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A multiconfiguration time-dependent Hartree algorithm for non-Born-Oppenheimer calculations

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We have embarked upon a project of performing dynamical calculations treating electrons and nuclei on exactly the same footing,
considering all particles as degrees of freedom of a dynamical system. In that way, the Born-Oppenheimer approximation is circumvented. The very concept of a potential energy surface is abolished and the problems associated with kinetic energy couplings or Berry phase simply vanish. Since an exact treatment of this kind would be prohibitive, we split the various degrees of freedom according to a MCTDH scheme.

Detailed analysis

According to the MCTDH scheme, in our code, the overall wavefunction of the system is expanded as a sum of configurations. Each configuration is a product of single degree of freedom (DOF) wavefunctions (orbitals) and has its own coefficient in the overall representation.

The single configuration limit is analogous to the Hartree-Fock limit in electronic structure calculations. The wavefunction is propagated according to a variational principle analogous to the time-dependent Schroedinger equation, both coefficients and orbitals being time-dependent.

All orbitals can be visualised throughout the calculation, thus providing a qualitative image of the dynamical progress. At each point in the calculation, the norm and the energy of the wavepacket are calculated in order to ensure their conservation. Moreover, the error introduced (into both orbitals and coefficients) by time discretisation into steps is estimated and the time step is accordingly modified. If necessary, care is also taken of Pauli antisymmetrisation.

Quantities of experimental interest are obtained throughout the calculation, such as autocorrelation functions and time-dependent flux functions.

Conclusions and Future Work

We are currently utilising our code for simple, prototype three-particle systems such as the collision between a H+ ion and a H atom to study the probabilities of inelastic scattering of the ion and/or transfer of the electron between atoms. Various initial angular momenta are considered and their effect on the overall process is evaluated.

In the future, we plan to extend our work to systems with more than one electrons. Such an extension is expected to scale very favorably with the number of degrees of freedom and the Pauli principle antisymmetrisation is very easy to implement.

Impact

The MCTDH method lends itself very conveniently to use in a grid environment. The decomposition of the overall problem into several single degree of freedom problems, where intercommunication is only necessary at the beginning of each time step, suggests the handling of each degree of freedom by a single processor and the consequent facilitation of the computation, both in terms of memory and computer time.

Moreover, going beyond the Born-Oppenheimer approximation entails many advantages. Problems traditionally associated with this approximation include nonadiabatic couplings and Berry phase effects, which simply cease to exist. Furthermore, the user can, at each point in time, visualise the orbitals for each degree of freedom separately. This provides unique visualisation opportunities which would be harder to implement in a more traditional
'exact' calculation.

As with any dynamics calculations, the quantities calculated throughout the process (autocorrelation function, time-dependent flux etc.) can be used to predict optical spectra and scattering cross sections. Comparison with the result of more traditional calculations can help to evaluate the effect of the approximation.

Keywords

wavepacket, MCTDH, wavefunction, orbital, flux, autocorrelation, algorithm

URL for further information

http://www.chm.unipg.it

Author: Dr SKOUTERIS, Dimitrios (University of Perugia)

Co-authors: Prof. LAGANA', Antonio (University of Perugia); Prof. GERVASI, Osvaldo (University of Perugia)

Presenter: Dr SKOUTERIS, Dimitrios (University of Perugia)

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