully compatible with teaching in condensed-matter physics. Other general questions can also be addressed like what chemical reactions are likely to be useful as the basis of quantum qubits, and, through exact quantum solution of simple model problems, what is required in high-level calculations taking on modern challenges in understanding non-adiabatic chemistry. Gaining an intrinsic understanding of chemistry and how it functions then leads back to the development of better methods for rigorous modelling.

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