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Definitions of non adiabatic PES

The concept of a Born-Oppenheimer (BO) potential energy surface (PES) has been extended to non-adiabatic wave functions by Hunter [1,2] and by Wilson [3]. A Hunter non-adiabatic PES corresponding to an excited vibrational state has a set of spikes superimposed on a BO-like PES. It was believed that Wilson PESs were spike-free. We have shown [4] that it was not the case and that the Wilson PES value at a given nuclear configuration was not the expectation value of a quantum observable but a quotient of such expectation values. Consequently, BO PESs have the quantum interpretation of quotients of approximate expectation values of observables.

References

- [1] G. Hunter, *Int. J. Quantum Chem. Symp* **8**, 413 (1974).
- [2] G. Hunter, *Int. J. Quantum Chem.* **9**, 237 (1975).
- [3] E. B. Wilson, *Int. J. Quantum Chem. Symp* **13**, 5-14 (1979).
- [4] P. Cassam-Chenaï, *Chem. Phys. Lett.* **420**, 354-357 (2006).