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Quantifying Electron Transfer Paths

As the name states, Physical Chemistry operates at the intersection of physics and chemistry. One fundamental difference between these sciences is that physics is governed by laws, whereas chemistry is mostly discussed in terms of concepts. This is not to say that chemistry is lawless – it, of course, is rooted in the laws of classical and quantum physics. But these laws are often too complex to execute for systems of chemical interest that exceed a few atoms and a few more electrons.

Chemical concepts are the result of making sense over the course of more than 100 years of carefully executed experiments, painstaking analyses, and critical observations combined with a deep knowledge of the characteristic behaviors of the elements. Chemical concepts have thus stood the test of time and become textbook knowledge. They are the foundation of the chemical intuition that is formed during a student's undergraduate degree and improved over a chemist's professional life. Despite the inevitability of chemical concepts when thinking about chemistry, some concepts are surprisingly fuzzy and require a lot of chemical context and background knowledge to use appropriately. On the other hand, some concepts that are used routinely in everyday chemistry arguments have clear-cut definitions that rely on physicochemical measurements. For instance, Pearson's principle of hard and soft acids and bases is of course defined via ionization potentials and electron affinities [1], but to use the concept neither the respective quantities nor the definition are needed. Spectroscopic measurements have been used to quantify concepts that are not defined via observables, one example being the covalency of metal-ligand bonds [2].

With the increasing applicability of quantum chemistry to larger and larger systems, the opportunities for quantifying chemical concepts grow. Especially the continuous improvement of density functional theory approaches, the development of reliable approximations to wavefunction methods, and the availability of highly parallel and memory-loaded computing resources have pushed quantum chemistry applications forward in most sub-disciplines of chemistry.

One concept that is fundamental to a broad range of chemistry is the Marcus model for electron transfer, expanded by Hush to systems with large electronic coupling [3, 4]. In the Marcus model, the electron donor and the electron acceptor sites are

represented by two harmonic potential energy surfaces, see Fig. 1. Electron transfer can occur if the surfaces have the same energy, and the probability for electron transfer is determined by Fermi's golden rule [5, 6]. Besides the temperature, important quantities for the electron transfer rate are thus the electronic coupling between the states, the free energy of activation, and a term for the reorganization energy. The reorganization energy can be determined from measurements of the intervalence charge transfer band, *i.e.*, the vertical excitation promoting the electron from the donor surface to the acceptor surface. The electronic coupling can mix the (diabatic) donor and acceptor states to yield (adiabatic) ground and excited states. If it is sufficiently strong, the donor and acceptor minima merge, resulting in a single minimum on the potential energy surface that corresponds to a ground state electronic structure with a fully delocalized electron. With a smaller coupling, the two minima remain separated by a small barrier. These considerations lead to the three classes of mixed-valent compounds put forward by Robin and Day [7]: a valence-trapped system with minimal coupling is a Class I system, a valence-delocalised system with a single minimum is a Class III system, and the intermediate case with a small, thermally surmountable barrier for electron transfer is a Class II system. Environmental influences, chiefly solvation effects, have a significant influence on the valence localisation behaviour.
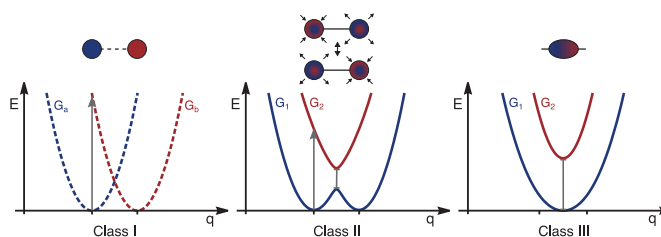

Fig. 1: One-dimensional potential energy curves for three classes of mixed-valent compounds according to Robin and Day. In Class I (left) there is minimal coupling and valence trapping; in Class II (middle) the coupling results in a double-well ground state potential allowing electron transfer; in Class III (right) the coupling is strong enough to result in a single minimum. The vertical arrows represent the reorganization energy in Class I and II, the vertical separation bars represent the electronic coupling in Class II and III.

