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## Vibronic computation and modeling in significant chemical problems

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The vibronic interactions have multiple impacts in various chemical and physical phenomena,<sup>1</sup> (supraconductivity, charge density and magnetism in mixed valence systems including the orbital ordering problems in manganites, stereochemistry and spectroscopy of various molecular species). The molecular dynamics and potential energy surface problems (topology, adiabaticity vs. non-adiabaticity) are also genuine vibronic topics. Such an extended relevance of the vibronic keyword faces also a certain fragmentation of the paradigm within rather disjointed areas of use, the methodologies ranging from semiempirical approaches to the state of the art *ab initio* calculations in certain restricted problems. The actual work follows the red line of our systematic interest in the coherent unification of the formal vibronic-type Hamiltonian models with the *ab initio* calculation apparatus. In a very general sense, the vibronic interactions are comprised in the force constants of a given normal coordinate under a form expressible as  $K_v = 2 \sum_{i=1}^{\infty} \sum_{n=1}^{wit} u_{ni}^{(1)} \cdot V_{in}^{(1)}$  where the *u* are coefficients related to the response of MO basis to coordinate perturbation and *V*, the vibronic constants, have effective mono-electronic meaning

whose concrete construction depends on the method of electronic structure calculation.<sup>2, 3</sup>



Figure 1. The vibronic orbitals for delocalized to localized mixed valence states in hypothetical molecule  $[Al_2Cl_6]^{2-}$ .

The general strategy is to connect vibronic formal definitions with analytical derivative and response theory techniques. Within the sketched frame, a new definition, the vibronic orbitals, was elaborated. Their obtaining concern the simultaneous diagonalization of the following matrices  $\mu_{ij} = \sum_{n=1}^{n} (u_{ni}^{(1)} \cdot V_{nj}^{(1)} + u_{nj}^{(1)} \cdot V_{ni}^{(1)})$  (*i*, *j* -occupied orbitals) and  $V_{mn} = \sum_{i=1}^{\infty} (u_{ni}^{(1)} \cdot V_{mi}^{(1)} + u_{mi}^{(1)} \cdot V_{ni}^{(1)})$  (*m,n* -virtual orbitals). The vibronic orbitals are designed as the functions most sensitive to the molecular geometry changes, whose transition density products offer the best partition of electron density flows during a distortion. An application is illustrated in fig.1 for the charge

density disproportionation in the hypothetical molecule  $[Al_2Cl_6]^{2-}$  taken as simple "academic" model for the vibronic treatment of the mixed valence.



**Scheme 1.** Generalized spin Hamiltonian used to fit potential energy surfaces of represented systems and their corresponding parameter definitions.

A series of particular applications was worked imbricating, in a new formalism, the spin-coupling and vibronic effective Hamiltonian models for sake of meaningful fit of potential energy surface data. In this way, treating the H<sub>3</sub> molecule, a particular description of the prototypical reaction coordinate and of the Jahn-Teller effect at the conical intersection was done. The same method comparatively applied to  $C_4H_4$  and  $C_6H_6$  allowed new analysis of  $\pi$ -distortions as key for antiaromaticity vs. aromaticity features. A general strategy, of setting vibronic-type Hamiltonians in order to rationalize the reaction coordinate data is proposed, proving the utility of vibronic paradigm in chemical reactivity problems.

## References

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