Theoretical Chemistry, Quantum Computing, Quantum Information and Quantum Simulation on Complex Reactive Systems

We develop new theoretical methods and the implementation of these into computational models. The methods are derived with an aim to help solve problems in biophysical chemistry, atmospheric chemistry and nano-material science.

Graph-theory-based Electronic Structure and Dynamics

**Graph-Theoretic Formalism**
- *ab initio* molecular dynamics is hindered by the scaling costs associated with electronic structure methods and basis set choice
- Geometric network, or simplex decomposition, of a chemical system

\[
E_{\text{graph} - \text{th}} = E_{\text{level},0} + \sum_{R} \sum_{m} R_{m} \cdot [-1]^{m} \cdot p_{m}^{(R)}
\]

- Hybrid ADMP/ROMD propagation scheme, no self-consistent field needed for ADMP propagation

\[
E_{\text{graph} - \text{th}} = \frac{1}{2} \text{Tr} [V^T MV] + \frac{1}{2} \text{Tr} \left[ \left( \mu^{1/4} W_{\mu}^{1/4} \right)^T \right] + \frac{1}{2} \text{Tr} \left[ V^T MV - E (R, P) - \eta (\bar{R}, \bar{R}) + \bar{R} \cdot [\bar{A} (PP - P)] \right]
\]

Multi-topology Fragmentation: accurate and efficient potential surfaces

Molecular potential surfaces computed by representing a molecular framework using multiple graph networks \( \{ G_{\lambda} \} \)

\[
(R, \tau) = \left( R, \{ G_{\lambda} | \{ (i,j) | \{ (\psi_{\lambda}(i), \tau) \} \} \right) \Rightarrow (R, G) \Rightarrow E_{\text{graph} - \text{th}}
\]

Potential surfaces obtained from a suitable interpolation scheme that includes multiple graphs.

\[
\langle E (R) \rangle = \sum_{\alpha \in C} \rho_{\alpha} (R) + E_{\text{graph} - \text{th}}
\]

Anion Photoelectron Spec.: Adiabatic, Sudden, and Multistage formalisms
- Experimental studies of anionic photoelectron spectra of \( \text{Sm}_{n}O_{2n}^{2-} \) clusters show an anomalous increase in the transition intensities of excited states (A,B) relative to ground state (X) at lower photon energies (collaboration with CJC group)
- This anomaly is attributed to the prolonged interaction of the photoelectron with the remnant neutral species in the low photon energy regime and the presence of dense spin states on the samarium centre.

\[
\text{Adiabatic limit: } \left( J_{f,j} ; \psi_{\lambda_{f,j}}^{\text{Sm}} | \rho_{\lambda_{f,j}} ^{\text{Sm}} \right) ^{2} \frac{1}{E_{\text{graph} - \text{th}}} \left( J_{j,k} ; \psi_{\lambda_{j,k}}^{\text{Sm}} | \rho_{\lambda_{j,k}} ^{\text{Sm}} \right) ^{2} \sin^{2} \left( x_{\lambda_{j,k}} \frac{\pi}{2} \right)
\]

\[
\text{Sudden limit: } \left( J_{f,j} ; \psi_{\lambda_{f,j}}^{\text{Sm}} | \rho_{\lambda_{f,j}} ^{\text{Sm}} \right) ^{2} \frac{1}{4E_{\text{graph} - \text{th}}} \left( J_{j,k} ; \psi_{\lambda_{j,k}}^{\text{Sm}} | \rho_{\lambda_{j,k}} ^{\text{Sm}} \right) ^{2}
\]

- A rigorous and more insightful treatment that reduces the computational complexity while preserving its accuracy can be developed by partitioning the composite system of the photoelectron and the remnant neutral into multiple stages through the inclusion of offsetting imaginary potentials.
- A time evolution of the system in each stage can be independently carried out by using TDDFT.
- The self-scattering and emitting potentials allow the coupling of the time evolved system between different stages.