The electron transfer coordinate, *i.e.*, the path in chemical space connecting the donor and acceptor minima, was thought of as an antisymmetric vibrational mode. In Class II mixed-valent systems, it mediates the movement of the unpaired electron from the donor to the acceptor, while in Class III systems with a single minimum on the potential energy surface, movement along this path leads to a larger degree of electron localization. Purely experimentally, the specifics of the electron transfer coordinate are not accessible. A computational approach for identifying and quantifying the electron transfer coordinate was thus needed, and ideally it would capture the

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connection between the vibrational modes of the system and the change in electronic structure associated with the electron transfer.

Our starting point was the realization that a single nuclear configuration will not be able to capture this connection between the electronic and geometric structure, and therefore we created a representative ensemble of molecules from a Wigner sampling procedure [8]. The central idea of Wigner sampling is to create a set of structures, each of which is distorted randomly along each normal mode of the system considering a given temperature. In each structure, the unpaired electron will be localized to different degrees on the three relevant fragments of a mixed-valent system, *i.e.*, the donor site, the bridge, and the acceptor site. On a technical note, local hybrid functionals are employed for the quantum chemistry calculations of each structure since they were shown by Kaupp and coworkers to produce reliable electronic structures [9, 10]. Since it is straightforward to quantify the spin population on different fragments, a measure for the progression along the electron transfer coordinate for Class III systems was found; for Class II systems the excitation energy is an appropriate measure. The remaining task was to identify how much each normal mode contributes to this progression, which was solved with a multicomponent fitting procedure under the assumption that the Marcus–Hush model is applicable. In short, our approach identifies a unique electron transfer coordinate from a linear combination of normal modes, see Figure 2 [8].

motions obtained in implicit solvation and in vacuum are virtually indistinguishable, but the scans recover the experimentally observed switch from Class II to Class III. Crucially, our method exclusively identifies those nuclear movements that contribute to electron transfer, which implies separability of the normal modes contributing to electron transfer from those that are 'electron transfer-innocent' as well as environmental effects.
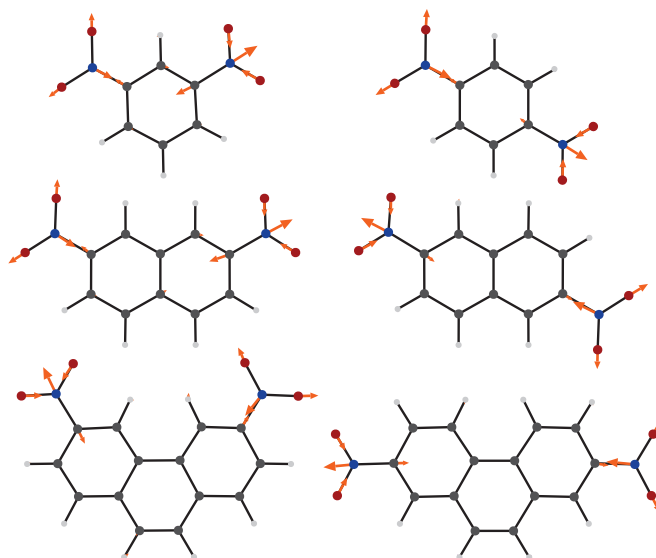

