ADIABATIC SEPARATION, BROKEN SYMMETRIES AND GEOMETRY OPTIMIZATION

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ABSTRACT. The identification of localized, broken symmetry, effective potentials is the main problem in the current discussions of localization, ergodicity and chaos. An effective potential based on an exact separation involving an extension of a conditional amplitude previously presented by Hunter can always be constructed. A generalization of the Hellmann-Feynman theorem (HFT) for non-adiabatic situations is presented. Its significance for geometry optimizations, localized excitations and collective electronic motions is discussed.

INTRODUCTION

John Coleman has addressed many times the problem of separability of functions of many variables into sums of products of functions of a lesser number of variables. One could paraphrase him and invoke that there is an "apostolic" succession: Schmidt, Löwdin-Shull, Coleman in connection with the problem. This article addresses the question from a different angle, namely: are there privileged coordinate systems for which the rank of the natural expansions can be shortened? We dedicate it to John Coleman with our sincere appreciation.

The separation and identification of fast and slow variables like the problem of identifying conditions for the validity of adiabatic separations of electronic and nuclear coordinates is an old one. The Born-Oppenheimer approximation (BOA) [1] is based on the smallness of a mass ratio.

Adiabatic separations involving a choice of a slow coordinate - like the hyperspherical radius- have been advocated by Fano [2] and others [3]. The question as to why such a separation is possible has been recently discussed by several authors [4,5]. It is clear that there are several examples where the method of adiabatic separation works extremely well, even for strong coupling situations or in the absence of small parameters [6,7].

The adiabatic separation and in its extreme form, the BOA, has been severely criticized by Woolley [8] because of its symmetry-breaking nature. Even more seriously, the adiabatic and the BOA cease to be valid at degeneracies of electronic energy surfaces. The conventional Jahn-Teller theorem for non-linear molecules leads then to a removal of

the electronic degeneracy through point-group symmetry-changing distortions [9]. Strictly speaking the total wave function, for joint electronic and nuclear motion, can no longer be truncated at the first term in the BO expansion, thus assailing the notion of conventional electronic energy surface. It would be imperative to have a generalization of the electronic energy surfaces in the neighborhood of a degenerate eigenvalue of the electronic Hamiltonian. Conventional geometry optimizations which have been inevitably based on the BOA can lead to questionable symmetry breakings as described by Davidson [10].

The fundamentals and mechanism of quantum localization in multidimensional correlated systems have been recently discussed by Hose, Taylor and Bai [11]. They argue that a BOA leads to dynamic potentials that make a non-obvious localization explicit. In a previous paper we showed how such dynamic potentials can arise through collective coordinates [5]. The problem is how to identify the appropriate coordinate system. In this paper we want to present a general treatment based on conditional probabilities. This leads to an adiabatic separation and energy surfaces for any choice of coordinate system. The choice of an optimal one, if any, for a given state can be made in a quantitative manner. Quantum chemical geometry optimizations can be carried out even in the case of vibronic degeneracies. A generalization of the conventional HFT [12] is also presented here.

SEPARATION OF ELECTRONIC AND NUCLEAR MOTION

In what follows q and Q will denote, collectively, the electronic and nuclear coordinates. They will later be used in a more general context. The Schrödinger equation has the form:

\[ H\psi(q,Q) = E\psi(q,Q) \]  

where the Hamiltonian

\[ H = T_q + T_Q + V(q,Q) = H_{el} + T_Q \]

involves the kinetic energy operators for the electrons and nuclei and the potential describing the Coulomb interactions. It is always possible to factorize the total wave function

\[ \psi(q,Q) = \psi(q,Q)\chi(Q), \chi(Q) \neq 0 \]

in terms of a conditional probability amplitude and a marginal one, the