Computing electronic structures: a new multiconfiguration approach for excited stat

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Authors
Éric Cancès CERMICS, École Nationals des Ponts et Chaussées, Cité Descartes, Marne-La-Vallée Cedex, Fr Rocquencourt, MICMAC Project, Domaine de Voluceau, Le Chesnay, France
Hervé Galicher CERMICS, École Nationals des Ponts et Chaussées, Cité Descartes, Marne-La-Vallée Cedex, Fr
Mathieu Lewin CERMICS, École Nationals des Ponts et Chaussées, Cité Descartes, Marne-La-Vallée Cedex, Fr Rocquencourt, MICMAC Project, Domaine de Voluceau, Le Chesnay, France

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ABSTRACT

We present a new method for the computation of electronic excited states of molecular systems. This method is based upon a recent theoretical definition of multiconfiguration excited states [due to one of us, see M. Lewin, Solutions of the multiconfiguration equations in quantum chemistry, Arch. Rat. Mech. Anal. 171 (2004) 83-114]. Our algorithm, dedicated to the computation of the first excited state, always converges to a stationary state of the multiconfiguration model, which can be interpreted as an approximate excited state of the molecule.The definition of this approximate excited state is variational. An interesting feature is that it satisfies a non-linear Hylleraas-Undheim-MacDonald type principle: the energy of the approximate excited state is an upper bound to the true excited state energy of the N-body Hamiltonian.To compute the first excited state, one has to deform paths on a manifold, like this is usually done in the search for transition states between reactants and products on potential energy surfaces. We propose here a general method for the deformation of paths which could also be useful in other settings.We also compare our method to other approaches used in Quantum Chemistry and give some explanation of the unsatisfactory behaviours which are sometimes observed when using the latters.Numerical results for the special case of two-electron systems are provided: we compute the first singlet excited state potential energy surface of the $H2$ molecule.

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↑ INDEX TERMS

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Collaborative Colleagues:

Éric Cancès: colleagues

Hervé Galicher: colleagues

Mathieu Lewin: colleagues