Fig. 3: **Some dinitroradical anions and their electron transfer paths from** *ab initio* **calculations.**
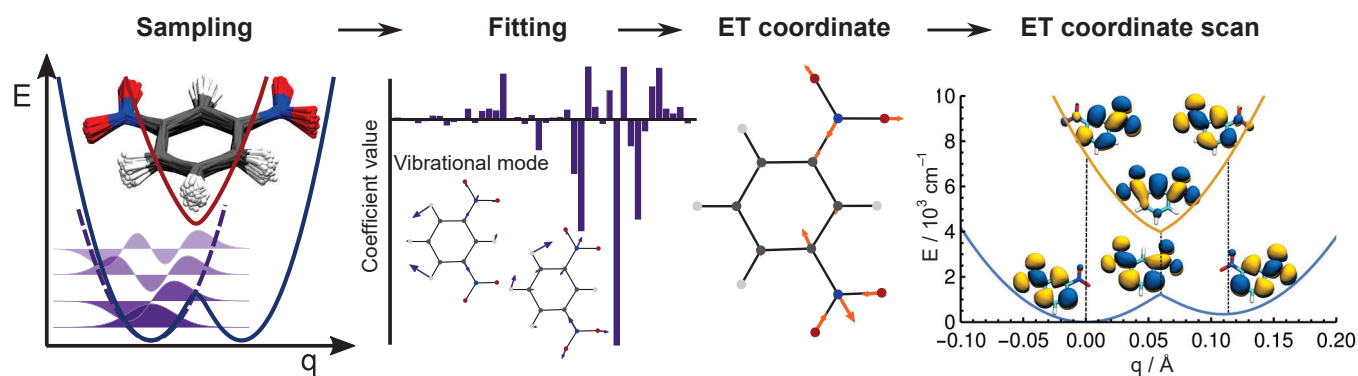

Fig. 2: **The methodology for obtaining the electron transfer coordinate from** *ab initio* **calculations: sampling generates an ensemble, which is subjected to a multi-component fitting procedure to yield the electron transfer coordinate as a linear combination of normal modes. A scan along this coordinate shows the expected Class II behavior; the change in electron position is shown with natural transition orbitals.**

For several examples, we found chemically intuitive electron transfer coordinates: they are antisymmetric motions involving the donor and acceptor sites, and similar molecules have similar motions. Thus, the electron transfer coordinate cannot be assigned to a single normal mode, but instead multiple normal modes contribute to the overall electron transfer in Class II systems, or partial electron localization in Class III systems. To verify that the motion obtained by our sampling-and-fitting approach indeed represents the electron transfer coordinate in the Marcus–Hush model, a scan along this motion revealed the correct Class II or Class III behavior for the respective systems both in terms of the potential shape and the electronic structure change. Interestingly, the motion we identify appears to be an intrinsic property of the system. For instance, for the *meta*-dinitrobenzene and 2,7-dinitronaphthalene radical anions, the

Being able to use quantum chemistry to quantify a concept also means that it can be interrogated in unique detail, its boundaries can be explored, and potential weaknesses or even failures can be discovered. Such studies may lead to the refinement of existing concepts or even the development of new concepts. Naturally, the reliability of the underlying quantum chemistry calculations must be known to prevent ill-founded conclusions. Whether through the trusted combination of theory and spectroscopy, or by referencing against higher levels of theory, there are many avenues to verify that a computational approach is accurate and robust. If a quantum chemical evaluation of a concept identifies a potential shortcoming or an unexpected behavior, this needs to be verified experimentally. A close dialogue between experiment and theory will hence be indispensable to evaluate and further develop chemical concepts. The

future looks bright in this regard: never before have experiment and theory had access to such sophisticated techniques and the ability to study chemistry with such high accuracy in the time, space and energy domains. The continued cooperation between experiment and theory will thus be able to push the frontiers of chemical concepts towards an unprecedented understanding of chemistry.

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Research in the Krewald group focusses on the electronic structure analysis of open-shell transition metal complexes and catalysts using density functional theory and wavefunction methods. The prediction of spin states and spectroscopic properties of transition metal complexes is a core research theme, with a particular focus on iron-based catalysts. A central topic is the light-driven activation and transformation of dinitrogen, for which the underlying photophysical and photochemical processes are analysed. Her group also investigates fundamental properties of transition metal complexes, including magnetic coupling and electron transfer paths, with modern computational tools.